Non-Steady-State Catalyst Characterization with Thin-Zone TAP Experiments

Evgeniy Redekop
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Non-Steady-State Catalyst Characterization with Thin-Zone TAP Experiments

by

Evgeniy A. Redekop

A dissertation presented to the Graduate School of Arts and Sciences of Washington University in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

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Rational catalyst design must be advanced beyond its state-of-the-art given the significant economic and environmental relevance of catalytic technologies. To address this challenge, precise kinetic characterization of industrial catalysts is required for elucidating complex reaction mechanisms, establishing structure-activity relationships, and building scientifically-sound microkinetic models of catalytic processes. In this thesis, a novel framework for non-steady-state high-throughput kinetic characterization of complex catalytic reactions is theoretically developed, experimentally validated, and applied to a catalytic reaction of considerable interest.

This novel framework of catalyst characterization is based on Temporal Analysis of Products (TAP) experiments. These pulse-response experiments employ Knudsen diffusion as a reliable standard process of gas transport to measure intrinsic rates of chemical transformations on catalysts. Specifically, this work focuses on the Thin-Zone (TZ) configuration of the TAP microreactor which allows monitoring of reaction kinetics for a well-defined and spatially uniform catalyst state with resolution on
the millisecond scale. In the TZ TAP reactor, a narrow catalytic sample is packed between two inert zones in order to minimize macroscopic concentration and temperature non-uniformities across the catalyst. Unlike traditional kinetic testing devices such as well-mixed or tubular reactors, the TZ TAP reactor maintains the catalyst in a highly uniform state for an extended range of reactant conversions. One of the main implications of maintaining TZ uniformity is the ability to effectively decouple reaction kinetics from external transport in the microreactor. Typically, TAP data analysis relies on a set of mechanistic assumptions about a reaction in order to obtain kinetic information from coupled reaction-diffusion data. In our framework, intra-pulse kinetic characteristics in the TZ including reaction rates, gaseous concentrations, and surface concentrations are reconstructed from exit flows via the 'model free' Y-Procedure and then used for elucidating the reaction mechanism and estimating kinetic parameters.

The core idea of the data analysis framework developed in this thesis is that the network of elementary steps behind a catalytic reaction can be revealed by examining how reconstructed kinetic characteristics evolve in relation to each other during a pulse-response experiment. Our results suggest, for example, that the temporal coherence between reactant consumption and product generation rates can provide compelling arguments in favor of one potential reaction mechanism over another. The analysis of rate-concentration data can also be used to estimate intrinsic kinetic parameters once the network of reaction steps is identified. These theoretical developments have been translated into a viable experimental methodology which has been validated using well-characterized oxygen uptake on polycrystalline platinum as a benchmark problem.
Finally, the Y-Procedure was applied to study CO oxidation and oxygen storage on the Au/SiO$_2$ catalyst prepared by magnetron sputtering. Oxygen was introduced to the catalyst during flow pretreatments under elevated pressure and then titrated off the catalyst by multi-pulse CO sequences under TAP vacuum conditions. The data indicate that oxygen is stored on the catalyst in two kinetically distinct reservoirs. Both reservoirs get filled with oxygen under flow pretreatment, but only one of them directly contributes oxygen for CO oxidation under vacuum. The two reservoirs exchange oxygen between each other and after one of them is depleted by the oxidation reaction during a CO pulse, the second reservoir resupplies oxygen before the next CO pulse arrives. Further research is needed to identify the chemical nature of the second oxygen reservoir. However, our findings testify to the utility of the Y-Procedure as an advanced tool for mechanistic research in catalysis. The thesis outlook section suggests several research directions which will be facilitated by the systematic application of the Y-Procedure.
Acknowledgments

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Evgeniy A. Redekop

Washington University in Saint Louis
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To my Dad, who taught me integrals, among other important things.

And to my Mom, who keeps telling me *Cum scuto, non in scuto.*
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B.1 Auxiliary device for pulse intensity calibrations
Chapter 1

Introduction

The major challenge for the chemical industry in the twenty first century is ensuring sustainable supplies of energy, fuels, and chemicals for a growing global population despite depletion of natural resources (Dudukovic, 2009, 2010). Catalytic technologies will play a pivotal role in addressing this challenge by enabling the utilization of alternative feedstocks, mitigation of greenhouse gases, and pollution abatement. In order to improve existing and develop novel industrial catalytic processes, tailored catalysts are needed for a number of chemical reactions such as dry reforming of hydrocarbons, water-gas-shift for hydrogen production, dehydrogenation of alkanes, and Fischer-Tropsch synthesis (Arakawa et al., 2001). Therefore, the rational design and optimization of catalysts must be advanced beyond their current abilities based on sound scientific knowledge about underlying catalytic phenomena.

Catalysts are designed and optimized via the Catalyst Development Cycle (CDC) comprised of an iterative process of preparing novel catalysts, testing their properties (structural and kinetic), and identifying further changes to improve their performance. Thus, accelerating the CDC is a major goal of catalytic science and nanotechnology which can be achieved only through developing a deeper understanding of structure-activity relationships. Kinetic characterization and modeling play a pivotal role in elucidating such relationships for technical catalysts\(^1\), but present daunting scientific tasks due to the inherent complexity of industrial catalytic processes (Chorkendorff and Niemantsverdriet, 2003).

\(^1\)By technical catalysts we understand often multi-component polycrystalline materials used in practical applications including the chemical industry.
1.1 Modern challenges in catalytic research

Industrial catalysis entails a plethora of physico-chemical interactions between solid surfaces and surrounding media across multiple length and time scales. These scales range from meters and hours for a catalytic reactor to angstroms and femtoseconds for molecules at a catalytic site; for examples see e.g. (Tian et al., 2004; Tariq et al., 2011). The disparity between scales leads to the disparity between physical models used to study them. The molecular scale fundamentals of surface chemistry and kinetics are mainly studied using model catalysts in Ultra-High Vacuum (UHV) chambers by surface science tools. However, the behavior of complex technical catalysts may be drastically different in a high pressure environment of a catalytic reactor. These problems are commonly called in the literature "materials gap" and "pressure gap". (Bonzel, 1977; van Santen, 1995; Zaera, 2002b). The materials gap arises because technical catalysts contain much more components than model catalysts. These components are arranged in elaborate geometric structures and are engaged in many intricate interactions. The pressure gap arises due to the effects of increased surface coverages such as lateral interactions of adsorbates, formation of new catalytic phases, or surface restructuring induced by elevated pressures. Likewise, the chemical complexity gap could be recognized as a way to acknowledge that the complexity of reaction networks involved in practical catalysis may exceed all expectations based on single crystal observations.

To respond to these seemingly overwhelming challenges, state-of-the-art catalytic research uses a diverse set of techniques to quantify and model catalytic kinetics on different levels of detail, according to the task at hand (Vlachos et al., 2006; Liu, 2007; Koci et al., 2010). Three general tasks of kinetic modeling can be distinguished:

1. **Fundamental and applied studies** employ kinetics to improve our mechanistic understanding of catalytic reactions and guide rational catalyst design.

2. **Catalyst selection** for commercial applications is accomplished by comparing different catalysts based on their kinetic properties.

3. **Reactor design** requires quantitative kinetic models to predict reactor performance and safety concerns.
For each task, scientifically sound models must be developed instead of merely empirical correlations (Lerou and Ng, 1996). Our work is concerned with a class of kinetic models which attempt to accurately represent catalytic reactions through a formal mechanism, as a combination of physico-chemically meaningful elementary steps (Dixon et al., 2006). In order to be relevant for engineering practices, such microkinetic models must relate molecular scale events on a catalytic surface to the apparent kinetic behavior in a catalytic reactor. However, these models are not intended for macroscopic reactor design or process-scale modeling. Instead, their purpose is to guide rational catalyst selection and optimization. They should also be applicable for mesoscopic transport-reaction models such as those of interstitial flow in packed beds, e.g. (Dixon et al., 2006). One of the important requirements for microkinetic models is that their parameters should represent intrinsic chemical characteristics free of transport effects. Microscopic transport (e.g. surface and micro-pore diffusion) may be indiscernible at this level, and parameters may have to be adjusted when they are coupled with a particular flow regime. Even when microkinetic models fail to predict the reactor performance quantitatively, they are still instructive qualitatively and can guide the construction of other phenomenological correlations.

Microkinetic modeling requires both gas- and surface-specific data since it explicitly accounts for the evolution of surface intermediates. An important breakthrough in gathering surface information came with the development of operando spectroscopies for probing catalytic surfaces across a wide pressure range (Somorjai and Rupprechter, 1999; Weckhuysen, 2003). Despite a wealth of information regarding surface intermediates and active sites provided by these methods, they are mainly qualitative and must always be complimented by a quantitative monitoring of the gas phase reagents/products. Gaseous kinetics has been studied extensively for more than 100 years, but the problem of mechanism identification has, in general, not been solved to date. Our work is focused on transient (non-steady-state) kinetic characterization methods, which are well-suited for this task.
1.2 Transient kinetic methods

Commonly used steady-state techniques of kinetic analysis often fail to provide sufficient details about catalytic reactions. Such details are required to reveal reaction mechanisms and relate their intrinsic kinetic parameters to a well-defined catalyst state. Unlike steady-state techniques, transient methods are particularly useful for mechanism identification and provide vast information on the inner workings of catalytic reactions (Biloen, 1993; Bennett et al., 1999; Bond, 2008; Berger et al., 2008).

In a transient experiment, rates of different elementary steps comprising the catalytic cycle are not equal, allowing for an improved mechanistic hypothesis to be posited and evaluated. Historically, transient studies of industrial catalysts have been performed under atmospheric pressure in reactors designed to approach one of the ideal flow patterns such as well-mixed or tubular reactors (CSTR, PFR), e.g. (Temkin et al., 1979). In spite of their simplicity, non-steady-state experiments in these reactors are burdened by complex hydrodynamics of turbulent flow which in itself is still poorly understood (Fox and Marin, 2006). Other complications include boundary layer effects, macroscopic non-uniformities of the catalytic sample, and low temporal resolution.

Steady-State Isotopic Transient Kinetic Analysis (SSITKA) avoids some of these complications by switching the isotopic composition of the feed stream during a steady-state kinetic measurement and monitoring the isotopic composition of the exit stream (Shannon and Goodwin, 1995; Balázhinimaev et al., 2009). While steady-state reaction rates and hydrodynamics remain intact when the streams are switched, transient isotopic signal in the effluent provides overall reaction kinetics, total concentration of isotope-containing surface intermediates, and their mean life-times. However, SSITKA uses non-steady-state isotopic characteristics only to measure steady-state characteristics and does not resolve individual reaction steps. Several other transient techniques have been developed, e.g. (Hu and Ruckenstein, 2003; Frennet et al., 2004; Herz, 2004; Ilić et al., 2008), but the systematic transient kinetic analysis of technical catalysts remains elusive. One of the more advanced transient techniques suitable for comprehensive mechanistic studies of complex multi-component catalysts is the Temporal Analysis of Products (TAP) introduced by (Gleaves et al., 1988). The TAP methodology and its improvement are the main focus of this thesis hereafter.
1.3 Temporal Analysis of Products (TAP)

Molecular Beam Scattering (MBS) experiments employed in surface science (Libuda and Freund, 2005) are exemplary for retrieving fundamental information on reaction mechanism and intrinsic kinetic parameters of individual steps, but in general they cannot accommodate the complex surfaces of technical catalysts. TAP experiments were originally devised as a simplified version of MBS which could operate on multi-component realistic catalysts with high specific surface areas and porous structures. Similarly to MBS, essential kinetic and mechanistic information is obtained in TAP by modulating the reactant flux, and measuring arrival times at the exit of unconverted reactants, products, and inert molecules. Continued efforts have been made since the first generation of TAP systems was introduced over twenty years ago in order to improve the quality and diversity of generated kinetic data (Gleaves et al., 2010). Modern TAP instruments, such as the one shown in Figure 1.1, integrate a number of enabling features including fast switching between Ultra-High Vacuum (UHV) and atmospheric modes, steady-state and transient regimes, and scrupulous control over the gas feed. The same sample of technical or model catalyst can be tested in the TAP system over a broad range of pressure ($10^5 - 10^{-6}$ (Pa)) and time ($10^3 - 10^{-4}$ (s)) scales. Detailed descriptions of the TAP reactor and references to its many practical applications may be found elsewhere, e.g. (Gleaves et al., 1997; Yablonsky et al., 2005; PÁrez-RamÁrez and Kondratenko, 2007).

1.3.1 Experimental hardware and principles of operation

The principal components of the third-generation TAP reactor setup (TAP-3) shown in Figure 1.1(a) are: (i) a feed system that supplies gas reactants for pulse and flow experiments at user defined temperatures and pressures; (ii) a temperature controlled (r.t. - 1000 C) packed bed microreactor; (iii) a quadrupole mass spectrometer (QMS) detector contained in (iv) a high-throughput vacuum system; and (v) a computer based control and data acquisition system. The signature type of TAP transient measurements is the pulse-response experiment conducted as follows. First, a very small pulse of gas mixture ($10^{13} - 10^{14}$ molecules) is introduced into the evacuated (< $10^{-3}$ Pa) microreactor by a high-speed pulse valve, as shown schematically in
Figure 1.1(c). The gas molecules traverse the reactor by means of Knudsen diffusion, encounter the catalyst on their way, and then escape into the vacuum chamber where they are monitored by the QMS. Exit flow curves of unconverted reactants and generated products recorded by the QMS contain rich kinetic information about reactions on the catalyst.

Kinetic information is extracted from TAP data using methods similar to classic kinetic studies, by comparing exit flow curves of reactants and products to those of an inert standard. What distinguishes TAP among other kinetic testing devices is the uniquely simple and reliable gas transport regime governed by Knudsen diffusion. Under this low-pressure regime located an the upper boundary of the surface science domain, gas molecules injected into the microreactor travel in interstitial voids independently of each other. As a result, effective diffusion coefficients of individual gases do not depend of the mixture composition or pulse-intensity\(^2\) and exit flow curves

---

\(^2\)As long as pulse-intensity stays within a certain range (nanomole quantities).
are remarkably reproducible. Another important advantage of the Knudsen regime is that external mass-transfer limitations are removed, and intrinsic kinetics can be decoupled more readily.

1.3.2 Interrogative Kinetics (IK) through various types of TAP experiments

The main goal of TAP experiments is to obtain a comprehensive picture of intrinsic reaction kinetics pertaining to a complex catalytic mechanism. Towards this goal, the TAP methodology employs a versatile toolkit of pulse-response experiments, such as single-pulse, multi-pulse, pump-probe, or temperature programmed experiments, which allow for controlled surface modifications and a simultaneous kinetic testing of resulting catalyst states. These experiments are collectively known as the Interrogative Kinetic (IK) approach to revealing reaction mechanisms and structure-activity relationships (Gleaves et al., 1997). In a dialog-like procedure, the catalyst is probed by the pulse initiating an experiment and exit flows of unconverted reactants, products, and side-products emerging from the microreactor in certain order are treated as responses to this probe.

Regarding surface modifications, two types of experiments are distinguished (Shekhtman et al., 1999): (1) state-defining and (2) state-altering. In the course of a state-defining experiment, the amount of gas molecules in the pulse is much smaller than the amount of active sites on the surface available for reaction. The catalyst is perturbed insignificantly during such a pulse, and the observed kinetics can be attributed to a particular catalyst state. Contrary to a state-defining experiment, the catalyst is altered appreciably during a state-altering experiment which can be used to study the effects of surface composition on the surface’s catalytic properties. For irreversible reactions, long series of small state-defining pulses are used to perform controlled state-altering experiments (multi-pulse) whereby the catalyst composition is changed gradually. Controlled state-altering experiments for reversible reactions are currently difficult to organize because all molecules desorb by the end of the pulse, leaving the catalyst unchanged.
While temporal and compositional changes of the catalyst surface are effectively manipulated as a part of the IK methodology, its spatial changes are minimized in order to link intrinsic kinetics to a specific rather than averaged catalyst state. Progressively higher levels of catalyst uniformity have been achieved by switching from one-zone to three-zone and then Thin-Zone TAP reactors. The Thin-Zone idea and its central role in precise kinetic characterization are discussed in the next subsection.

1.3.3 The importance of spatial catalyst uniformity and the Thin-Zone idea

For spatially distributed gas and surface compositions in the catalyst, transport processes are strongly coupled with chemical reactions which might lead to ambiguous results upon data analysis. Consequently, spatial uniformity of the catalyst sample is paramount in accurately measuring the intrinsic kinetics (Moulijn et al., 1991). Generally, the macroscopic concentration non-uniformity in a catalytic reactor can be characterized by a ratio of the total concentration difference across the catalyst to the inlet concentration value (i.e. $\Delta C/C_{in}$). In reactors traditionally used for kinetic testing (Continuous Stirred-Tank Reactor (CSTR) and Differential Plug-Flow Reactor (d-PFR)), the mass transport is dominated by convection for which non-uniformity is directly proportional to conversion $\Delta C/C_{in} \propto X$. Kinetic measurements in such reactors are restricted to low conversions in order to minimize non-uniformity in the catalytic sample (Bennett et al., 1999).

In the TAP reactor, concentration gradients cannot be avoided since they are the driving force of gas transport in the Knudsen regime. Nevertheless, the non-uniformity $\Delta C/C_{in}$ can be minimized in the Thin-Zone (TZ) TAP reactor proposed by Shekhtman and Yablonsky in (Shekhtman et al., 1999) where a narrow ($\Delta L_{cat} < L$) catalyst sample is sandwiched between two inert zones. Here, $\Delta L_{cat}$ is the thickness of the catalyst zone, and $L$ is the total reactor length. It was shown in (Shekhtman and Yablonsky, 2005) that under Knudsen flow conditions, the catalyst non-uniformity in the TZ is determined by a purely geometrical factor $\Delta C/C_{in} \propto \Delta L_{cat}/L$ for a not-very-fast reaction. This non-uniformity can be minimized by using a catalyst sample which is much thinner than the total reactor length. In other words, the mixing of gas by diffusion on the small local scale of the Thin-Zone decreases the non-uniformity.
faster than the reaction increases it. Due to this property, TZ TAP experiments are favorable for a systematic characterization of intrinsic catalytic kinetics.

There are two commonly used strategies for translating exit flow data into kinetic characteristics of a uniform catalyst sample located in the thin-zone (Tantake et al., 2007): model regression and moment analysis. Both methods require strong assumptions about the reaction mechanism to be made in advance which may significantly reduce the value of extracted information and lead to data misinterpretation. Often, only qualitative assessments of data are reported in the literature due to complexities of the quantitative data collection and analysis. The second method, moment analysis, dramatically decreases the temporal resolution of data by integrating thousands of time points over the pulse length to give only three moment values. The disadvantages of conventional data analysis strategies have been alleviated by an algorithm suggested by (Yablonsky et al., 2007) that translates exit flow curves into thin-zone reaction rates and gas concentrations with no assumptions on the reaction mechanism while preserving their temporal resolution. This algorithm, called the Y-Procedure, is the theoretical frontier of the TAP methodology, since it has not yet been developed beyond a single numerical example for a simple first order reaction and has not been applied to experimental data.

1.4 Motivation and thesis objectives

Non-steady-state TZ TAP experiments demonstrate a unique set of features which enable more elaborate kinetic characterization than any other technique suitable for studying technical catalysts. However, procedures currently used for extracting intrinsic kinetic information from TZ TAP data have a number of limitations hindering wide-scale application of advanced TAP methodologies. These limitations stem from the fact that exit flow analysis typically relies on a priori mechanistic assumptions and/or pulse-averaged moments instead of the explicit transient physico-chemical characteristics of a catalytic reaction. With the development of the Y-Procedure, it is now possible to directly reconstruct reaction rates and gas concentrations in the catalytic zone and unlock a new level of detail in transient kinetic characterization. This work is motivated by the transformative potential of the Y-Procedure to enhance
microkinetic modeling of complex reaction mechanisms, thereby assisting in design of industrial catalytic processes. Specific thesis objectives are as follows:

1. Theoretically explore the possibilities for mechanism identification brought about by the analysis of TZ TAP data using the Y-Procedure.

2. Develop and validate a practical data interpretation framework based on these possibilities.

3. Apply the developed framework to study a novel catalytic system of considerable interest.

1.5 Thesis outline

Chapter 2 provides a concise overview of theoretical foundations developed over the last decade to model and analyze TAP pulse-response experiments in the Knudsen transport regime. The Thin-Zone TAP reactor is discussed in the context of a general theory of TAP reactors which also includes one-zone and three-zone configurations. After introducing mathematical models and some of their solutions for standard TAP reactors, the chapter discusses how kinetic characteristics of catalytic reactions are extracted from exit flow data and what are the limitations of different data analysis strategies. The Y-Procedure is presented as the current frontier in TAP data analysis.

Chapter 3 presents novel theoretical developments of the Y-Procedure approach which form a basis for further practical applications. First, the primary data post-processing and visualization are described which effectively relate gaseous kinetic characteristics to the catalyst composition within each pulse. Second, numerical simulations of irreversible and reversible adsorption steps are used to explicate the intra-pulse data analysis and parameter estimation. Finally, the principle of temporal kinetic coherence is formulated for multi-step mechanisms and its utility in mechanism identification is demonstrated by numerical simulations of two-route CO oxidation and irreversible reaction with a hidden surface step.

Chapter 4 addresses practical matters of the Y-Procedure. The chapter begins with the Pulse Intensity Modulation (PIM) protocol of data acquisition specifically
designed for the Y-Procedure. Then, the experimental validation of the Y-Procedure approach is presented which utilized oxygen uptake on polycrystalline platinum as a benchmark. Finally, an experimental study of CO oxidation on the novel Au/SiO$_2$ catalyst is described in which the Y-Procedure was used to reveal the mechanism of oxygen storage.

In **Chapter 5**, conclusions are drawn from our findings and future research directions are outlined for the Y-Procedure analysis of TZ TAP experiments within the broader context of catalytic science and technology.
Chapter 2

The theory of TAP experiments: state of the art

The purpose of this chapter is to review the theory of TAP pulse-response experiments which has been developed to quantitatively describe physico-chemical processes in the TAP microreactor and guide experimental design. The chapter is divided into two sections corresponding to the interconnected aspects of TAP theory: modeling and data analysis. Although extracting reaction kinetics from exit flow data is the primary goal of TAP theory, in practice it is mathematical models of microreactors that enable systematic data analysis. Only when gas transport and transport-chemistry interactions during a pulse-response experiment are understood through mathematical models can data analysis methods be developed and applied.

The first section 2.1 summarizes such models and their solutions developed for various configurations of the TAP microreactor. Rather than adhering to the chronological order in which these models appeared in the literature, the section opens with the formulation of governing equations with unspecified boundary conditions for a generic packing zone of arbitrary dimensions. These equations and their solution in the Laplace domain constitute a universal segment of a general multi-zone reactor model. Specific configurations of the microreactor are then described as particular cases constructed from such segments. The main focus of this thesis is the Thin-Zone configuration, but other models were also included in the chapter in order to introduce the nomenclature, theoretical concepts, and solution methods used thereafter.

The second section 2.2 is devoted to data analysis techniques used for processing exit flow measurements in order to retrieve kinetic information. These techniques
have evolved from a simple qualitative assessment of exit flow curves to more advanced quantitative methods such as moment analysis and the Y-Procedure. The overall trend in the development of these techniques has been to decrease the stringency of kinetic assumptions needed for extracting intrinsic kinetic characteristics from reaction-diffusion data. The interpretation of multi-pulse sequences is also summarized in this section. The chapter concludes with several critical remarks on the state of the art and current limitations of the theory of TAP experiments which motivate further research.

2.1 Mathematical modeling of TAP experiments

Mathematical models of TAP pulse-response experiments rest on the assumption that within a certain range of experimental conditions, including background pressure and pulse intensity, the transport of gas through the microreactor occurs solely via Knudsen diffusion. The validity of this assumption must be established experimentally for different gases and packing materials, but it is generally accepted that the assumption holds when the microreactor is evacuated to approximately $10^{-3}$ (Pa) and the pulse intensity does not exceed $10^{14}$ molecules. Under these conditions, TAP experiments can be described by a one dimensional diffusion equation containing a reaction source term and supplied with appropriate boundary and initial conditions. As a model outcome, we seek to predict the exit flow as a function of time for a given set of transport and kinetic parameters.

2.1.1 General model of a packing zone and its transfer matrix

Consider a reactor zone $l$ of length $\Delta_x$ (m) packed with a uniform material, whether inert or catalytically active, depicted schematically in Figure 2.1. The transport of gas through the packing obeys the following system of partial differential equations (PDEs) (Gleaves et al., 1997)

$$
e^{(t)} \frac{\partial C^{(t)}_g}{\partial t} = D^{(t)} \frac{\partial^2 C^{(t)}_g}{\partial x^2} - S_v^{(t)} (1 - e^{(t)}) R^{(t)} (k^{(t)} , C^{(t)}_g , C^{(t)}_s) , \quad (2.1)$$

13
\[
\frac{\partial C_s^{(l)}}{\partial t} = R^{(l)}(k^{(l)}, C_g^{(l)}, C_s^{(l)}).
\] (2.2)

Here, \(C_g(x, t)\) \((mol \cdot m_G^{-3})\) is the bulk gas concentration (in the void), \(C_s(x, t)\) \((mol \cdot m_S^{-2})\) is the surface concentration, \(R(k, C_g, C_s)\) \((mol \cdot m_S^{-2} s^{-1})\) is the surface reaction rate, \(D\) \((m_G^3 m_T s^{-1})\) is the effective diffusion coefficient, \(\epsilon\) \((m_G^3 m_T^{-3})\) is the fractional voidage of the bed, \(S_v\) \((m_S^2 m_S^3)\) is the specific surface area (non-porous), and \(k\) is a set of intrinsic kinetic parameters. All these quantities are specific to zone \(l\), as indicated by the superscript. In what follows, we will omit the superscript where it is unnecessary. The independent variables are time \(t\) \((s)\) and axial distance \(x\) \((m_T)\). Subscripts \(T\), \(G\), and \(S\) referring to the total, gas, and surface are often not shown hereafter for brevity. It should also be mentioned that quantities \(C_g\), \(C_s\), \(R\), and \(D\) are generally vectors whose elements correspond to different substances. The subscripts may change accordingly in order to refer to a specific species.

Figure 2.1: **Schematic representation of a general packed zone of length \(\Delta x\) in the TAP reactor** Unspecified conditions on the left and right boundaries are shown for concentration values \(C(x, t)\) \((mol \cdot m^3)\) and molecular flows \(F(x, t)\) \((mol \cdot s)\) as blue and red circles, respectively. Solid lines connecting the boundary conditions represent corresponding variables as functions of their position. Concentrations of surface intermediate are also defined at every position in the zone (shown as a solid line at the bottom), but do not require boundary conditions because their governing equation does not contain spatial derivatives.

The reactor zone is assumed to be completely evacuated in the beginning of each pulse-response experiment, meaning that gas concentrations are initially zero everywhere:

\[
C_g(x, t = 0) = 0.
\] (2.3)
Surface concentrations are generally not zero because some of them represent surface sites or surface intermediates irreversibly adsorbed during previous pulses, flow-pretreatments, or other events in the history of a given catalyst state. However, a homogeneous initial condition equivalent to (2.3) can be used to treat surface concentrations with non-zero initial distribution \( C_{s,\text{init}}(x, t = 0) \) after a new variable is introduced, such that \( C'_{s} = C_{s} - C_{s,\text{init}} \). For this new variable, the initial condition is

\[
C'_{s}(x, t = 0) = 0. \tag{2.4}
\]

Once a pulse is introduced into the zone, gas molecules travel through the packing by means of Knudsen diffusion. When this mode of gas transport dominates, the mean free path of gas molecules is larger than interstitial distances and the effective diffusion coefficient depends only on the geometry of packing, temperature, and molecular weights:

\[
D = \frac{\epsilon}{\tau} D_{Kn} = \frac{\epsilon d_{i}}{3\tau} \left( \frac{8RT}{\pi M_{a}} \right)^{1/2}, \tag{2.5}
\]

where \( \tau \left( m_{G}^{2} m_{T}^{-1} \right) \) is the bed tortuosity, \( R \) is the universal gas constant, \( T \, (K) \) is the absolute temperature, \( M_{a} \, (kg \, mol^{-1}) \) is the molecular weight of the gas, and \( d_{i} \,(m) \) is the diameter of interstitial voids related to the particle diameter \( d_{p} \,(m) \) as

\[
d_{i} = \frac{2\epsilon}{3(1-\epsilon)} d_{p}.
\]

Apart from Knudsen diffusion, gas molecules may participate in various processes such as adsorption, surface reactions, or intra-particle diffusion which are encompassed by the reaction source term in equation (2.1). If gases do not interact with the particle surface because they are inert or the packing material is inert, the reaction term is set to zero. Otherwise, it is a sum of rates of various elementary steps in which a particular gas participates multiplied by stoichiometric coefficients. Generally, the rate form is a non-linear function of concentrations and must be treated numerically. For simplicity, we temporarily restrict the discussion to a simple reversible adsorption

\[^{3}\text{The kinetic model has to be changed accordingly.}\]
of gas $A$ on the catalyst site $Z$, i.e. $A + Z \rightleftharpoons ZA$, for which the reaction term is assumed to be

$$R_A = C_{Z,\text{tot}} k^+ C_A - k^- C_{ZA},$$

where $C_A$ is the gas concentration, $C_{ZA}$ is the surface concentration of adsorbed $A$, $C_{Z,\text{tot}}$ is the total concentration of adsorption sites, $k^+$ ($m^3 mol^{-1}s^{-1}$) is the adsorption constant, and $k^-$ ($s^{-1}$) is the desorption constant.

This particular model reaction is chosen for two reasons. First, practically all catalytic cycles are initiated by a similar step in which one of the gaseous reactants binds to the surface. Second, the kinetic equation (2.6) can be reduced to the irreversible case by setting the desorption constant to zero or the entire reaction term can be eliminated by setting both constants to zero. Thus, the solution valid for this model can also be used for both irreversible adsorption and pure diffusion. It should be noted that the adsorption constant does not depend on the concentration of adsorbate $C_{ZA}$, implying that the pulse is assumed to be so small that it does not change the surface composition significantly $C_Z = C_{Z,\text{tot}}$ (i.e. a state-defining pulse). This assumption ensures that the rate form is linear with respect to gas and surface concentrations, a condition necessary for further analytical derivations.

When the rate form is linear, the model for gas $A$ can be conveniently solved in the Laplace domain (Constales et al., 2001a). The application of the integral Laplace transform defined as

$$(\mathcal{L} f) (s) = \int_{t=0}^{+\infty} e^{-st} f(t)dt$$

(2.7)

to governing equations (2.1) and (2.2) with initial conditions (2.3) and (2.4) leads to

$$\epsilon s \mathcal{L} C_A = D_A \frac{\partial^2 C_A}{\partial x^2} - S_v (1 - \epsilon) \left( C_{Z,\text{tot}} k^+ \mathcal{L} C_A - k^- \mathcal{L} C_{ZA} \right),$$

(2.8)
\[ s \mathcal{L} C_{ZA} = C_{Z, tot} k^+ \mathcal{L} C_A - k^– \mathcal{L} C_{ZA}. \] (2.9)

From (2.9) it follows that

\[ \mathcal{L} C_{ZA} = \frac{C_{Z, tot} k^+ \mathcal{L} C_A}{s + k^-}, \] (2.10)

substituting which into equation (2.8) results in

\[ \frac{1}{\mathcal{L} C_A} \frac{\partial^2 C_A}{\partial x^2} = \frac{s}{D} \left( \epsilon + S_v (1 - \epsilon) \frac{C_{Z, tot} k^+}{s + k^-} \right) = \lambda^2, \] (2.11)

where \( \lambda \) is a positive square root of the right hand side for \( s \geq 0 \). Equation (2.11) has the following general solution

\[ \mathcal{L} C_A = A(s) \cosh(\lambda x) + B(s) \sinh(\lambda x), \] (2.12)

where \( A(s) \) and \( B(s) \) are constants uniquely determined by zone-specific boundary conditions. Some of these boundary conditions are later defined for molecular flows rather than concentrations. According to Fick’s first law, the molecular flow (of gas \( A \)) \( F_A(x, t) \) (mol s\(^{-1}\)) is proportional to the concentration gradient:

\[ F_A = -AD_A \frac{\partial C_A}{\partial t}(x, t). \] (2.13)

It is convenient to differentiate solution (2.12) with respect to the axial distance \( x \), obtaining the following equation for the molecular flow

\[ \mathcal{L} F_A = A(s) \lambda \sinh(\lambda x) + B(s) \lambda \cosh(\lambda x). \] (2.14)
After expressing constants \( A(s) \) and \( B(s) \) through gas concentrations and flows on two boundaries of the packing zone, equations (2.12) and (2.14) can be combined into a compact matrix form:

\[
\begin{pmatrix}
\mathcal{L} C_A^{left}(s) \\
\mathcal{L} F_A^{left}(s)
\end{pmatrix} = M(u, w)
\begin{pmatrix}
\mathcal{L} C_A^{right}(s) \\
\mathcal{L} F_A^{right}(s)
\end{pmatrix},
\]

(2.15)

where \( C_A^{left/right} \) and \( F_A^{left/right} \) refer to gas concentrations and molecular flows on the left and right boundaries of the packing zone respectively. The transfer matrix \( M(u, w) \) in (2.15) is defined as

\[
M(u, w) = \begin{pmatrix}
cosh(u) & \frac{\sinh(u)}{uw} \\
\frac{uw}{u} & \frac{\sinh(u)}{cosh(u)}
\end{pmatrix}.
\]

(2.16)

Here, variables \( u \) and \( w \) are

\[
u = \sqrt{s\tau + \frac{s\psi^2}{s+k}}, \quad w = \gamma,
\]

(2.17)

where \( \tau = \epsilon \frac{(\Delta x)^2}{D_A} (s) \) and \( \gamma = \frac{D_A}{\Delta x} (m \ s^{-1}) \) are transport parameters of the zone, and \( \psi = \sqrt{\epsilon \Delta x (1 - \epsilon) C_{Z,tot}^k / \epsilon} \) is the dimensionless adsorption/diffusion parameter.

Matrix equation (2.15) linearly relates four boundary conditions for an arbitrary packing zone and can be used to calculate any two of them, given that the other two are known. This result stems from the fact that equation (2.1) is a second order PDE and requires two boundary conditions for its solution. As will be shown in the subsequent sections of this chapter, equation (2.15) can be used to construct mathematical models for other microreactor configurations by applying specific sets of boundary conditions. The transfer matrix formalism of this equation also played an important role in advancing the strategies of data analysis discussed in section 2.2.
2.1.2 One-zone reactor

In the simplest case, the entire TAP microreactor of length $L$ is packed with the same material and has only one zone shown in Figure 2.2. This case, known as the one-zone reactor, can be readily modeled by equations developed in the previous section with the boundaries of an arbitrary packing zone coinciding with the inlet and outlet ends of the microreactor. One of the two required boundary conditions is imposed at the exit $(x = L)$ though which the reactor is exposed to the evacuated chamber. Once gas molecules escape into the vacuum system, they have a very low probability of returning back into the microreactor. Correspondingly, the gas concentration at the reactor exit is always assumed to be zero:

$$C_A^{\text{right}} = C_A(x = L, t) = 0. \quad (2.18)$$

The second boundary condition is imposed at the inlet $(x = 0)$ through which the pulse-valve injects gases into the microreactor. Typically, this inlet pulse is represented as a time-dependent condition for the molecular flow:

$$F_A^{\text{left}} = -AD_A \frac{\partial C_A}{\partial t}(x = 0, t) = N_{PA} \delta(t - 0^+) \cdot ,. \quad (2.19)$$

where $N_{PA} (mol)$ is the amount of A molecules in the pulse, $A (m^2)$ is the reactor cross section, and $\delta(t - 0^+) (s^{-1})$ is Dirac delta function localized at time zero. The realistic non-ideal inlet pulse can be modeled by an appropriate function of time instead of the delta function, but it was concluded that “the model with ideal BIC [boundary and initial conditions] is proven to be completely adequate to the description and interpretation of transport-reaction data obtained with TAP-2 reactors.” (Constales et al., 2006).

Substituting these boundary conditions into the transfer matrix equation (2.15) leads to

$$1 = M_{21}(u) \cdot 0 + M_{22}(u) \cdot \mathcal{L}F(x = L, s), \quad (2.20)$$
Figure 2.2: The one-zone TAP reactor of length $L$ and the boundary conditions for its mathematical model

from where the Laplace transform of exit flow can be found as

$$\mathcal{L} F_{exit}^A(x = L, s) = \frac{1}{M_{22}(u)} = \frac{1}{\cosh(u)}. \quad (2.21)$$

Upon inversion of the Laplace transform, expression (2.21) yields the exit flow curve $F_{exit}^A(t)$ experimentally observed in a pulse-response experiment. The same curve can be obtained by solving the model equations in the time domain via the separation of variables technique (Gleaves et al., 1997). According to this solution, the exit flow divided by the pulse intensity, i.e. Pulse Intensity (PI) normalized flow, is given by

$$\frac{F_{exit}^A(t)}{N_{PA}} = \frac{D_A \pi}{\epsilon L^2} \sum_{n=0}^{\infty} (-1)^n (2n+1) \left[ A_n \exp \left( r_- \frac{tD_A}{\epsilon L^2} \right) + (1-A_n) \exp \left( r_+ \frac{tD_A}{\epsilon L^2} \right) \right], \quad (2.22)$$

where

$$r_{\pm} = - \left( p_n^2 + \tilde{k}^+ + \tilde{k}^- \right) \pm \sqrt{\left( p_n^2 + \tilde{k}^+ + \tilde{k}^- \right)^2 - 4 p_n^2 \tilde{k}^-}, \quad (2.23)$$

$$p_n = (n + 0.5) \pi, \quad (2.24)$$
\[ A_n = \frac{(r_+ + p_n^2 + \bar{k}^+)}{r_+ - r_-}, \]  
(2.25)

and the dimensionless adsorption/desorption constants are defined as

\[ \bar{k}^+ = k^+ \frac{S_v(1 - \epsilon)L^2C_{Z,tot}}{D}, \]  
(2.26)

\[ \bar{k}^- = k^- \frac{\epsilon L^2}{D}. \]  
(2.27)

The most important result is obtained when \( k^+, k^- = 0 \) and the exit flow represents purely diffusional transport through the microreactor:

\[ \frac{F_A^{\text{exit}}(t)}{N_{P_A}} = \frac{D_A \pi}{\epsilon L^2} \sum_{n=0}^{\infty} (-1)^n (2n + 1) \exp \left(-\left(n + 0.5\right)^2 \frac{tD_A}{\epsilon L^2} \right). \]  
(2.28)

The curve described by equation (2.28) is called the Standard Diffusion Curve (SDC) because its shape does not depend on the composition or size of the inlet pulse. The properties of this curve are discussed in section 2.2.1 in the context of data analysis. In conclusion of this brief account of the one-zone TAP reactor it should be noted that the main shortcoming of this configuration is significant temperature and concentration gradients developing along the microreactor during an experiment. These non-uniformities are very difficult to quantify, control, and account for and therefore obstruct data analysis. The need to minimize these non-uniformities has necessitated development of the three-zone reactor configuration.

### 2.1.3 Three-zone reactor

The original idea behind the three-zone reactor was to place the catalytic layer between two inert zones in order to minimize temperature gradients in the catalyst (Gleaves et al., 1997). This configuration is schematically shown in Figure 2.3 where zones are numbered by \( l = 1, 2, 3 \). Each layer of packing can be modeled as a separate
zone defined by equations (2.1), (2.2), (2.3), and (2.4) with zone-specific voidage $\epsilon_l$ and diffusion coefficients $D_l$. It is assumed that transport parameters are identical within all inert zones because they are packed with the same material. For the catalytic zone, $\epsilon_l$ and $D_l$ are often thought to be equal to those in inert zones. This simplification is justified in practice when the sizes of inert and catalytic particles are closely matched. Zone-specific reaction terms in governing equations follow the same convention as previously described.

Figure 2.3: The three-zone TAP reactor, global boundary conditions for its mathematical model, and transfer conditions between two adjacent zones

Concentrations of surface intermediates are defined only within the catalytic zone and are represented by the third solid line at the bottom of the middle section.

The outer boundaries of inert zones coincide with the reactor inlet and outlet, subject to global boundary conditions (2.18) and (2.19). Additional transmission conditions are imposed on the inner boundaries located between the catalytic zone and two inert zones:

$$C_g^{(l)}(x_l, t) = C_g^{(l+1)}(x_l, t), \quad (2.29)$$

$$-AD_l \frac{\partial C_g^{(l)}}{\partial t}(x_l, t) = -AD_{l+1} \frac{\partial C_g^{(l+1)}}{\partial t}(x_l, t), \quad (2.30)$$

where $x_l$ is the boundary position between zones $l$ and $l+1$, $l = 1, 2$. These conditions ensure concentration and flow continuities across inter-zone boundaries.
In the Laplace domain, the three-zone TAP reactor with linear rate form (2.6) in the catalyst can be modeled by the following transfer matrix equation (Constales et al., 2001a)

\[
\begin{bmatrix}
\mathcal{L}C(x = 0, s) \\
\mathcal{L}F(x = 0, s)
\end{bmatrix}
= P(s) \begin{bmatrix}
\mathcal{L}C(x = L, s) \\
\mathcal{L}F(x = L, s)
\end{bmatrix},
\]

(2.31)

where the $2 \times 2$ global transfer matrix $P(s)$ is formed by multiplying matrix relations (2.15) for all three zones and taking into account equations (2.29) and (2.30):

\[
P(s) = \begin{pmatrix}
P_{11}(s) & P_{12}(s) \\
P_{21}(s) & P_{22}(s)
\end{pmatrix} = \prod_{i=1}^{3} M(u_i, w_i).
\]

(2.32)

Substituting Laplace transforms of global boundary conditions (2.19) and (2.18), i.e. $\mathcal{L}F(x = 0, s) = 1$ and $\mathcal{L}C(x = L, s) = 0$ respectively, into equation (2.31) leads to

\[
1 = P_{21}(s) \cdot 0 + P_{22}(s) \cdot \mathcal{L}F(x = L, s),
\]

(2.33)

from where the exit flow can be obtained as the Laplace inversion of

\[
\mathcal{L}F^{\text{exit}}(x = L, s) = \frac{1}{P_{22}(s)},
\]

(2.34)

where $P_{22}(s)$ is the lower right element of the transfer matrix. Exact expressions for elements of matrix $P(s)$ are rather complicated and can be found elsewhere (Constales et al., 2001a).

The transfer matrix formalism developed for the three-zone configuration was later extended to include an arbitrary number of zones (Constales et al., 2001a), three dimensional geometry (Constales et al., 2001b), multiple gaseous substances with different diffusion rates (Constales et al., 2004), and non-ideal boundary conditions (Constales et al., 2006). To date, this mathematical apparatus gives the most comprehensive account of TAP microreactors which has led to many valuable analytical
results in data analysis. The Thin-Zone reactor, a limiting case of the three-zone configuration, is particularly useful for precise kinetic measurements due to its superior uniformity.

### 2.1.4 Thin-Zone reactor

The Thin-Zone (TZ) reactor was suggested as a way to further minimize macroscopic gradients of gas concentrations and catalyst composition during a pulse-response experiment (Shekhtman et al., 1999). Although the Thin-Zone configuration can be accurately modeled as a three-zone reactor, it is more useful to consider the limiting case in which the catalytic zone is represented by an infinitely thin reactive interface between two adjacent inert zones shown in Figure 2.4. Such a simplification is possible only under the assumption of complete catalyst uniformity which we further refer to as the Thin-Zone hypothesis.

![Figure 2.4: The Thin-Zone (TZ) TAP reactor with the catalyst represented as reactive interface and the boundary conditions for its mathematical model](image)

Surface concentrations are defined only on the reactive interface and are represented by the circle at the bottom of the TZ.

Mathematically, the catalyst uniformity assumption corresponds to the collapse of partial differential equation (2.1) for the TZ into the following boundary conditions between inert zones

\[
C_g^{(I)}(x = L_{TZ}, t) = C_g^{(II)}(x = L_{TZ}, t) = C_g^{TZ}(t), \quad (2.35)
\]
\[ F^{in}(t) - F^{out}(t) = -AD \frac{\partial C_g^{(I)}}{\partial x}(x = L_{TZ}, t) + AD \frac{\partial C_g^{(II)}}{\partial x}(x = L_{TZ}, t) = S_{cat} R^{TZ}(k, C_g, C_s^{TZ}), \]

where \( F^{in} \) and \( F^{out} \) are molecular flows entering and leaving the TZ, \( S_{cat} = A \Delta L_{cat} S_v (1 - \epsilon_{cat}) \) \((m^2)\) is the total catalytic surface area, \( \Delta L_{cat} \) \((m)\) is the thickness of the catalytic zone, \( L_{TZ} \) \((m)\) is the position in the middle of TZ, and indices I and II refer to first and second inert zones. Surface concentrations on the TZ interface \( C_s^{TZ} \) are still described by equation (2.2), but they are no longer functions of position within the catalyst.

Equivalently in the Laplace domain, internal boundary conditions (2.35) and (2.36) can be represented by the following limiting case of the transfer matrix\(^4\) (2.16) (Constales et al., 2001a)

\[ M^{TZ} = \begin{pmatrix} 1 & 0 \\ \kappa s & 0 \\ s + k^- & 1 \end{pmatrix}, \]

where \( \kappa = S_v (1 - \epsilon_{cat}) C_{Z, tot} k^+ \Delta L_{cat} \) \((m s^{-1})\) is the Thin-Zone activity parameter. With this alteration, equation (2.34) can still be used to predict the exit flow for given linear kinetics.

Physically, equation (2.35) ensures that gas concentrations are continuous across the reactive interface and equation (2.36) states that chemical transformation rates are equal to the difference between incoming and outgoing molecular flows. The latter equation constitutes the local mass balance of the uniform catalytic zone and can be compared to mass balance equations of classical kinetic testing reactors. The mass balance of a steady-state Continuously Stirred Tank Reactor (CSTR) is

\[ F^{in} - F^{out} = v^{in} C^{in} + v^{out} C^{out} = S_{cat} R(k, C_g, C_s), \]

\(^4\)Linear rate form (2.6) is assumed for simplicity and substituted in equation (2.36).
where the inlet $v^{in}C^{in}$ and outlet $v^{out}C^{out}$ flows are driven by convection, $v$ (m$^3$s$^{-1}$) being the volumetric flow rate. Similarly, the mass balance of a steady-state differential Plug-Flow Reactor (dPFR) is

$$F^{in} - F^{out} = v^{in}C^{in} + v^{out}C^{out} = S_{cat}R(k, \bar{C}, \bar{C}'),$$

(2.39)

where spatial-average concentrations are defined as $\bar{C} = \frac{C^{inlet} + C^{outlet}}{2}$.

The macroscopic spatial non-uniformity $x\Delta C$ can be estimated as the ratio of the total concentration difference developed across the catalyst and the maximum concentration value, which for reactants is typically the initial value $C^{inlet}$:

$$x\Delta C \approx \frac{C^{inlet} - C^{outlet}}{C^{inlet}}.$$  

(2.40)

For convection-driven reactors such as CSTR or dPFR, this non-uniformity is directly proportional to the conversion $x\Delta C \propto X$. Kinetic experiments in these devices are usually limited to low conversions in order to maintain uniform composition. In the TZ TAP reactor, on the other hand, the transport is diffusion-driven and the non-uniformity is governed by a combination of geometric and kinetic factors. For example, the non-uniformity of the catalytic zone located in the middle of the microreactor can be estimated as (Shekhtman and Yablonsky, 2005)

$$x\Delta C \approx \frac{2 - X}{1 + (1 - X)L/\Delta L_{cat}}.$$  

(2.41)

The pulse conversion $X$ is defined as

$$X = \int_{0}^{t_{pulse}} \frac{F^{in}(t) - F^{out}(t)}{F^{in}(t)} dt,$$  

(2.42)

where $t_{pulse}$ is the pulse length.
According to this expression for $\Delta L_{\text{cat}}/L$ ratio of 1/30, the non-uniformity does not exceed 20% as long as conversion of a gaseous product remains below 80%. Numerical simulations further corroborate the validity of the Thin-Zone hypothesis within a broad range of conversions (Phanawadee et al., 2003). Therefore, the TZ TAP reactor significantly expands the window of spatially uniform gas and surface compositions accessible for kinetic interrogation and systematic mapping of structure-activity relationships. Spatial uniformity also has important implications for data analysis because it allows kinetically ‘model free’ decoupling of intrinsic reaction kinetics from exit flow curves.

2.2 Data analysis techniques

The main objective of TAP data analysis is to relate exit flow curves to reaction kinetics on the catalyst, specifically, to deduce how the reaction term in equation (2.1) depends on gas and surface concentrations as well as to extract intrinsic kinetic parameters $k$. A number of strategies have been developed for interpreting exit flow data based on models of transport and chemical processes occurring in the TAP reactor. These approaches are described below in order of increasing quality of their resulting kinetic information. The main difference between these methods is the strength of assumptions employed to extract the intrinsic kinetics from transient reaction-diffusion data.

2.2.1 The Standard Diffusion Curve (SDC) and kinetic fingerprints

The Standard Diffusion Curve (SDC) given by equation (2.28) represents purely diffusive passage of gas molecules through the TAP microreactor. A well tuned TAP apparatus reproduces the SDC rather well, as exemplified by the following experiment. The ascending sequence of argon pulses shown in Figure 2.5(a) was recorded for a series of pulses whose intensities increased due to slowly rising feed pressure. Although the pulse intensity and, therefore, the peak argon concentration in the microreactor increased by more than 6 times within the sequence, all exit flow curves
closely match the SDC when properly scaled. Figure 2.5(b) compares the analytical SDC with the experimental points corresponding to the smallest and largest pulses, illustrating that transport models based on 1D Knudsen diffusion are indeed accurate. The SDC provides a remarkably reliable transport standard for evaluating the intrinsic kinetics of catalytic reactions in the transient regime.

Figure 2.5: The Standard Diffusion Curve (a) Argon exit flow (a.u.) as a function of time for pulse intensities gradually increasing by a factor of six between the first and the last curves. (b) Experimental exit flows for pulses 1 and 130 compared to the Standard Diffusion Curve (SDC). Also shown are the curves corresponding to the irreversible and reversible reactions. All curves are scaled to the dimensionless exit flow $\tilde{F} = \frac{F}{N_P \epsilon L^2}$ and time $\tilde{t} = \frac{t D}{\epsilon L^2}$.

Physico-chemical interactions between gas molecules and packing particles in the microreactor cause the exit flow shape to deviate from purely diffusive behavior. Two such examples generated for the one-zone reactor using solution (2.22) are shown in Figure 2.5(b) in comparison with the SDC. When gases irreversibly adsorb or react on particle surfaces ($k^+ \neq 0$, $k^- = 0$), their normalized exit flow curves are located below the SDC due to the decrease in the amount of molecules leaving the reactor at any given time. Reversible processes ($k^+, k^- \neq 0$), on the other hand, do not change the total amount of escaping molecules and only introduce additional residence time spent by molecules on the surface or in the pores of catalytic particles. Consequently, the exit flow curve of gases reversibly interacting with packing is broader than the SDC and intersects with it when desorbing molecules balance those that are just being adsorbed. In this case, the area between the exit flow curve and the SDC
up to the point of intersection is equal to the area between these curves after the intersection. Other examples of characteristic curve shapes include the double peak and the narrow peak with a long tail, both reminiscent of fast adsorption accompanied by slow desorption, e.g. (Gleaves et al., 1997; Kondratenko et al., 1999; Goguet et al., 2006). These and other features of exit flow shapes serve as 'kinetic fingerprints' profiling simple chemical reactions against the background of the SDC. Similarly, a great deal of mechanistic insights can be gained about complex reactions by examining the order in which reactant and product molecules emerge from the microreactor. This initial qualitative assessment of exit flow curves provides valuable guidance for the quantitative analysis that follows.

2.2.2 Model fitting

The most straightforward approach to the quantitative analysis of TAP data is model fitting, a technique widely applied for parameter estimation in chemical kinetics. In brief, the experimental data are regressed with an appropriate mathematical model of a TAP reactor coupled with a candidate kinetic model of catalytic reactions. Regression routines minimize the sum of squares of residuals between experimental $F_{\text{exp}}(t)$ and model $F_{\text{mod}}(t)$ exit flow curves containing $N$ time points:

$$\sum_{i=1}^{N} (F_{\text{exp}} - F_{\text{mod}})^2 \rightarrow \text{min}.$$  \hspace{1cm} (2.43)

by adjusting the values of kinetic parameters $k$. The minimization is performed by one of several commonly used methods including the Levenberg-Marquardt, Nelder-Mead, and Powell algorithms (Press et al., 1999).

The model exit flow curves are obtained from analytical solutions if they are available or via numerical simulations utilizing mathematical models as outlined in Appendix A. This numerical modeling is typically based on the Method of Lines (MOL) in which governing equations are discretized on a computational grid using finite differences for spatial derivatives (Schiesser, 1991). The discretization turns the model from a system of PDEs to a system of time-dependent ODEs describing the evolution
of model variables at every point on the grid. The ODE system is then solved in
time by Runge-Kutta, Adams, or other available integration methods (Press et al.,
1999). More details about the methodology of model fitting applied to TAP data and
statistical assessment of estimated parameters can be found in (van der Linde et al.,
1997; Schuurman, 2007).

The advantage of fitting a numerical model is that practically any reaction mechanism
can be simulated, including those with non-linear kinetics. Usually, several kinetic
models are evaluated and the best fit is then used for estimating kinetic parameters,
e.g. (Kondratenko and Baerns, 2004). However, a major shortcoming of this approach
is that reaction mechanisms and their corresponding kinetic models must be assumed
in advance. Not only is it possible that the true mechanism was not included in
the list of candidate models, but also multiple models may describe the same set
of kinetic data with comparable accuracy, e.g. (Biegler et al., 1986; Prasad et al.,
2009). Besides this model uncertainty, fitting routines may result in time-consuming
computations which motivate development of faster techniques for data analysis such
as the method of moments.

2.2.3 Moment analysis

The \( n \)th exit flow moment is defined as

\[
M_n = \int_0^{+\infty} t^n F_{\text{exit}}(t) dt, \tag{2.44}
\]

where \( n = 0, 1, 2, \ldots \) is the number of the moment with dimension \( (s^n) \). In practice,
the upper integration limit is the duration of recorded pulses.

The zeroth moment \( (n = 0) \) is simply the area under the curve which gives the
amount of gas molecules that escaped the reactor over the course of a pulse-response
experiment. When the exit flow curve is normalized by the pulse intensity (PI), \( M_0 \)
is related to the total conversion \( X \) by
The ratio of first \((n = 1)\) and zeroth moments is the mean residence time in the microreactor for escaped gas molecules

\[
\tau_{res} = \frac{M_1}{M_0}.
\]  (2.46)

If gas molecules undergo only Knudsen diffusion without side processes such as intra-particle diffusion or chemical reactions, the residence time is determined only by their diffusion coefficient and reactor geometry according to

\[
\tau_{res,\text{diff}} = \frac{\epsilon L^2}{D}.
\]  (2.47)

Relations (2.46) and (2.47) are used to determine the diffusion coefficient of the inert gas from the experimental exit flow. Taking into account equation (2.5), diffusion coefficients of other gases can then be calculated from the diffusion coefficient of the inert gas using the following expression for the ratio of any two Knudsen diffusion coefficients

\[
\frac{D_1}{D_2} = \sqrt{\frac{T_1 M_{a,2}}{T_2 M_{a,2}}}.
\]  (2.48)

If in addition to Knudsen diffusion gas molecules participate in chemical reactions on their way through the microreactor, basic analysis of exit flow moments can provide essential mass balance and kinetic characteristics for these reactions. The mass balance can be assessed by examining reactant conversions given by equation (2.45) and product selectivities calculated as ratios of product zeroth moments and reactant conversions. Conversions can then be used to calculate first order apparent kinetic constants if the residence time in the catalytic zone is known. In the TZ case, the residence time is given by

\[
M_0 = 1 - X.
\]  (2.45)
\[
\tau_{res}^{TZ} = \tau \frac{\Delta L_{cat} \Delta L_{in2}}{D},
\]  

(2.49)

where \(\Delta L_{cat} \ (m)\) is the length of the catalytic zone and \(\Delta L_{in2} \ (m)\) is the length of the second inert zone.

For the first order reaction, the apparent kinetic constant for a particular reactant can be found, analogously to the CSTR (see equations (2.36) and (2.38)), from its conversion and residence time using the following simple expression

\[
k_{app} = \frac{X}{1 - X} \frac{1}{\tau_{res}^{TZ}}.
\]  

(2.50)

While in a state-defining single-pulse experiment this apparent constant characterizes a uniform well-defined catalyst state, in a state-altering single-pulse experiment it represents the time-average activity of a range of uniform catalytic states. For this reason, the quality of kinetic analysis critically depends on whether a particular pulse-response experiment is state-defining or state-altering. Currently, a distinction between these two types is made solely based on rules-of-thumb such as the variability of several sequential exit flow curves in the course of a multi-pulse experiment. Pulses are assumed to be state-defining if their shapes and moments do not change considerably from pulse to pulse. This rule, of course, makes sense only for conversions below 100 %. Provided such an assertion is justified, equation 2.50 is the simplest way to relate the observed catalytic activity to a particular catalyst state.

Kinetic parameters of more complex multi-step mechanisms can be estimated from reactant and product exit flow moments using a set of algebraic equations. These equations can be derived for a particular mechanism using one of the following two methods:

1. First, the reactor model formulated as a system of PDEs for gas and surface concentrations, such as equations (2.1) and (2.2), is analytically differentiated with respect to space. This translates governing equations for concentrations into equations for molecular flows. Then, flow equations are integrated with

---

The mechanism must still be assumed in advance.
respect to time which, according to the definition of moments (2.44), leads to a system of ODEs for the distribution of moments along the reactor axis (Yablonskii et al., 1998). The solution of this system at $x = L$ provides analytical expressions for exit flow moments as functions of kinetic and transport parameters.

2. Alternatively, existing analytical solutions for the exit flow obtained via separation of variables or Laplace domain techniques can be substituted directly into the definition of moments (2.44). This approach was eloquently presented in (Constales et al., 2001a) where it was shown that the global transfer matrix can be related to exit flow moments by

$$\mathcal{L} F^{\text{exit}}(x = L, t) = \frac{1}{P_{22}(s)} = M_0 - M_1 \frac{s}{1!} + M_2 \frac{s^2}{2!} - \cdots. \tag{2.51}$$

Thus, exact mathematical expressions can always be obtained for a general multi-zone TAP reactor with linear and pseudo-linear mechanisms.

With the help of these two methods, analytical expressions for exit flow moments in terms of kinetic and transport parameters have been obtained for numerous model mechanisms in one-zone (Gleaves et al., 1997; Yablonskii et al., 1998), three-zone (Phanawadee et al., 1999; Dewaele and Froment, 1999), and Thin-Zone (Shekhtman et al., 1999) reactors. Although such expressions are very convenient for parameter estimation, their use is merely a modified model fitting routine and shares the major disadvantages of assuming the reaction mechanism in advance. Subsequent developments in TAP data analysis have been focused on those methods that are capable of decoupling chemical kinetics from transport phenomena with minimal a priori assumptions about the reaction mechanism.

### 2.2.4 Primary kinetic coefficients

The first partially 'model free' extraction of intrinsic physico-chemical characteristics from reaction-diffusion TAP data has been suggested in (Shekhtman et al., 2003) where exit flow moments were linked to primary kinetic coefficients. The main idea behind the method of primary coefficients is to express transient reaction rates as
functions of only concentrations of gas substances and time-derivatives thereof using a phenomenological representation of the form

\[
R(t) = r_0 C_g(t) + \sum_{n=1}^{\infty} r_n \frac{d^n C_g(t)}{dt^n}, \quad n = 0, 1, 2, ...
\]  

(2.52)

Surface concentrations, intrinsic kinetic parameters, and the structure of the reaction mechanism enter this expansion only implicitly through primary kinetic coefficients \( r_n \). Under certain restrictions placed on the reaction mechanism, numerical values of these primary kinetic coefficients can always be extracted from exit flow moments and do not require a particular kinetic model. Below, we summarize mechanistic restrictions needed to derive expression (2.52) and define the range of validity of this data analysis method.

First, it is assumed that the rate of an elementary step in which a given gas substance is consumed by the surface is linear with respect to this gas. This widely accepted assumption for gas-solid reactions implies that only one gas molecule participates in every elementary step. This is usually the case because the probability of two gas molecules simultaneously colliding with the same site on a catalytic surface is very low. Second, the experiment is assumed to be state-defining with respect to surface concentrations. If these two assumptions are valid, then the reaction rate for gas \( i \) is linear with respect to all gas and surface concentrations:

\[
R_{g,i}(k_{CS}, C_g, C_s) = k_{CS,i} C_{g,i}(x,t) + \sum_q k_{CS,q} C_{s,q}(x,t),
\]

(2.53)

where kinetic parameters \( k_{CS} \) depend on the catalyst state and also include stoichiometric coefficients. These kinetic parameters are determined by intrinsic kinetic constants \( k \) and surface concentrations \( C_{CS} \) which define catalytic properties but are themselves assumed not to change within a pulse, i.e. \( k_{CS} = \{k, C_{CS}\} \). Dynamic surface concentrations \( C_s \) do change inside the pulse, but not significantly enough to cause any changes in \( C_{CS} \). Concentrations of these dynamic surface species \( C_s \) can be expressed as a linear combination of gas concentrations in the Laplace domain:
\[ \mathcal{L} C_{s,q}(x, s) = \sum_q \alpha_{q_i}(k_{CS}, s) \mathcal{L} C_{g,i}(x, s), \]  

(2.54)

where coefficients \( \alpha_{q_i}(s) \) do not depend on the axial position. Substituting this linear combination into the Laplace transform of (2.53) results in

\[ \mathcal{L} R_{g,i}(k_{CS}, x, s) = \sum_j r^{ij}(k_{CS}, s) \mathcal{L} C_{g,j}(x, s), \]  

(2.55)

where \( r^{ij}(k_{CS}, s) \) are elements of the reactivity matrix which relates the vector of gas concentrations to the vector of reaction rates in the Laplace domain.

Next, another mechanism restriction is made by considering only catalytic processes with one reagent in which products can not be converted back into the reagent. For such a process, the reactivity \( r^{ij} \) of gas \( i \) with respect to the only reagent \( j \) can be expanded as a series around the Laplace variable \( s = 0 \) in powers of \( s \):

\[ \mathcal{L} R_{g,i}(k_{CS}, x, s) = (r^i_0(k_{CS}) + r^i_1(k_{CS})s + r^i_2(k_{CS})s^2 + \cdots) \mathcal{L} C_{g,i}(x, s) \]  

(2.56)

or equivalently in the time domain

\[ R_{g,i}(k_{CS}, x, t) = r^i_0(k_{CS})C_{g,j}(x, t) + r^i_1(k_{CS}) \frac{dC_{g,j}(x, t)}{dt} + r^i_2(k_{CS}) \frac{d^2C_{g,j}(x, t)}{dt^2} + \cdots, \]  

(2.57)

where \( r^i_n \) are primary kinetic coefficients. The zeroth coefficient \( r^i_0 (s^{-1}) \) represents an apparent kinetic constant for gas \( i \), the dimensionless first coefficient \( r^i_1 \) represents an apparent constant of the release of gas \( i \) from preceding surface intermediate, and the second coefficient \( r^i_2 (s) \) represents an apparent time delay caused by surface or

\(^{6}\) Reactivity \( r^{ij} \) is self-reactivity when \( i = j \).
intra-particle processes. Coefficients of higher orders have no clear physico-chemical meaning and are not considered further.

As mentioned earlier, primary kinetic coefficients $r_n$ are functions of the reaction mechanism, surface concentrations, and intrinsic kinetic parameters and represent the kinetic effect that a catalytic surface has on a given gaseous substance. For a given reactor configuration, these coefficients can be found directly from exit flow moments $M_n$ using algebraic equations derived in (Shekhtman et al., 2003). This data analysis step, i.e. ($\{M_n\} \rightarrow \{r_n\}$), does not require a particular rate form, as long as the reaction mechanism complies with previously discussed linearity assumptions. Once a mechanistic hypothesis is independently formulated, primary coefficients can be interpreted in terms of intrinsic parameters of the corresponding kinetic model, i.e. ($\{r_n\} \rightarrow \{k\}$). The relationship between model parameters and primary kinetic coefficients for a number of useful mechanisms can be found in Table 1 of (Shekhtman et al., 2003).

In our work, we have used the method of primary kinetic coefficients to characterize reversible CO adsorption on gold catalysts (see Chapter 4 section 4.3.1). For reversible processes with zero total conversion, coefficient $r_0$ is always zero and coefficients $r_1$ and $r_2$ can be found from exit flow moments using

$$\frac{M_1}{M_0} = \left( \frac{\Delta L_{in2}}{D_{in2}} + \frac{\Delta L_{cat}}{2D_{cat}} \right) \left( 2\Delta L_{in2}\epsilon_{in2} + \Delta L_{in2}(\epsilon_{cat} + r_1) \right),$$  \hspace{1cm} (2.58)

$$\frac{M_2}{M_0} - \frac{5}{3} \left( \frac{M_1}{M_0} \right)^2 = \frac{(\Delta L_{in2})^2 (\Delta L_{cat})^2}{3} \left( \frac{\epsilon_{cat} + r_1}{D_{in2}} - \frac{\epsilon_{in2}}{D_{cat}} \right)^2 - r_2\Delta L_{cat} \left( \frac{2\Delta L_{in2}}{D_{in2}} + \frac{\Delta L_{cat}}{D_{cat}} \right).$$  \hspace{1cm} (2.59)

The absolute value of the first primary coefficient is related to the apparent equilibrium constant by

$$|r_1| = \frac{k_a}{k_d},$$  \hspace{1cm} (2.60)
where \( k_a \) (s\(^{-1}\)) is the apparent adsorption constant including the total concentration of active sites and \( k_d \) (s\(^{-1}\)) is the desorption constant. The latter can be found from the absolute value of the ratio of second and first primary coefficients:

\[
\left| \frac{r_2}{r_1} \right| = \frac{1}{k_d}.
\]  

(2.61)

More experimental applications of this method can be found in (Shekhtman et al., 2003, 2008; Morgan et al., 2010). Importantly, the only restriction placed on reaction mechanisms in order to obtain primary kinetic coefficients is that of linearity with respect to gas and surface concentrations. Therefore, this method is an important step towards kinetically 'model free' decoupling of catalytic kinetics from transport processes which was not fully achieved until development of the Y-Procedure.

### 2.2.5 The Y-Procedure

The most advanced method for TZ TAP data analysis is the Y-Procedure suggested by Yablonsky in (Yablonsky et al., 2007). This algorithm extracts transient reaction rates \( R^{TZ}(x = L_{TZ}, t) \) and gas concentrations \( C_g^{TZ}(x = L_{TZ}, t) \) in the catalyst zone from exit flows of reactants and products \( F_{\text{exit}}(x = L, t) \) with no prior assumptions about the mechanism of the catalytic reaction or its corresponding rate form. In essence, the Y-Procedure uses transport and kinetic properties of inert zones to reconstruct the local mass balance of the catalytic zone for every time point from the global mass balance of the entire reactor. Two key factors enabling such a reconstruction are 1) the well-defined transport process across inert zones, and 2) the macroscopic uniformity of the catalyst zone. When these conditions are met, it is possible to solve the inverse diffusion problem for the mathematical model of TZ TAP experiments outlined in section 2.1.4, thereby relating experimentally measured exit flow at \( x = L \) to boundary conditions on the catalyst zone (2.35) and (2.36) at \( x = L_{TZ} \).

In order to solve the inverse diffusion problem, we recall that inert zones in the microreactor satisfy the transfer matrix equation (2.15). Furthermore, the Thin-Zone TAP reactor is fully described by two such matrix equations which linearly relate eight quantities, namely, \( C_g(x = 0, t), C_g^{(I)}(x = L_{TZ}, t), C_g^{(II)}(x = L_{TZ}, t), C_g(x = L, t), \)


$F(x = 0, t), F^{(I)}(x = L_{TZ}, t), F^{(II)}(x = L_{TZ}, t)$, and $F(x = L, t)$. Two of these quantities are known in advance through boundary conditions (2.18) and (2.19). The exit flow is measured experimentally, and one more quantity is accounted for due to the concentration continuity across the Thin-Zone (2.35). Consequently, we can find the other four missing quantities as schematically shown in Figure 2.6.

Figure 2.6: Schematic representation of the Y-Procedure The TZ gas concentration and flow leaving the TZ are determined using two boundary conditions known at the reactor exit. The flow entering the TZ is determined (along with the gas concentration at the reactor entrance) using the flow boundary condition at the reactor entrance and TZ gas concentration. The TZ reaction rate is then obtained as a difference between flows entering and leaving the TZ.

The experimental exit flow is a discrete signal measured by the QMS and is subject to noise (Roelant et al., 2007). Because the inverse diffusion operation is mathematically ill-posed, high-frequency components of this noise will be amplified by the Y-Procedure. For practical reasons of handling discrete noisy signals, the algorithm operates with the Fourier domain equivalent of the transfer matrix equation obtained from the original Laplace domain solution using the following mapping

$$\mathcal{L} f(s) \mapsto \mathcal{F} f(\omega), \quad s = i \omega, \quad (2.62)$$

where $\mathcal{F}$ denotes the Fourier transform and $i$ is the imaginary unit. Additionally, a smoothing function is introduced for filtering out the high-frequency noise.

The full derivation of Y-Procedure equations can be found in (Yablonsky et al., 2007); Here, we present their final version used in practice. Combining transfer matrix equations (2.15) for two inert zones, all known boundary conditions, and the TZ
mass balance (2.36), Y-Procedure equations in the Fourier domain take the following form

\[ \mathcal{F} C^{TZ}(\omega) = Y_c(\omega) \mathcal{F} F_{\text{exit}}(\omega) W(\omega), \]  
\[ \mathcal{F} R^{TZ}(\omega) = Y_r(\omega) \left( \mathcal{F} F_{\text{ctrl/exit}}^{\text{exit}}(\omega) - \mathcal{F} F_{\text{exit}}(\omega) \right) W(\omega), \]  

where \( \omega \) is the collection of frequencies for a signal measured at \( N \) equally spaced time points (\( N \) is even) separated by small intervals \( h \):

\[ \omega = 2n\pi/Nh \quad n = -N/2 + 1, \ldots, N/2. \]  

For pure Knudsen diffusion in inert zones, functions \( Y_c(\omega), Y_r(\omega), \) and \( W(\omega) \) in equation (2.64) are defined as

\[ Y_c(\omega) = \left( \frac{\sinh \sqrt{i\omega\tau_2}}{\gamma_2 \sqrt{i\omega\tau_2}} \right), \]  
\[ Y_r(\omega) = \left( \cosh \sqrt{i\omega\tau_2} + \frac{\tau_1}{\tau_2} \left( \frac{\sinh \sqrt{i\omega\tau_1}}{\cosh \sqrt{i\omega\tau_1}} \right) \right), \]  
\[ W(\omega) = e^{-\omega^2 h^2 \sigma^2/2}, \]

where dimensionless parameter \( \sigma \) controls the degree of noise filtering. Functions \( Y_c(\omega) \) and \( Y_r(\omega) \) depend only on geometric and transport properties of inert zones. Therefore, the Y-Procedure is a kinetically 'model free' algorithm and does not require prior assumptions about the reaction mechanism for reconstructing catalytic kinetics from exit flows.

In equation (2.64), \( F_{\text{exit}}^{\text{ctrl}} \) is the exit flow which represents gas transport in the absence of catalytic reactions. In the ideal case when the inlet pulse approaches Dirac delta
function and the gas transport is purely Knudsen, this term is equivalent to the SDC. However, \( F_{\text{exit}}^{\text{ctrl}} \) should be always measured independently in order to account for possible deviations of the inlet pulse shape from delta function and interactions of gases with inert material.

In practice, the reconstruction of catalytic kinetics involves the following steps:

1. Measure control exit flows with inert packing only.
2. Measure exit flows in catalytic experiments.
3. Calculate Fourier transforms of gas exit flows \( \mathcal{F} F_{\text{exit}}^{\text{ctrl}}(\omega) \) and \( \mathcal{F} F_{\text{exit}}(\omega) \) by using Fast Fourier Transform (FFT) algorithms.
4. Calculate Fourier transforms of gas concentrations and reaction rates in the catalyst zone by applying equations (2.63) and (2.64).
5. Recover gas concentrations \( C_{TZ}(t) \) and reaction rates \( R_{TZ}(t) \) from their Fourier transforms using Inverse FFT algorithms.

Previously, the Y-Procedure was illustrated in the literature by only one numerical example concerning a state-defining experiment with a simple first order irreversible reaction on the catalyst (Yablonsky et al., 2007). As expected, the reconstructed reaction rate was linear with respect to the reconstructed gas concentration and the slope of this dependency was equal to the apparent kinetic constant. The Y-Procedure analysis of more complex mechanisms, non-linear kinetics, and state-altering experiments has not been reported.

### 2.2.6 Analysis of multi-pulse sequences

Hitherto, the discussion of TAP data analysis has been focused on extracting mass balance and kinetic characteristics from a single pulse-response experiment. Practical TAP experiments usually involve sequences of many such pulses in order to examine how catalytic behavior changes as a function of the catalyst state. Multi-pulse experiments can be classified into several categories depending on their objectives:
• **Simple titration.** The main goal of simple titration is to estimate the total concentration of empty surface sites or previously adsorbed species by measuring the amount of probe molecules adsorbed or released over the entire multi-pulse sequence. For example, multi-pulse oxygen uptake followed by CO titration can be used for measuring the total oxygen storage capacity of supported metal catalysts, e.g. (Nishiguchi et al., 2003; Widmann et al., 2010). Another example of the multi-pulse titration technique is determining the amount of coke on the catalytic surface by burning carbon deposits off with a sequence of oxygen pulses while monitoring the total amount of produced carbon dioxide (Basso et al., 1991).

• **Titration with kinetic analysis.** TAP titration experiments can reveal more subtle mechanistic details if the evolution of kinetic properties within multi-pulse sequences is analyzed in addition to the total gas consumption. For instance, (Shekhtman et al., 2008) postulated the presence of two types of active sites on the Pt/CeO$_2$ catalysts based on two distinct regions of kinetic behavior observed in multi-pulse CO oxidation experiments.

• **Temperature ramp.** Thermally programmed multi-pulse sequences are performed in order to screen reaction kinetics over a wide temperature range. Such experiments provide data for estimating activation parameters, e.g. (Fushimi et al., 2005), and are in many ways equivalent to conventional Temperature Programmed Reaction (TPR) methods (Falconer and Schwarz, 1983). A unique example worth mentioning is that of thermally programmed CO titration of oxygen on palladium catalysts which revealed kinetic oscillations, suggesting complex interactions between different atomic layers near the catalytic surface or between metallic and oxide phases (Fushimi et al., 2007).

• **Pump-probe cycles.** In pump-probe multi-pulse experiments, two gaseous reactants are always pulsed sequentially. The pump-pulse prepares a short-lived catalyst state which is then sampled by the following probe-pulse. Lifetimes of surface intermediates and 'hidden' surface steps of catalytic reactions can be revealed by determining how the product formation depends on the time delay between pump and probe pulses. Examples of pump-probe experiments can be found in (Hinz, 1999; Perez-Ramirez et al., 2005; Goguet et al., 2006),
From the theoretical point of view, the idea common to all these categories is to prepare a well defined state of the catalyst and then characterize it kinetically. Preferably, each pulse in a sequence should be state-defining so that kinetic behavior and catalyst states can be assessed separately. Within a single state-defining pulse, many simplifications of the reaction mechanism can be assumed in order to extract apparent kinetic parameters by one of the methods presented earlier. Gradual catalyst modification over many pulses, either by the kinetic probe itself, other reagents, or temperature, leads to parametric dependencies of apparent kinetic parameters on the catalyst state:

\[ k_{app} = f(C_{CS}, k(T)). \] (2.69)

Kinetic properties \( k_{app} \) can be presented on the normalized scale of catalyst states, which spans two extreme values of surface compositions \( C_{CS,\text{min}} \) and \( C_{CS,\text{max}} \). These characteristics form the 'kinetic passport' of a given catalyst, providing a quantitative basis for comparing performances of different catalysts. The interpretation of such dependencies can help to refine the reaction mechanism and estimate its intrinsic kinetic parameters \( k \). To date, a unified theoretical framework for interpreting multipulse experiments has not been suggested.

### 2.3 Concluding remarks

It is safe to assert that the theory of TAP pulse-response experiments in the Knudsen transport regime is well developed and can be used to accurately predict exit flow curves for various reactor configurations, given that the kinetic model for reactions on the catalyst is known. A general solution of the direct problem, i.e. simulating exit flow curves, is given for an arbitrary linear reaction mechanism in a multi-zone TAP reactor by equation (2.34). Reactor models with non-linear reaction mechanisms can also be solved via numerical methods. Within this theoretical framework, the Thin-Zone TAP reactor corresponds to a limiting case of the three-zone reactor when the entire catalytic zone is reduced to the reactive interface between two inert zones. This configuration enables precise measurements of intrinsic kinetic properties.
of multi-component technical catalysts and relates these properties to a macroscopically uniform catalyst state. Despite significant progress recently achieved by the TAP methodology, the inverse problem of deducing reaction kinetics in the catalytic zone from exit flow curves is far from being unambiguously solved.

Commonly used regression of exit flow curves with numerical or analytical models relies on strong kinetic assumptions about reaction mechanisms in order to solve the inverse problem. The same is true for primitive moment analysis which relates exit flow moments to kinetic parameters of an \textit{a priori} postulated reaction mechanism. These model-dependent approaches should not be used for model discrimination, unless the mechanism is proven independently. Instead, TAP data should be initially analyzed in the 'model free' manner using the concept of primary kinetic coefficients to gain physico-chemical insights into the nature of catalytic reactions. These coefficients can then be related to parameters of a particular kinetic model which is consistent with experimental observations over a wide range of catalyst states and operating temperatures. In spite of its clear advantages over simple data regression, the method of primary kinetic coefficients has not to date been systematically applied in practice in part due to the mathematical complexity of algebraic equations which translate exit flow moments into primary kinetic coefficients.

Unlike kinetic characteristics of gaseous species, the evolution of surface intermediates is usually not directly monitored in TAP experiments. Changes of surface concentrations have been deduced from the overall pulse-to-pulse mass balance, that is, how many molecules were consumed or released during previous pulses. Albeit modifications of catalyst composition in multi-pulse TAP experiments are significantly more resolved than both steady-state and SSITKA data, the temporal resolution of interpulse mass balances was still limited to seconds because exit flow curves must be integrated in order to calculate moments. To conclude, the integral moment analysis has major inherent shortcomings including:

- Non-linear kinetic models cannot be analyzed.
- It is insensitive to fast surface reactions on the sub-second time scale.
- Surface intermediates in reversible reactions completely desorb by the end of each pulse and cannot be tracked by the pulse-to-pulse mass balance.
The general matrix form for primary kinetic coefficients of a multi-response reaction network is not available.

The Y-Procedure alleviates the limitations of moment analysis by reconstructing transient reaction rates and gas concentrations in the catalytic zone from exit flow curves. These non-steady-state kinetic characteristics are more advantageous for microkinetic analysis than primary kinetic coefficients because they can be directly related to the standard formalism of chemical kinetics. Furthermore, the Y-Procedure is devoid of a priori mechanistic assumptions and is, therefore, applicable to non-linear kinetics and state-altering experiments. These advantages motivate further research towards the development of a comprehensive methodology for unraveling complex catalytic mechanisms based on a systematic application of the Y-Procedure. In the next chapter, further developments of the Y-Procedure methodology are presented and exemplified by numerical simulations.
In the previous chapter we concluded that the Y-Procedure is a superior TAP data analysis method because of the intra-pulse\textsuperscript{7} kinetic characteristics it provides, including rates of reactions and gas concentrations in the catalytic zone. These quantities are obtained with millisecond time resolution and are free of any prior assumptions about the reaction mechanism. In this chapter, we show how gas phase kinetic information given by the Y-Procedure can be further scrutinized to reveal time-dependent catalyst composition, facilitate elucidation of reaction pathways, and estimate intrinsic kinetic parameters. These theoretical developments are validated by experimental applications in the following chapter and form a solid foundation for advanced non-steady-state catalyst characterization using Thin-Zone TAP experiments.

In section 3.1, a post-processing step is introduced in which the reaction rates of gaseous substances are used for calculating transient surface storages which are defined as uptake minus release of certain atoms or groups of atoms by the catalytic surface. These storages coincide, in some cases, with concentrations of surface intermediates and can be used as compositional descriptors of the catalyst state evolving within each pulse. In section 3.2, we also suggest a simple geometric representation of intra-pulse transient data obtained via the Y-Procedure as trajectories in the kinetic rate/composition space.

\textsuperscript{7}Hereafter, the term “intra-pulse“ is used as a synonym of ”within the pulse”.

45
The remaining sections of this chapter focus on numerical simulations of model reactions with a special emphasis on mechanism identification and parameter estimation. The main purpose of analyzing model reactions is to identify characteristic features of their transient behavior which can be used as kinetic fingerprints for corresponding mechanistic motifs and facilitate the interpretation of experimental data for more realistic reactions. Synthetic exit flow data for model reactions were generated using numerical simulations of the Thin-Zone TAP reactor described in Appendix A and then analyzed via the Y-Procedure and novel post-processing steps. First, irreversible and reversible adsorption steps with coverage-dependent kinetics are discussed in sections 3.3 and 3.4. Next section 3.5 introduces the principle of temporal kinetic coherence for a robust discrimination between multi-step reaction mechanisms. This principle is then demonstrated using two-route CO oxidation in section 3.6 and irreversible isomerisation in section 3.7. Concluding remarks in the end of the chapter provide a short discussion on our key theoretical and numerical findings.

### 3.1 Relating gaseous kinetics to surface storages

In concluding remarks 2.3 to Chapter 2 it was noted that precise characterization of the catalyst composition during TZ TAP experiments is hindered by the low temporal resolution of moment analysis. On the contrary, the Y-Procedure enables direct calculation of surface storages within each pulse from reconstructed reaction rates in the catalytic zone. By a surface storage we understand the difference between the total uptake and release of certain moieties, such as individual atoms or groups of atoms, from the catalytic surface up to a given point in time. These storages can be found by integrating the sum of reaction rates of those elementary steps in which the moiety participates. Taking into account stoichiometric coefficients and standard sign convention, a surface storage at time \( t \) elapsed since the beginning of the pulse is given by

\[
C_s(t) = C_{s,\text{in}} + \int_0^t \left( \sum_i \nu_i R_i^+(t') - \sum_i \nu_i R_i^-(t') \right) dt',
\]  

(3.1)
where $C_{s,in}$ is the initial storage, $\nu_i$ is the stoichiometric coefficient of moiety with surface concentration $C_s$ in the $i$th step. The plus sign corresponds to the reaction steps in which the moiety is emitted into the gas phase and the minus sign to those steps in which it is consumed. In essence, equation (3.1) expresses the non-steady-state mass balance of the catalytic surface.

The relationship between surface storages and kinetically individual surface intermediates is determined by the particular reaction mechanism under analysis. Regardless of stoichiometry, elementary steps of all catalytic reactions can be categorized into three general types which differ by the amount of molecules exchanged between gas and surface phases:

1. **Type 1: only one gas is involved** Examples falling into this category include molecular adsorption steps $Z + A = ZA$, dissociative adsorption steps $2Z + A_2 = 2ZA$, and surface reactions with gas release $ZA + ZB = 2Z + AB$. Empty surface sites are also treated as intermediates. Such reaction steps couple each surface intermediate to only one gas.

2. **Type 2: two gases are involved** Steps of this type, which can be represented as $Z + G = Z'' + G'$, couple each surface intermediate to two gas substances ($G$ and $G'$). One of the gases is consumed while the other is released.

3. **Type 3: no gases are involved** Only surface substances participate in this type of steps, i.e. $Z + Z' = Z'' + Z'''$.

If only elementary steps of types 1 and 2 occur in the mechanism, the net rates of all surface species can be uniquely expressed as linear combinations of gas reaction rates. For example, consider a reaction in which gas $A$ is oxidized by oxygen according to the combination of steps shown in Table 3.1. Here, gas $AO_2$ is produced in parallel to gas $AO$. In another combination of steps shown in Table 3.2, $AO_2$ is produced sequentially from $AO$. Subscripts $s$ and $g$ in these tables indicate surface and gas, respectively, but are not shown further. Consider also both combinations of steps simultaneously.

In these reaction mechanisms, oxygen appears on the surface only as intermediate $ZO$ whose net reaction rate can be expressed through gas substances as
Table 3.1: **Elementary steps involved in the parallel oxidation mechanism**

<table>
<thead>
<tr>
<th>Elementary step</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>(1) $O_2,g + 2Z_s = 2ZO_s$</td>
<td>$r_1$</td>
</tr>
<tr>
<td>(2) $A_g + Z_s = ZA_s$</td>
<td>$r_2$</td>
</tr>
<tr>
<td>(3) $ZO_s + ZA_s = 2Z_s + AO_s$</td>
<td>$r_3$</td>
</tr>
<tr>
<td>(4) $2ZO_s + ZA_s = 3Z_s + AO_{2,g}$</td>
<td>$r_4$</td>
</tr>
</tbody>
</table>

Table 3.2: **Elementary steps involved in the sequential oxidation mechanism**

<table>
<thead>
<tr>
<th>Elementary step</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>(1) $O_2,g + 2Z_s = 2ZO_s$</td>
<td>$r_1$</td>
</tr>
<tr>
<td>(2) $A_g + Z_s = ZA_s$</td>
<td>$r_2$</td>
</tr>
<tr>
<td>(3) $ZO_s + ZA_s = 2Z_s + AO_s$</td>
<td>$r_3$</td>
</tr>
<tr>
<td>(5) $ZO_s + AO_g = Z_s + AO_{2,g}$</td>
<td>$r_5$</td>
</tr>
</tbody>
</table>

\[
R_{ZO} = [\text{Uptake} - \text{Release}] = [2R_{O_2}] - [R_{AO} + 2R_{AO_2}] = 2r_1 - r_3 + r_5 - 2(r_4 + r_5) = 2r_1 - r_3 - 2r_4 - r_5. \tag{3.2}
\]

Similarly, the net rate of surface intermediate $ZA$ is given by

\[
R_{ZA} = [\text{Uptake} - \text{Release}] = [R_A] - [R_{AO} + R_{AO_2}] = r_2 - r_3 + r_5 - (r_4 + r_5) = r_2 - r_3 - r_4. \tag{3.3}
\]

The rate of free active sites $Z$ can then be expressed from the total surface mass balance $C_{Z,\text{tot}} = C_Z + C_{ZO} + C_{ZA}$ as

\[
R_Z = [\text{Gain} - \text{Loss}] = -[R_{ZO} + R_{ZA}] = -2r_1 - r_2 + 2r_3 + 3r_4 + r_5. \tag{3.4}
\]
In the combined mechanism, product $AO_2$ is produced via two routes: steps (1,2,4) and steps (1,2,3,5). An important observation is that net rates of surface intermediates can still be determined individually because some elementary rates cancel out. Section 3.6 elaborates on the implication of this property for mechanism identification by considering another example of a two-route mechanism, $CO$ oxidation.

If steps without exchange with gas phase (type 3) also occur in the mechanism, it is generally impossible to express net rates of all surface intermediates as a combination of gaseous reaction rates. For these and more complex mechanisms which do not permit isolation of the net rates of all intermediates, only the combined concentrations of several surface intermediates can be uniquely characterized. However, these combined storages may still be used for elucidating purely surface reaction steps of type 3 as discussed further in section 3.7. The direct measurement of individual surface intermediates in complex mechanisms with surface steps of type 3 may be achieved in future generations of TAP systems which may be coupled with *in situ* spectroscopy. The next subsection introduces a physical metaphor which can facilitate the analysis of individual reaction steps in a TAP pulse-response experiment and the estimation of intrinsic kinetic parameters.

### 3.2 Pulse-response experiments as trajectories in the rate/composition space

The Y-Procedure analysis of TZ TAP data followed by the calculation of surface storages provides transient kinetic characteristics in the catalytic zone summarized in information flow diagram 3.1. In order to use these characteristics for gaining deeper insights into reaction mechanisms, we suggest a simple geometric interpretation of pulse-response experiments as transient trajectories of a reacting system\(^8\) in a space spanned by gas concentrations, surface concentrations, and reaction rates in the catalyst zone treated as independent coordinates, i.e. $\{C_g, C_s, R\}$. We refer to this space hereafter as the rate/composition (RC) space. For a particular reaction step $i$, the rate form $R_i(k, C_g, C_s)$ relates these coordinates to each other and defines a specific

---

\(^8\)By the reacting system we understand a combination of time dependent chemical variables describing gaseous and surface phases in the catalytic zone.
surface in the RC space. In order to avoid possible confusions, we will use the term RC surface for this mathematical construct to distinguish it from the catalyst surface. The behavior of the reacting system during a pulse-response experiment can be understood as follows.

![Information flow in the proposed data analysis framework](image)

Figure 3.1: **Information flow in the proposed data analysis framework** The original exit flow data are translated into gas concentrations and reaction rates via the kinetically model-free Y-Procedure. For certain mechanisms, reaction rates can be integrated to give concentrations of surface intermediates.

When we perturb the reacting system from its initial state in the RC space, it travels along a certain trajectory confined to the RC surface. In a pulse-response experiment, the perturbation is driven by the external concentration gradient. After the perturbation is removed, i.e. all molecules escape the microreactor, the reaction system will relax into its final position where it will stay until the next pulse. The final state of the system can coincide with the initial state only if the overall process is completely reversible. In this framework, each pulse of TZ TAP experiments corresponds to a trajectory in the RC space and the problem of data analysis can be formulated as determining parameters of the RC surface based on experimentally recorded trajectories. The geometric interpretation of TAP pulse-response experiments is particularly useful when the RC space is three-dimensional and kinetic trajectories can be easily visualized as illustrated in the following two sections by simple irreversible and reversible adsorption steps.

### 3.3 Irreversible adsorption

We begin the discussion of Y-Procedure analysis of model catalytic reactions with irreversible molecular adsorption of gas A on the catalyst site Z:

---

9This is often the case, since elementary steps involving more than two reactants are highly unlikely. Kinetic trajectories of higher dimensions can in principle be analyzed via numerical methods.
\[ A + Z \xrightarrow{k} ZA. \]

The non-steady-state rate for this reaction is given by

\[ R_A(t) = k \left( C_{Z,tot} - C_{ZA}(t) \right) C_A(t), \quad (3.5) \]

where \( k \) is the intrinsic adsorption constant; \( C_{Z,tot} \) is the total concentration of active sites. Numerical simulations for this model reaction were performed with parameters listed in Table 3.3. In our simulations, the effective diffusion coefficient was assumed to be the same for probe gas \( A \) and inert. We varied the pulse intensity between \( 10^{-11} \) and \( 10^{-8} \) moles of gas \( A \) per pulse in order to control the degree to which the surface was covered by irreversibly adsorbed \( A \). Each simulated pulse contained an equal amount of the inert standard and it was assumed that the gas transport remained in the Knudsen regime for given pulse intensities.

Table 3.3: Simulation parameters used for virtual TZ TAP experiments with irreversible adsorption

<table>
<thead>
<tr>
<th>System parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reactor length, L (m)</td>
<td>0.0254</td>
</tr>
<tr>
<td>Cross-sectional area, A (m²)</td>
<td>1.1 \cdot 10^{-5}</td>
</tr>
<tr>
<td>TZ (catalyst) length, L_{cat} (m)</td>
<td>\frac{1}{20} L (unless otherwise specified)</td>
</tr>
<tr>
<td>Position of the TZ middle from the entrance, L_TZ (m)</td>
<td>\frac{1}{2} L (unless otherwise specified)</td>
</tr>
<tr>
<td>Bed voidage, ( \varepsilon )</td>
<td>0.4</td>
</tr>
<tr>
<td>Specific catalyst area, S (m⁻¹)</td>
<td>1 \cdot 10^{8}</td>
</tr>
<tr>
<td>Number of discretization points in the grid, N_g</td>
<td>200</td>
</tr>
<tr>
<td>Effective diffusion coefficient, D (m² s⁻¹)</td>
<td>0.8 \cdot 10^{-3}</td>
</tr>
<tr>
<td>Intrinsic adsorption constant, k (m³ mol⁻¹ s⁻¹)</td>
<td>1 \cdot 10^{3}</td>
</tr>
<tr>
<td>Total concentration of active sites, C_{Z,tot} (mol m²)</td>
<td>5 \cdot 10^{-9}</td>
</tr>
</tbody>
</table>

All simulated experiments belong to either the single-pulse or multi-pulse category. Figure 3.2(a) shows Pulse Intensity (PI) normalized exit flow curves (s⁻¹) for a number of single-pulse experiments with an increasing number of molecules per pulse (indicated by the arrow). The pulse intensity clearly affects the shape of these curves and the total conversion. Figure 3.2(b) shows the multi-pulse result where PI normalized exit flow curves of gas \( A \) are ascending towards the inert exit flow as the number
of consecutive pulses increases. The decreasing conversion is due to irreversible uptake of A on the catalyst.

**Figure 3.2:** Virtual TZ experiments with irreversible adsorption

(a) Pulse Intensity (PI) normalized exit flow curves of gas A are shown which correspond to different single-pulse experiments. The arrow points towards increasing pulse intensity. (b) PI normalized exit flow curves of gas A corresponding to the multi-pulse experiment are shown with $0.5 \cdot 10^{-9}$ moles per pulse (one of the pulses above).

Figure 3.3 shows an example of the Y-Procedure analysis. The original exit flow data (inert and reagent A) corresponding to $0.5 \cdot 10^{-9}$ moles of A per pulse are plotted in Figure 3.3(a). The area difference between the curves indicates that 86% of A molecules underwent irreversible adsorption on the catalyst. Similar conclusions can be drawn from the reconstructed TZ gas concentrations depicted in Figure 3.3(b). The reconstructed reaction rates are presented in panel (c) which shows that the rate of A consumption also assumed the shape of a pulse, following the evolution of its gas concentration. The zero rate of inert is plotted for comparison. The inset of panel (c) shows the accumulation of ZA on the catalyst surface with relation to the total number of available active sites (dotted line).
Figure 3.3: **Example Y-Procedure results for irreversible adsorption** (a) Exit flow curves of gas A and the inert standard (pulse intensity $0.5 \cdot 10^{-9}$ moles). (b) Gas concentrations of A and the inert standard. (c) Reaction rates of A and the inert standard. The inset shows the surface concentration of $Z_A$.

The time-dependent data from panels (b), (c), and inset of (c) characterize the evolution of three coordinates in the rate/composition space, and are plotted as a single trajectory marked with a star symbol in Figure 3.4(a). The same plot shows a number of other trajectories which were obtained for pulses of various intensities. The blue solid lines represent trajectories reconstructed from exit flows via the Y-Procedure, and the black dotted lines next to them represent the original trajectories from the simulation itself. Slight deviations between reconstructed and simulated data are due to the fact that the Y-Procedure is based on a continuous representation of the diffusion equation, while numerical simulations utilize a finite discretization of the latter. The plot also contains the RC surface defined by equation (3.5). Below, kinetic trajectories in the RC space are analyzed separately for single- and multi-pulse experiments.
Figure 3.4: **The interpretation of transient kinetic characteristics for irreversible adsorption** (a) Blue solid lines show reconstructed trajectories. Black dotted lines show simulated trajectories. Black solid lines show trajectories projected onto $R - C_g$ plane. The RC surface defined by equation (3.5) is also shown (wire frame). The white arrow indicates increasing pulse intensity $N_P$. The pulses marked with star symbols are used in other panels. (b) Rate vs. gas concentration plot for the pulse which is smaller than *. (c) $R/C \cdot 10^6$ ($m \cdot s^{-1}$) ratio as a function of $ZA$ concentration for the pulse marked with ***. The inset shows the corresponding data range. (d) Rate vs. gas concentration plot for the multi-pulse experiment (pulses * through **). (e) The apparent kinetic constant as a function of $ZA$ concentration.
3.3.1 Single-pulse experiment

In Figure 3.4(a), single-pulse trajectories emanate from the same initial condition: a clean catalyst surface with zero coverage ($C_{ZA} = 0$) and zero gas concentration ($C_A = 0$). In the beginning of an experiment, the gas concentration and reaction rate increase under external forcing by the diffusive molecular flux of $A$. The time direction is indicated by the black curved arrow. After the forcing is removed, the system ‘rolls down’ the RC surface and finally rests on the surface concentration axis. The final position is shifted from the initial condition along this axis by a total amount of gas $A$ adsorbed during a pulse. The two largest simulated pulses ($0.8 \cdot 10^{-8}$ and $1 \cdot 10^{-8}$ moles per pulse) both end up at $C_{Z_{tot}}$ where the surface is fully occupied.

The patch of the RC surface sampled by a trajectory grows as the pulse intensity increases in the direction indicated by the broad white arrow. Importantly, the shape of the trajectory is also changing in this direction. The larger the sampled area, the more non-linear the kinetic surface. This shape change is best illustrated by projecting trajectories onto the $R - C_g$ plane of the graph (black solid lines). When the pulse is sufficiently small, the projection appears to be linear as illustrated in panel (b) for a very small state-defining pulse of $1 \cdot 10^{-10}$ moles. The pulse is too small to be seen in panel (a) below the pulse marked with a star, and is therefore marked as $< \star$. This $R - C_g$ projection corresponds to a classic rate vs. concentration linear plot from which only one kinetic parameter can be extracted. This parameter is the apparent adsorption constant for a clean surface $k_{app} \approx kC_{Z_{tot}}$ given by the slope of the line.

On the contrary, larger pulses (state-altering) clearly demonstrate the non-linear behavior as evident from their petal-like projections on to the $R - C_g$ plane in panel (a). Although the reaction rate is still linear with respect to the apparent adsorption constant and gas concentration, the former is now time dependent, and changes within the pulse. The decrease in the apparent kinetic constant during such state-altering experiments can be used to extract both the total concentration of active sites and the intrinsic adsorption constant from a single transient kinetic experiment. It should be emphasized that this information can be obtained by observing the transient behavior of the catalyst, rather than via steady-state measurements or integral moment.
analysis. The parameters can be conveniently extracted from these data by dividing equation (3.5) by the gas concentration:

\[
\frac{R_A(t)}{C_A(t)} = kC_{Z,tot} - kC_{ZA}(t).
\] (3.6)

Figure 3.7(c) plots state-altering data in coordinates \( R_A(t)/C_A(t) \) vs. \( C_{ZA}(t) \) for the pulse of \( 0.4 \cdot 10^{-8} \) moles marked with three star symbols. The slope provides the intrinsic kinetic constant, while the x-intercept gives the total concentration of active sites. The data plotted in Figure 3.4(c) cover only a fraction of the entire pulse. The representative part of the original exit flow curve is bounded by two vertical lines in the inset. Outside these limits, the \( R_A(t)/C_A(t) \) ratio deviates from the straight line and then demonstrates spurious oscillations. This deviation can be attributed to the discrepancy between simulated and reconstructed values, whereas oscillations in the curve tail are caused by the division operation between two small numbers. The issue of determining the data range with optimal information content and sensitivity must be addressed in future studies.

### 3.3.2 Multi-pulse experiment

During a multi-pulse experiment, the pulse intensity was kept constant at \( 0.5 \cdot 10^{-9} \) moles per pulse. The first and last pulses in the multi-pulse sequence are marked in Figure 3.4(a) by star and double star symbols, respectively. Each successive trajectory in the sequence starts from the final point of the previous trajectory, since the adsorption is irreversible and the surface composition does not change between pulses. These trajectories visualize how the surface was gradually covered from one pulse to the next.

Panel (d) of Figure 3.4 shows rate vs. gas concentration plots for the multi-pulse sequence. The change of the apparent adsorption constant within each pulse is manifested by their petal-like shapes which still resemble the straight line from panel (b). Using all trajectories generated in this sequence, we calculated apparent kinetic constants by two different means:
1. **Moment analysis** The conversion for each pulse was calculated as \( X = 1 - M_0 \), where \( M_0 \) is the area under Pulse Intensity (PI) normalized exit flow curve of gas \( A \). Assuming a first order reaction, the apparent kinetic constant was found from equation (2.50) with the residence time in the catalytic zone given by equation (2.49).

2. **Slope** The apparent kinetic constant was estimated as a slope of a straight line passing through the origin and the point of maximum reaction rate (tip of the petal).

Figure 3.4(e) shows apparent kinetic constants calculated by these two methods as functions of surface composition for different pulses in the sequence. Similarly, as in panel (c), the intrinsic adsorption constant and total concentration of active sites were estimated from plotted data. These estimates are compared to real parameter values used for the simulation in Table 3.4. Analysis of petal slopes agreed well with the moment analysis, although both methods slightly overestimated kinetic parameters.

<table>
<thead>
<tr>
<th>Table 3.4: Kinetic parameters estimated via different methods for the multi-pulse virtual experiment with irreversible adsorption</th>
</tr>
</thead>
<tbody>
<tr>
<td>( k ) (( m^3 \text{ mol}^{-1} \text{ s}^{-1} ))</td>
</tr>
<tr>
<td>Simulation</td>
</tr>
<tr>
<td>Method of moments</td>
</tr>
<tr>
<td>Petal slopes</td>
</tr>
</tbody>
</table>

Summarizing single- and multi-pulse numerical experiments presented in this section, we conclude that intra-pulse kinetic characteristics reconstructed from exit flows by the Y-Procedure are consistent with more conventional method of moments. The major advantage of the Y-Procedure is that the dependence of apparent kinetic parameters on the changing catalyst composition can be obtained within a single state-altering pulse while the catalyst is ‘at work’, rather than from integral moment values. The ability to track compositional changes within pulse-response experiments has even greater implications for reversible reactions, as shown in the following section for a reversible molecular adsorption.
3.4 Reversible adsorption

Consider a single-site reversible molecular adsorption:

\[ A + Z \xrightleftharpoons[k^-]{k^+} ZA. \]

The kinetics of this reaction are governed by the following rate equation

\[
R_A(t) = k^+ \left( C_{Z,\text{tot}} - C_{ZA}(t) \right) C_A(t) - k^- C_{ZA}(t). \tag{3.7}
\]

Similarly to the irreversible case, we investigated the influence of pulse intensity \((10^{-11} - 10^{-8} \text{ moles per pulse})\) on the non-steady-state kinetics of this reaction. The kinetic parameters were set to \(k^+ = 1 \cdot 10^3 \text{ (m}^3/\text{mol/s}), k^- = 10 \text{ (1/s)},\) and \(C_{Z,\text{tot}} = 0.5 \cdot 10^{-9} \text{ (mol/m}^2),\) while other parameters listed in Table 3.3 were the same as for the irreversible case.

Figure 3.5(a) demonstrates for a number of single-pulse experiments that while the area under exit flow curves remains constant, their shapes are affected by the pulse intensity which increases in the direction marked by the arrow. Figure 3.5(b) presents the multi-pulse experiment with constant pulse intensity. As expected for a truly reversible process, all curves are the same because the catalyst returns in to its original state by the end of each pulse.

Figure 3.6(a) shows an example of simulated data corresponding to \(0.5 \cdot 10^{-9}\) moles of \(A\) per pulse. The exit flow curve of gas \(A\) intersects the inert exit flow curve, demonstrating the kinetic fingerprint of reversibility. Likewise, the reconstructed TZ concentration of gas \(A\) crosses the reconstructed TZ concentration of the inert standard as seen in panel (b). The reconstructed reaction rate and surface concentration of \(ZA\) also exhibit features characteristic of reversibility. After the initial peak, the reaction rate intersects the time axis and asymptotically approaches zero from the negative side as seen in panel (c). The peak region of this curve is dominated by adsorption, while the region of negative reaction rate is controlled by desorption.
Figure 3.5: **Virtual TZ experiments with reversible adsorption** (a) Pulse Intensity (PI) normalized exit flow curves of gas A corresponding to different single-pulse experiments. The arrow points towards increasing pulse intensity. (b) PI normalized exit flow curves of gas A corresponding to the multi-pulse experiment with $0.5 \cdot 10^{-9}$ moles per pulse.

Another characteristic feature of the reversible reaction is that the surface concentration shown in the inset of panel (c) passes through a maximum and then decays as molecules desorb.

The full set of reconstructed transient trajectories is shown in Figure 3.7(a) plotted in the RC space. All trajectories are closed due to complete reversibility. For small pulse intensities, trajectories are contained within an approximately planar surface. This can be used as a fingerprint of state-defining experiments for reversible adsorption. In this region, surface coverage does not affect adsorption kinetics significantly ($C_{ZA}(t) \ll C_{Z,tot}$). As the pulse intensity increases, trajectories become increasingly non-planar due to significant changes in surface coverage ($C_{ZA}(t) \sim C_{Z,tot}$). This feature is the fingerprint of state-altering experiments for reversible adsorption.

The plane trajectory for state-defining experiment can be presented as
Figure 3.6: Example Y-Procedure results for reversible adsorption (a) Exit flow curves of gas $A$ and inert (pulse intensity $0.5 \cdot 10^{-9}$ moles). (b) Gas concentrations of $A$ and inert. (c) Reaction rates of $A$ and inert. The inset shows the surface concentration of $ZA$.

$$\frac{R_A(t)}{C_A(t)} \approx k^+ C_{Z,tot} - k^- \frac{C_{ZA}(t)}{C_A(t)}. \tag{3.8}$$

Expression (3.8) follows from equation (3.7) by omitting the cross-term $k^+ C_{ZA} C_A$ and dividing by $C_A(t)$. The state-defining trajectory in these coordinates is depicted in Figure 3.7(b) for a pulse marked with a single star symbol. The slope gives the value of the intrinsic desorption constant and the y-intercept gives the apparent adsorption constant which is a product of the intrinsic adsorption constant and total concentration of active sites. The inset of panel (b) shows the plotted data range.

In order to decouple the intrinsic adsorption constant and active sites concentration, a state-altering trajectory can be linearized in the following form
Figure 3.7: The interpretation of transient kinetic characteristics for reversible adsorption (a) Trajectories in the rate/composition space ($R\ (nmol/m^2/s)$ vs. $C_g \cdot 10^2\ (mol/m^3_G)$ vs. $C_{ZA}\ (nmol/m^2_S)$). Blue solid lines show reconstructed trajectories. Black dotted lines show simulated trajectories. Black solid lines show the trajectories projected onto $R - C_g$ plane. The kinetic surface defined by equation (3.7) is not shown. The positive direction of time is depicted as a curved black arrow. The white arrow shows the increasing pulse intensity $N_P$. The pulses marked with star symbols are used in other panels. (b) $R/C\ (nm/s)$ ratio as a function of $C_{ZA}/C_g\ (nm)$ ratio for the pulse marked with *. The inset shows the corresponding data range. (c) $(R + k^-C_{ZA})/C_g\ (nm/s)$ ratio as a function of $ZA$ concentration for the pulse marked with **.
\[
\frac{R_A(t) + k^- C_{ZA}(t)}{C_A(t)} = k^+ C_{Z,\text{tot}} - k^+ C_{ZA}(t).
\] (3.9)

The value of the desorption constant in the left hand side of this expression is known from a state-defining experiment. Therefore, the intrinsic adsorption constant can be determined as a slope of the plot corresponding to expression (3.9). Figure 3.7(c) shows such a plot for the largest simulated pulse marked with double star. The plot deviates from the straight line due to reasons discussed previously in section 3.3 for irreversible adsorption. The surface coverage increases along the lower trajectory branch, and decreases along the upper branch.

One of the most interesting features of transient RC trajectories for reversible processes is the presence of special points in time where adsorption is instantaneously balanced by desorption, turning the net rate to zero. Such points, further referred to as the Momentary Equilibrium (ME) points, are marked in Figures 3.6(c) and 3.7(a) by red circles. The following subsection discusses their physico-chemical status in more detail.

### 3.4.1 Momentary Equilibrium (ME)

The net transient rate of reversible reactions reaches zero in the classical chemical equilibrium of closed systems (Denbigh, 1981). Typically, the reaction rate approaches zero and kinetic characteristics approach their equilibrium values monotonously, as shown in Figure 3.8(a) for the reversible adsorption of species \( A \) on a catalyst surface. The non-monotonous behavior of reversible reactions in such closed systems can result only from considerable non-linearities of their kinetics and is encountered extremely infrequently (Yablonskii, 1991; Gorban et al., 2006). On the contrary, the net reaction rate of even the simplest reversible adsorption in a TAP pulse-response experiment demonstrates complicated behavior depicted in Figure 3.8(b). Here, the reaction rate as well as gas and surface concentrations of species \( A \) are shown as functions of time within a single pulse. The rate reaches its maximum, decreases until it changes sign at the ME point, and then approaches zero from below as all molecules desorb from the catalyst. If \( A \) does not participate in other reactions on the catalyst, the area under the reaction rate curve before the ME point must be equal to the area after the
ME point, and the time when surface concentration reaches maximum must coincide with the time of ME. These properties are also valid for a more general case of pulse experiment with arbitrary but well-defined transport.

Figure 3.8: Transient behavior near (a) the classical chemical equilibrium and (b) the Momentary TAP equilibrium All units are arbitrary.

Similarly to the classical chemical equilibrium, adsorption characteristics including the intrinsic equilibrium constant and total concentration of active sites can be inferred from gas and surface concentrations at the ME point. Setting the net reaction rate in equation (3.7) to zero, we arrive at the following equation

\[ C_{Z,eq} = \frac{C_{Z,tot} C_{A,eq}}{C_{A,eq} + 1/K_{eq}} \]  

where \( C_{Z,eq} \) and \( C_{A,eq} \) are surface and gas concentrations at the ME and \( K_{eq} = k^+ / k^- \) is the intrinsic equilibrium constant. Expression (3.10) relates compositions of gas and surface phases in the ME point and is equivalent to the Langmuir isotherm (Langmuir, 1916). From this equation it follows that shifting the ME position in the RC space (changing \( C_{Z,eq} \) and \( C_{A,eq} \)) can be used for estimating \( K_{eq} \) and \( C_{Z,tot} \). The ME position, in turn, can be manipulated by controlling the composition and size of TAP pulses. We suggest the following TZ TAP experiment employing the principle of shifted equilibria to characterize reversible adsorption on a catalyst.

- First, a sequence of pulses should be recorded at a given temperature \( T^{(j)} \) and constant pulse intensity \( N_{P,A}^{(i)} \). For a truly reversible adsorption, pulses should
not differ within the sequence and can be averaged for further analysis in order to improve the signal-to-noise ratio. In what follows, superscripts \((j)\) and \((i)\) refer to particular temperatures and pulse intensities, respectively. The Y-Procedure analysis of the averaged exit flow curve followed by the calculation of surface uptake will result in a single RC trajectory passing through the ME point with coordinates \(C_{Z,A,eq}^{(i)}\) and \(C_{A,eq}^{(i)}\).

- The same measurement should be repeated for multiple pulse compositions and sizes. Appendix B describes the experimental protocol designed for such modulations of pulse intensity. The full set of trajectories corresponding to different pulse intensities can then be used to calculate the intrinsic equilibrium constant and concentration of sites at a given temperature \((K_{eq}^{(j)}\) and \(C_{Z,tot}^{(j)}\)) by a linear regression of ME points \(\left\{C_{Z,A,eq}^{(i)}, C_{A,eq}^{(i)}\right\}\) with the linearized form of equation (3.10):

\[
\frac{1}{C_{Z,A,eq}^{(i)}} = \frac{1}{C_{Z,tot}^{(j)}} + \frac{1}{K_{eq}^{(j)}} \frac{C_{Z,tot}^{(j)}}{C_{A,eq}^{(i)}}. \tag{3.11}
\]

- Next, the entire set of pulse-modulated experiments should be repeated for several temperatures. If the hypothesis that molecules of gas \(A\) undergo simple adsorption governed by equation (3.7) was correct, the estimate of the concentration of sites should be constant within a certain temperature range, i.e. \(C_{Z,tot}^{(j)} \neq f(T^{(j)})\). The equilibrium constant, on the other hand, should depend on the temperature according to the Van’t Hoff equation (Atkins and Paula, 2009)

\[
\ln(K_{eq}^{(j)}) = -\frac{\Delta H_{ads}}{RT^{(j)}} + \frac{\Delta S_{ads}}{R}, \tag{3.12}
\]

where \(\Delta H_{ads}\) (kJ mol\(^{-1}\)) is the heat of adsorption and \(\Delta S_{ads}\) (J mol\(^{-1}\) K\(^{-1}\)) is the entropy of adsorption, which can be estimated via a linear regression of \(\ln(K_{eq}^{(j)})\) vs. \((T^{(j)})^{-1}\).

The proposed experiment is a novel method for measuring the number of working active sites for reversible catalytic steps and their intrinsic thermodynamic parameters. This method should be used in combination with the analysis of individual trajectories to elucidate intrinsic kinetic parameters of a reaction step from state-defining and
state-altering experiments. Table 3.5 summarizes all kinetic parameters recoverable
by this combination of experiments for reversible and irreversible adsorption steps.

Table 3.5: Kinetic parameters which can be obtained for irreversible and reversible adsorptions via the Y-Procedure

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Irreversible reaction</th>
<th>Reversible reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>State-defining</td>
<td>$k_{app} = k(C_{Z,tot} - C_{ZA})$</td>
<td>$k_{app}^+ = k^+C_{Z,tot}; k^-$</td>
</tr>
<tr>
<td>State-altering</td>
<td>$k; C_{Z,tot}$</td>
<td>$k^+; C_{Z,tot}$ (if $k^-$ is known)</td>
</tr>
</tbody>
</table>

Besides adsorption of gaseous reactants, the techniques of kinetic analysis introduced
in this and previous sections are also applicable to an arbitrary reaction step, as
long as its rate and concentrations of participating species (gaseous or surface) are
individually known from the Y-Procedure. In the next section we turn to the problem
of identifying the network of steps for a complex mechanism which must be solved in
order to isolate and analyze individual elementary reactions.

3.5 The temporal kinetic coherence of transient kinetic characteristics

For a reaction mechanism consisting of multiple steps, the Y-Procedure complemented
by the calculation of surface storages yields intra-pulse reaction rates and concentra-
tions for different gaseous and surface species. We have already noted in section 3.1
that the kinetics of these substances may be coupled to each other through several
types of elementary steps. In order to deduce a particular combination of elemen-
tary steps leading to the observed intra-pulse kinetic characteristics, it is instructive
to examine the temporal coherence of experimental data. By temporal coherence of
kinetic characteristics we understand the synchronization of their behavior, such as
coincidence of their peak-times or time-independence of their ratios, which is rooted
in the underlying reaction mechanism.

Although temporal coherency as an experimental observation is a more fundamen-
tal concept than kinetic model, it can be best understood as consistency of reaction
rates and/or concentrations with a particular kinetic model used to represent the
reaction mechanism. For example, reaction rates of two species should appear synchronized when both species participate in the same elementary step or sequence of such steps and do not participate in any other processes. Ideally, completely synchronized reaction rates are equal to each other when scaled according to the proper stoichiometric coefficients. If experiments suggest that they are not synchronized, it can be concluded that data are inconsistent with the model or visa versa. Besides such a rate-rate coherency, there is also a rate-concentration coherency which directly follows from the law of mass action for an elementary step. The principle of temporal kinetic coherence between transient kinetic characteristics is exemplified in the following section for the two-route \( CO \) oxidation mechanism.

### 3.6 Two-route mechanism of \( CO \) oxidation

We begin the analysis of multi-step catalytic reactions by considering the oxidation of carbon monoxide by oxygen on precious metals. \( CO \) oxidation can be described by two possible mechanisms: Langmuir-Hinshelwood (LH) and Eley-Rideal (ER). Both mechanisms assume that oxygen dissociates irreversibly and occupies two surface sites \( Z \). According to the ER mechanism, oxidation proceeds through the direct reaction between surface oxygen and gas phase \( CO \). The LH mechanism, on the contrary, postulates that \( CO \) requires reversible preadsorption in the form of \( ZCO \) before it can react with surface oxygen. Elementary steps of these mechanisms are summarized in Tables 3.6 and 3.7. In rate expressions, also given in these tables for each elementary step, \( \Theta_i \) is the fractional surface coverage of \( i \)th intermediate defined as the ratio of its concentration and the total concentration of active sites:

\[
\Theta_i = \frac{C_{s,i}}{C_{Z,total}}. \tag{3.13}
\]

Rate equations are given in terms of coverages rather than surface concentrations in order to keep the dimensionality of intrinsic kinetic constants in accordance with the commonly accepted convention for this reaction, e.g. (Krischer et al., 1992; Nekhamkina et al., 2003).
Table 3.6: Elementary steps involved in the impact CO oxidation mechanism and their reaction rates

<table>
<thead>
<tr>
<th>Elementary step</th>
<th>Reaction rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1) $O_2 + 2Z \rightarrow 2ZO$</td>
<td>$r_1 = C_{Z,tot}k_1^+\Theta_Z^2CO_2$</td>
</tr>
<tr>
<td>(2) $ZO + CO \rightarrow Z + CO_2$</td>
<td>$r_2 = C_{Z,tot}k_2^+\Theta_ZCO$</td>
</tr>
</tbody>
</table>

Table 3.7: Elementary steps involved in the adsorption CO oxidation and their reaction rates

<table>
<thead>
<tr>
<th>Elementary step</th>
<th>Reaction rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1) $O_2 + 2Z \rightarrow 2ZO$</td>
<td>$r_1 = C_{Z,tot}k_1^+\Theta_Z^2CO_2$</td>
</tr>
<tr>
<td>(3) $CO + Z \rightleftharpoons ZCO$</td>
<td>$r_3 = C_{Z,tot}k_3^+\Theta_ZC\Theta_CO - C_{Z,tot}k_3^-\Theta_ZCO$</td>
</tr>
<tr>
<td>(4) $ZO + ZCO \rightarrow 2Z + CO_2$</td>
<td>$r_4 = C_{Z,tot}k_4^+\Theta_ZO\Theta_ZCO$</td>
</tr>
</tbody>
</table>

The ER scheme, also known as the impact mechanism, is the combination of steps (1,2). The LH scheme, often called the adsorption mechanism, is the combination of steps (1,3,4). Desorption of $CO_2$ is considered to be very fast and is usually lumped with $CO_2$ generation step, whether it is produced in step (2) or (4). In practice, the reaction may proceed through both routes simultaneously and may involve all four elementary steps from Tables 3.6 and 3.7. Yet another possibility is the ER mechanism accompanied by reversible $CO$ adsorption where $ZCO$ acts as a spectator species, i.e. steps (1,2,3). The problem of mechanism discrimination for this model reaction has a long history (Yablonskii, 1991; Freund et al., 2011) and often serves as a benchmark for novel techniques of kinetic analysis such as the Y-Procedure. In the following two subsections, the principle of temporal kinetic coherence is applied to discriminate between possible combinations of elementary steps in $CO$ oxidation.

### 3.6.1 Testing the rate-rate temporal coherency

The first step towards discerning the mechanism of $CO$ oxidation is to compare $CO_2$ generation and $CO$ consumption rates which are available from the Y-Procedure. Figure 3.6.1 shows two numerical examples generated to illustrate the rate comparison.
using geometric and transport parameters from Table 3.3 and kinetic parameters from Table 3.8. Both simulations represent a single pulse of CO/argon mixture (0.5 \cdot 10^{-9} \text{ (mol)} of each gas) over a catalyst previously covered with oxygen (80 % of all sites). Exit flow curves shown in Figures 3.6.1(a) and (b) correspond to impact and adsorption mechanisms of CO oxidation, respectively. The kinetic parameters of individual steps from Tables 3.6 and 3.7 were chosen in such a way that for both mechanisms the total conversion reached \( \sim 30\% \) by the end of the pulse. Determining the mechanism from either set of exit flux data by conventional moment analysis or curve fitting would have been a formidable challenge since exit flow shapes and conversions are very similar. Conclusions of such a determination would crucially depend on some \textit{a priori} mechanistic assumptions.

Table 3.8: \textbf{Kinetic parameters used for virtual TZ TAP experiments with two-route CO oxidation mechanism}

<table>
<thead>
<tr>
<th>System parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>( k_2^+ ) (\text{m}^3 \text{mol}^{-1} \text{s}^{-1})</td>
<td>120</td>
</tr>
<tr>
<td>( k_3^+ ) (\text{m}^3 \text{mol}^{-1} \text{s}^{-1})</td>
<td>( 1 \cdot 10^3 )</td>
</tr>
<tr>
<td>( k_5^- ) (\text{s}^{-1})</td>
<td>50</td>
</tr>
<tr>
<td>( k_7^- ) (\text{s}^{-1})</td>
<td>50</td>
</tr>
<tr>
<td>Total concentration of active sites, ( C_{Z,\text{tot}} ) (\text{mol m}^2)</td>
<td>( 5 \cdot 10^{-9} )</td>
</tr>
</tbody>
</table>

Contrary to the exit flow data, reconstructed thin-zone reaction rates shown in Figures 3.6.1(c) and (d) clearly demonstrate the difference between the two mechanisms. For the impact mechanism, the \( CO \) consumption rate is equal to the rate of \( CO_2 \) production for all time points during the pulse (rate-rate coherence). For the adsorption mechanism, there is an apparent lag between the two rates. Namely, the rate of \( CO \) consumption is peaking before the rate of \( CO_2 \) formation and is more narrow. This difference is a result of the appreciable surface life-time of \( ZCO \) intermediate before it reacts with the surface oxygen.

The same conclusion can be made from temporal evolutions of surface intermediates \( ZCO \) and \( ZO \) calculated as

\[
C_{ZCO}(t) = C_{ZCO,\text{init}}(t) + \int_0^t (R_{CO}(t') - R_{CO_2}(t')) \, dt',
\]

(3.14)
Figure 3.9: **Model CO oxidation** (a)-(b) Exit flow curves for ER and LH mechanisms, \((nmol \, s^{-1})\). (c)-(d) TZ reaction rates for ER and LH mechanisms, \((nmol \, m^{-2} \, s^{-1})\). Insets of (c)-(d) show concentrations of surface intermediates, \((nmol \, m^{-2})\).

\[
C_{ZO}(t) = C_{ZO,init}(t) + \int_0^t (2R_{O_2}(t') - R_{CO_2}(t')) \, dt',
\]

where, in this case, the initial \(ZCO\) concentration is zero, the initial \(ZO\) concentration is 0.8\(C_{Z,\text{tot}}\), and the rate of oxygen is zero.

In accordance with a remark made in section 3.1, intra-pulse storages of \(CO\) and oxygen atoms given by equations (3.14) and (3.15) are correctly calculated regardless of the reaction route.Insets of Figures 3.6.1(c) and (d) present surface storages for purely impact and adsorption mechanisms. For the impact mechanism, there is no \(ZCO\) accumulation within the pulse. For the adsorption mechanism, \(ZCO\) concentration peaks in the beginning of the pulse and then slowly decays until all \(ZCO\) is reacted with surface oxygen.

In brief, the coherency between transient \(CO\) and \(CO_2\) reaction rates provides a strong argument in favor of the impact mechanism, while their decoherency suggests the adsorption mechanism. However, the decoherency alone does not rule out the possibility
of more complicated reaction schemes. For example, a combination of impact and adsorption mechanisms (steps (1-4)) or the impact mechanism accompanied by a buffer step of CO adsorption (steps (1-3)) may also result in the difference between CO and CO$_2$ reaction rates. For this reason, it is necessary to test the entire set of transient kinetic characteristics, including reaction rates, gas, and surface concentrations, for consistency with different models as described in the next subsection.

### 3.6.2 Testing the rate-concentration temporal coherency

The dependence of reaction rates on gas and surface concentrations is specific to the underlying combination of elementary steps and must be examined within each pulse in order to further clarify mechanistic details. The rate of CO$_2$ production via the impact step (2) in Table 3.6 divided by ZO concentration and CO concentration gives the intrinsic kinetic parameter $k_3^+$:

$$\frac{R_{CO_2}(t)}{C_{ZO}(t)C_{CO}(t)} = k_2^+.$$  \hspace{1cm} (3.16)

Similarly for step (4) of the adsorption mechanism in Table 3.7, CO$_2$ production rate divided by $C_{ZO}$ and $C_{ZCO}$ gives the intrinsic kinetic parameter $k_4^+$:

$$\frac{R_{CO_2}(t)}{C_{ZO}(t)C_{ZCO}(t)} = k_4^+.$$  \hspace{1cm} (3.17)

Only for pure impact or adsorption mechanisms should these ratios of intra-pulse characteristics be equal to intrinsic reaction parameters and therefore stay constant throughout the pulse. Generally, the intrinsic parameters are not known in advance. One of these ratios is time-independent only when the reaction rate in the numerator and the product of concentrations in the denominator are synchronized. When gaseous CO and(or) surface intermediates participate in the reaction not according to impact or adsorption mechanisms, apparent parameters calculated as ratios of intra-pulse rates and concentrations 3.16 and 3.17 will be themselves time-dependent. This rate-concentration coherency or lack thereof provides a powerful additional test
for mechanistic hypotheses. To illustrate this point, consider the coherency of CO oxidation kinetics for various combinations of elementary steps.

Figure 3.6.2 shows kinetic parameters obtained according to equations (3.16) and (3.17) for several possible combinations of elementary steps as functions of time within a single-pulse experiment described in the previous section, i.e. CO pulse over the oxidized catalyst. In Figure 3.6.2(a), the kinetic parameter \( \frac{R_{CO_2}}{CZO^2C_{CO}} \) remain constant in time during the pulse only for mechanisms without the surface reaction step (ER and ER with the buffer step). Similarly, only the LH mechanism which does not involve \( CO_2 \) production via the impact step demonstrates the time-independent kinetic parameter \( \frac{R_{CO_2}}{CZO^2C_{ZCO}} \), as evident from Figure 3.6.2(b).

\[
\text{(a)} \quad \frac{R_{CO_2}}{CZO^2C_{CO}} \quad \text{(b)} \quad \frac{R_{CO_2}}{CZO^2C_{ZCO}}
\]

The internal coherency of intra-pulse kinetics completes the set of fingerprints for determining the combination of elementary steps involved in a given realization of the model CO oxidation reaction. The mechanism decoding procedure can be summarized as a decision tree presented in Figure 3.11. For equal CO and \( CO_2 \) rates, if the apparent kinetic constant given by equation (3.16) does not depend on time, then CO oxidation proceeds only via the impact mechanism. If the apparent kinetic constant changes within the pulse, it can be deduced that surface oxygen species \( ZO \) participate in other reaction(s) parallel to the impact step. For non-equal CO and \( CO_2 \) rates, time-independence of the kinetic parameter given by equation (3.17).
suggests that $CO$ oxidation proceeds through the adsorption mechanism. Alternatively, the other combination of rate/concentration data given by equation (3.16) has to be tested for time-independence. If it is constant, $CO$ oxidation via the impact mechanism is accompanied by the buffer step of reversible $CO$ adsorption. If it is not constant, the combination of impact and adsorption mechanisms can be conjectured. Without the Y-Procedure, the choice between these possibilities based on the model-dependent data fitting or method of moments would have been ambiguous.

![Decision Tree](image)

**Figure 3.11:** The decision tree for mechanism discrimination for $CO$ oxidation

Abbreviations: ER - Eley-Rideal; LH - Langmuir Hinshelwood; AOP - Additional Oxygen Process on the surface; buffer - reversible adsorption of $CO$ as a spectator.

The methodology described in this section is applicable to a broader class of reaction mechanisms which consist only of elementary steps involving gas uptake or release by a catalyst (see types 1 and 2 in section 3.1). Decision trees similar to the one in Figure 3.11 can be constructed for such reactions and then used to interpret experimental data sets. Should a step with no communication between gas and surface phases occur in the reaction (see type 3 in section 3.1), mechanism identification becomes more cumbersome because surface-only reaction steps do not allow calculation of individual intermediate concentrations. It is nevertheless possible to reveal the presence of hidden surface steps by excluding other possibilities, as demonstrated above for the
additional oxygen process on the surface or via another example of rate-concentration decoherency discussed in the next section.

3.7 Elucidating a hidden surface step

One of the basic examples where introduction of a surface step is necessary to explain experimental data is the case of catalytic isomerisation of gas $A$ into gas $B$. Consider two simple irreversible mechanisms for this reaction which consist of elementary steps shown in Tables 3.9 and 3.10. In the first mechanism (two-step) comprised of steps (1) and (2), desorption of $B$ immediately follows after adsorption of $A$. In the second mechanism (three-step) comprised of steps (1), (3), and (4), there is a hidden surface step between adsorption of $A$ and release of $B$. The apparent kinetic behavior exhibited by each mechanism may vary and is determined by the relative rates of elementary steps.

**Table 3.9: The two-step mechanism of isomerisation of $A$ to $B$**

<table>
<thead>
<tr>
<th>Elementary step</th>
<th>Reaction rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1) $A + Z \rightleftharpoons ZA$</td>
<td>$r_1 = k_1^+ C_ZC_A - k_1^- C_{ZA}$</td>
</tr>
<tr>
<td>(2) $ZA \rightarrow B + Z$</td>
<td>$r_2 = k_2^+ C_{ZA}$</td>
</tr>
</tbody>
</table>

**Table 3.10: The three-step mechanism of isomerisation of $A$ to $B$**

<table>
<thead>
<tr>
<th>Elementary step</th>
<th>Reaction rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1) $A + Z \rightleftharpoons ZA$</td>
<td>$r_1 = k_1^+ C_ZC_A - k_1^- C_{ZA}$</td>
</tr>
<tr>
<td>(3) $ZA \rightleftharpoons ZB$</td>
<td>$r_3 = k_3^+ C_{ZA} - k_3^- C_{ZB}$</td>
</tr>
<tr>
<td>(4) $ZB \rightarrow B + Z$</td>
<td>$r_4 = k_4^+ C_{ZB}$</td>
</tr>
</tbody>
</table>

In a limiting case when step (1) is much slower than all other steps, the kinetics of both mechanisms will be equivalent to that of a single step in which the catalyst’s role is reduced to merely a reaction medium, i.e. $A + Z \rightleftharpoons B + Z$. In all other cases, the formation of $B$ will be delayed behind the consumption of $A$. It is also easy to
see that when step (3) is much faster than step (4) or vice versa, the second mechanism will demonstrate apparent kinetics indistinguishable from the first mechanism. Namely, there will be no time delay between the depletion of intermediate $ZA$ and the formation of gas $B$. There will be, however, a parametric range in which the two mechanisms are distinguishable; it is this parametric range that we explore here.

Table 3.11: Kinetic parameters used for virtual TZ TAP experiments with irreversible isomerisation mechanisms

<table>
<thead>
<tr>
<th>System parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k^+_1$ ($m^3$ $mol^{-1}$ $s^{-1}$)</td>
<td>$1 \cdot 10^3$</td>
</tr>
<tr>
<td>$k^-_1$ ($s^{-1}$)</td>
<td>50</td>
</tr>
<tr>
<td>$k^+_2$ ($s^{-1}$)</td>
<td>5</td>
</tr>
<tr>
<td>$k^+_3$ ($s^{-1}$)</td>
<td>10</td>
</tr>
<tr>
<td>$k^+_4$ ($s^{-1}$)</td>
<td>10</td>
</tr>
<tr>
<td>Total concentration of active sites, $C_{Z, tot}$ ($mol$ $m^2$)</td>
<td>$5 \cdot 10^{-9}$</td>
</tr>
</tbody>
</table>

Figures 3.12(a) and (b) show exit flow curves of gases $A$ and $B$ which were obtained in simulations with two- and three-step mechanisms respectively using geometric and transport parameters from Table 3.3, kinetic parameters from Table 3.11, and pulse intensity of 1(nmol) of $A$. The kinetic parameters where set in such a way that both mechanisms produce the same conversion (35%). Clearly, model fitting or moment analysis are not able to distinguish the two mechanisms unambiguously because exit flow data appear to be very similar. The two mechanisms can be discriminated by examining the coherency between the rate of $B$ production and the total surface storage which can be calculated as

$$C_{\Sigma}(t) = \int_0^t (R_A(t') - R_B(t')) dt'.$$

(3.18)

If $B$ is produced via the two-step mechanism, then $ZA$ is the only kinetically important intermediate whose concentration coincides with the total surface storage of $A$, i.e. $C_{\Sigma}(t) = C_{ZA}(t)$. According to the rate equation for step (2) in Table 3.9, $ZA$ concentration should be coherent with the rate of $B$ generation. On the other hand, if $B$ is produced via the three-step mechanism, the total storage represents the sum of $ZA$ and $ZB$ intermediates, i.e. $C_{\Sigma}(t) = C_{ZA}(t) + C_B(t)$, which must not be coherent with the rate of gas $B$. Height-normalized $R_B$ and $C_{\Sigma}$ shown in
Figures 3.12(c) and (d) as functions of time within the pulse suggest that temporal decoherency between them can be used as kinetic signature of the hidden surface-only step (3) in the mechanism of irreversible isomerisation.

Figure 3.12: The two- versus three-step isomerisation mechanism (a)-(b) Exit flows for two-step and three-step mechanisms, (nmol s\(^{-1}\)). (c) The temporal kinetic coherence between the TZ reaction rate \(R_B\) and combined surface storage \(C_\Sigma\) for the two-step mechanism; all units are arbitrary. (d) The temporal kinetic decoherence between the TZ reaction rate \(R_B\) and combined surface storage \(C_\Sigma\) for the three-step mechanism.

3.8 Concluding remarks

In this chapter, a theoretical apparatus has been introduced for interpreting intrapulse reaction rates and gas concentrations in the TZ which were reconstructed by the Y-Procedure. One of the key results enabling mechanism identification and parameter estimation is the calculation of transient surface storages by integrating an appropriate linear combination of gaseous reaction rates. This novel post-processing step of TAP data analysis in effect resolves the mass balance of the catalyst surface and provides a description of catalyst composition with millisecond temporal resolution. Contrary to exit flow moments, this information enables a truly transient analysis.
of reaction rates as functions of both gas and surface compositions and has several implications for the TAP methodology. First of all, state-defining and state-altering pulses can be easily distinguished on the basis of rate-concentration dependencies. Second, intrinsic kinetic parameters including the total concentration of working active sites can be estimated for irreversible and reversible reaction steps from a single transient measurement while the act of catalysis is in progress. Finally, previously avoided single-pulse state-altering TAP experiments can now be utilized for probing non-linear kinetic effects of increased surface coverages.

The ability to observe the evolution of catalyst composition within the pulse is especially advantageous for reversible reactions, since the net compositional change from pulse to pulse is zero for such reactions. The analysis of intra-pulse trajectories corresponding to reversible adsorption revealed a new type of chemical equilibria, the Momentary Equilibrium (ME), where the net reaction rate instantaneously passes through zero. Unlike "TAP equilibrium" described in (Yablonskii et al., 1998) as “the state [...] that a single-pulse experiment naturally evolves toward and would reach if the reactor length were infinitely long”, the ME phenomenon takes place in a finite microreactor at a finite time and can be precisely characterized by means of the Y-Procedure. One practical application of the ME is measuring adsorption isotherms in the pulse intensity modulated experiment suggested in section 3.4.1.

Moreover, intra-pulse surface dynamics is instrumental for identifying multi-step reaction mechanisms. For a broad class of mechanisms involving exchange of molecules with the gas phase in every elementary step, concentrations of kinetically individual surface intermediates\(^\text{10}\) can be obtained from gaseous reaction rates. Such mechanisms can be completely characterized based on kinetics within a single TAP pulse-response experiment using the principle of temporal kinetic coherence which can be expressed in the following two statements. First, a direct comparison of reaction rates of reagents and products elucidates whether products were formed in the same elementary steps as reagents were consumed or if additional surface processes preceded their formation. Second, every combination of elementary steps results in a temporal coherency between certain kinetic characteristics such as reaction rates, concentrations of gaseous substances, and surface storages. This principle unambiguously determines whether

\(^\text{10}\)The term “kinetically individual” is used in order to avoid referring to chemically individual intermediates because the two are not, generally, the same.
experimental data comply with a hypothesized mechanism, as we have demonstrated for the two-route CO oxidation mechanism. For a more general class of reactions containing surface-only elementary steps, intra-pulse storages represent combined rather than individual surface concentrations. Combined storages are still informative for kinetic analysis, as we have shown by elucidating a hidden surface-only step for simple irreversible isomerisation based on the decoherency between a combined surface storage and a product generation rate.

It should be noted that the reaction mechanism suggested by transient kinetics within a state-defining experiment is specific to a particular catalyst state. There are various reasons for the mechanism or its parameters to change as a function of the catalyst state including lateral interactions between adsorbates (Zaera, 2002a), formation of new catalytic phases like surface oxides on metals (Zorn et al., 2011), or poisoning of active sites (Moulijn et al., 2001). Three scenarios are possible: 1) changing catalyst state does not affect either the reaction mechanism or its parameters, 2) changing catalyst state does not affect the mechanism but changes mechanism parameters, and 3) changing catalyst state results in the change of the reaction mechanism itself. In order to assess the relationship between significant changes of the catalyst state and reaction kinetics, surface coverages must be varied in multi-pulse, pump-probe, and pulse intensity modulated TAP experiments. The Y-Procedure analysis combined with these experimental techniques is a powerful new tool for interrogative kinetic studies of complex catalytic reactions. The next chapter addresses several issues associated with practical realization of this tool and provides two experimental applications of the Y-Procedure analysis, both related to CO oxidation on precious metals.
Chapter 4

Experimental applications: Oxygen and carbon monoxide on precious metals

The previous chapter introduced several novel opportunities for advanced kinetic characterization of technical catalysts emerging from Y-Procedure-based analysis of Thin-Zone TAP experiments. Particularly, it was shown that transient kinetics reconstructed by the Y-Procedure can be used for identifying reaction mechanisms and estimating intrinsic kinetic parameters. Practical implementation of these opportunities posits several methodological challenges which are briefly discussed in the opening section 4.1 of this chapter. Then, two experimental studies employing the Y-Procedure are described in sections 4.2 and 4.3, both related to oxidation reactions on precious metals.

The first study was designed to validate the Y-Procedure methodology by investigating oxygen uptake on polycrystalline platinum, an important initial step of oxidation reactions. The intrinsic adsorption constant and concentration of active sites estimated via the Y-Procedure were in close agreement with more conventional moment analysis of the same data set as well as previously published findings. The second study investigated CO oxidation on Au/SiO₂ catalysts prepared via magnetron sputtering. This reaction is not only industrially relevant, but is also a valuable model for studying catalytic mechanisms because it exhibits a number of prototypical kinetic features (Freund et al., 2011; Royer and Duprez, 2011).
The focus of our study of gold catalysts was on two specific mechanistic questions: whether the reaction proceeds through impact or adsorption pathways and what is the mechanism of oxygen storage on the catalyst? To answer these questions, the Y-Procedure was used in combination with moment analysis of CO titration of surface oxygen which was introduced by oxygen flow pretreatments at elevated pressures. Our findings suggest that in the explored range of experimental conditions, CO oxidation can be described by an apparent impact mechanism and that oxygen is stored on the Au/SiO$_2$ catalysts in two kinetically distinct reservoirs. Although these mechanistic details could be hypothesized based on moment analysis alone, strong evidence in their support such as intra-pulse non-steady-state kinetics could be obtained only via the Y-Procedure. Importantly, the capacity of an additional reservoir was investigated in a wide range of oxygen pretreatment pressures, providing an example experimental strategy linking TAP studies to more realistic operating conditions.

4.1 Some practical considerations

4.1.1 Accounting for reversible adsorption in inert zones

In Thin-Zone TAP experiments, the catalytic sample is sandwiched between two zones packed with other material (quartz or silicon carbide) whose role is to provide an inert medium for diffusion of gas molecules to and from the catalyst. As evident from the data analysis methodology discussed in Chapter 2, quantification of gas transport through this material is essential for obtaining reaction characteristics from exit flow curves, and any deviations from the Knudsen model can have a significant impact on extracted catalytic kinetics. Unfortunately, experimental practice shows that seemingly inert materials may in fact adsorb certain gases to a small but measurable extent. If a gas is adsorbed irreversibly, it is likely that those few surface sites that are available on the inert material for gas adsorption will be quickly occupied during pretreatments and will not present a problem for the actual pulse-response experiments. In reality, gases such as CO adsorb on such inert material reversibly and the effects of this adsorption interfere with experimental results. Recently, mathematical corrections were introduced into the method of moments in order to factor in reversible adsorption in inert zones (Goguet et al., 2011).
In order to introduce similar corrections for the Y-Procedure, recall that equations (2.63) and (2.64) for the reconstruction of thin-zone kinetics were derived from the transfer matrix equation (2.15) written for two inert zones in the TZ TAP reactor. Transfer matrices $M(u, w)$ given by expression (2.16) were, in turn, defined for a general zone with linearized reversible adsorption. When the original Y-Procedure equations were formulated, variables $u$ and $w$ given by equation (2.17) were simplified to $u = \sqrt{s \tau}$ and $w = \gamma$ because zones were considered completely inert\textsuperscript{11}. Therefore, the adsorption-corrected Y-Procedure can be obtained by using non-simplified variables $u$ and $w$ for defining matrices $M(u, w)$. The following expressions give the corrected Y-Procedure functions for equations (2.63) and (2.64)

\begin{align*}
Y_{c}^{corr}(\omega) &= \left( \frac{\sinh u_2(\omega)}{u_2 w_2} \right), \\
Y_{r}^{corr}(\omega) &= \left( \cosh u_2(\omega) + \frac{u_1(\omega)w_1}{u_2(\omega)w_2} \frac{\sinh u_1(\omega)\sinh u_2(\omega)}{\cosh u_1(\omega)} \right). 
\end{align*}

Here, zone-specific variables $u$ and $w$ are

\begin{equation}
\begin{aligned}
u &= \sqrt{s \tau + \frac{s \psi^2}{s + k_d}}, \\
w &= \gamma, 
\end{aligned}
\end{equation}

where $\tau = \epsilon \frac{(\Delta x)^2}{D}$ (s) and $\gamma = \frac{D}{\Delta x} (m \ s^{-1})$ are transport parameters of each zone, $\psi = \sqrt{k_a \tau}$ is the dimensionless adsorption/diffusion parameter, $k_a$ and $k_d (s^{-1})$ are apparent adsorption and desorption constants. These apparent constants and the control exit flow $F_{exit}^{ctrl}(t)$ for equation (2.64) have to be determined in a separate experiment when the entire microreactor is packed with the non-so-inert material.

\textsuperscript{11}Here, $\tau$ and $\gamma$ are zone-specific and superscript $^{(i)}$ is simply omitted.
4.1.2 The Pulse Intensity Modulation (PIM) protocol

In Chapter 3 we have shown that pulse intensity modulations can be used to control the catalyst composition in TZ TAP experiments, providing a sensitive tool for studying the dependence of apparent kinetics on surface coverages. Pulse-modulated experiments are particularly useful for decoupling the concentration of active sites and intrinsic kinetic parameters. In order to exploit this novel tool in practice, the intensity of TAP pulses must be scrupulously controlled and measured. Precise calibration of pulse size can be experimentally challenging due to the technical complexity of TAP hardware and significant uncertainties within its control parameters. Experimental factors influencing the pulse intensity in a typical TAP reactor setup include spring and bellows tensions in the pulse-valve, total pressure in the feed line, voltage applied to the pulse-valve, and width of electronic pulses sent from the pulse generator. Typically, these factors are adjusted before an experiment in an iterative trial-and-error process whose objective is to tune pulse-valves such that they produce stable pulses with exit flow curves demonstrating Knudsen behavior. Once the initial tuning is completed, the pulse intensity is typically kept constant for an entire set of planned TAP experiments. At best, the pulse size is measured periodically to confirm that it does not drift over time. Since TAP experiments often involve variations of reactant ratios, the quantity of gases injected with every pulse is varied by changing the feed mixture composition.

The systematic application of the Y-Procedure methodology necessitates more flexible procedures for manipulating the supply of reactants to the catalyst as well as more refined protocols for data collection and post-processing. We have heuristically developed the Pulse Intensity Modulation (PIM) protocol for performing TAP pulse-response experiments with precisely controlled pulse intensity specifically designed to be analyzed via the Y-Procedure. The protocol can be found in Appendix B. The case study presented in the next section utilized this protocol and is the first experimental validation of the Y-Procedure approach.
4.2 Oxygen uptake on polycrystalline Pt

The first experimental example of the Y-Procedure analysis examines oxygen uptake on polycrystalline platinum. Although it was shown that this reaction proceeds through multiple physisorbed and chemisorbed oxygen intermediates, e.g. (Gee and Hayden, 2000; Yang et al., 2010), its macroscopic kinetics are often described by the dissociative adsorption model, for example in (Verdasca et al., 2002; Elokhin et al., 2009). This model implies that oxygen molecules dissociate upon adsorption on two platinum sites to form two surface-bound oxygen atoms in a single elementary step:

\[ O_2 + 2Z \rightarrow 2ZO. \]

TAP experiments reported in the literature (Hoebink et al., 1997; Nijhuis et al., 1997) and prior experience in our laboratory suggest that under Knudsen conditions oxygen uptake on polycrystalline platinum can be considered irreversible. Therefore, this model reaction presents a convenient benchmark for confirming the validity of data analysis approach developed in Chapter 3 section 3.3 for irreversible adsorptions. Transient kinetic characteristics discussed here (oxygen gas concentration and adsorption rate) were extracted from exit flow TAP data in a kinetically 'model free' manner via the Y-Procedure and then interpreted in the light of dissociative adsorption model. The Y-Procedure results were in agreement with conventional moment analysis.

4.2.1 Experimental data

The experimental data were collected using a TAP-2 reactor system (Mithra Tech.) previously described elsewhere (Gleaves et al., 1997). For calibration measurements, the stainless steel microreactor \((L = 36.5\text{ mm}, \ d = 4.8\text{ mm})\) was packed with inert material (SiC, 60 mesh, City Chemical LLC). The microreactor was evacuated to the background pressure of \(10^{-6}\) \(\text{torr}\), resistively heated to 673 K, and conditioned at this temperature for 30 minutes. To burn-off carbon containing contaminants, a 1 : 5 mixture of argon (Cee-Kay Supply) and oxygen (UHP grade, Airgas) was pulsed into the microreactor until no carbon dioxide was observed by the QMS. Oxygen
pretreatment was followed by pulsing a 1 : 10 argon and hydrogen (UHP grade, Praxair) mixture until no water was observed in the exit flow. Then, the microreactor was cooled to 423 K, and a set of calibration experiments was performed with various argon / oxygen mixtures. These preliminary measurements demonstrated that both argon and oxygen were transported through the microreactor via Knudsen diffusion, and did not interact with inert material otherwise.

For the catalytic measurements, the microreactor was packed in the thin zone configuration ($L_{TZ} = 23.1$ mm, $L_{cat} \sim 1$ mm) with 17 mg of polycrystalline platinum powder (max. particle size 150 micron, 99.95% purity, Good Fellow) sandwiched between two SiC zones. The catalyst sample was conditioned before catalytic measurements following the procedure described above for inert packing. After the reduction in hydrogen at 673 K and cooling to 423 K, a few pulses of argon / CO (99.99%, CeeKay) 1 : 10 mixture were introduced, but no $\text{CO}_2$ production was observed, confirming that the catalyst was fully reduced. The uptake of oxygen on the catalyst was recorded by pulsing a 5 : 1 argon / oxygen mixture. The evolution of two mass fragments in time was followed, namely, 40.1 a.m.u. for argon and 32.0 a.m.u. for oxygen. Since the QMS switched from one mass to the other between pulses, the oxygen signal was recorded only for every odd pulse starting with pulse one. The amount of oxygen consumed during every even pulse was assumed to be the average between two adjacent odd pulses. After uptake experiments, the microreactor was repacked with inert, and the total pulse intensity was measured to be $\sim 0.65 \cdot 10^{-9}$ (mol) by monitoring the pressure drop in the feed line of known volume.

Figure 4.1(a) shows PI normalized oxygen exit curves corresponding to the multi-pulse uptake experiment. In the beginning of the sequence, there was almost no oxygen coming out of the reactor due to complete conversion. As the catalyst surface approached saturation, the peak value of oxygen exit flow rapidly increased until the area under successive curves stopped changing from one pulse to the next. In Figure 4.1(b), the exit flow of oxygen from this final portion of the multi-pulse sequence is compared with the exit flow of argon and the standard diffusion curve. All three curves are plotted in dimensionless coordinates in order to account for the difference in diffusivities. This figure clearly shows that argon and oxygen traveled through the microreactor via Knudsen diffusion without adsorption on the catalyst and that all active sites on the catalyst were occupied. The total oxygen uptake achieved
by the end of our experiment was estimated to be $6 \cdot 10^{-7}$ ($mol_{ZO}/g_{cat}$) which is comparable to the total oxygen capacity of polycrystalline platinum reported in the literature (Hoebink et al., 1997). The concentration of active sites in this section is also expressed in ($mol_{ZO}/g_{cat}$) for consistency of notation.

![Figure 4.1: Experimental results for oxygen uptake on Pt (a) Exit flow curves of oxygen and argon (pulse intensity $0.65 \cdot 10^{-9}$ mol). (b) Dimensionless exit flow curves of oxygen and argon for the pulse marked with a star symbol compared to the standard diffusion curve. The dimensionless coordinates are $\tilde{F} = \frac{F \epsilon L^2}{N_P D}$, and $\tilde{t} = t \frac{D}{\epsilon L^2}$.](image)

**4.2.2 Moments vs. the Y-Procedure**

In order to evaluate the Y-Procedure methodology, we first calculated the apparent adsorption constant $k_{app}$ (1/s) for each pulse according to equation (2.50). The mean surface coverage for each $i$th pulse, that is midway between the coverage at the end of pulse (i-1) and the beginning of pulse (i+1), was calculated as
\[ \Theta_i = \frac{C_{ZO,i}}{C_{Z,tot}} = \frac{C_{ZO,i-1} + \frac{1}{2} \cdot 2X_i \frac{N_p}{m_{cat}}}{C_{Z,tot}}, \quad (4.4) \]

where the second term in the numerator represents half of oxygen atoms adsorbed during pulse \( i \).

With increasing surface coverage the apparent constant declined. This decline was steeper than linear (graph is not shown), suggesting that oxygen adsorption is dissociative and not molecular. In the mean field approximation, the rate of dissociative oxygen adsorption on two catalyst sites \( Z \) is

\[ R_{O_2} = C_{Z,tot} k (1 - \Theta)^2 C_{O_2}. \quad (4.5) \]

where \( k \) (\( m^3/mol/s \)) is the intrinsic adsorption constant.

Apparent adsorption constants can be related to the surface coverage and intrinsic kinetic constant by

\[ k_{app} = \frac{m_{cat}}{V_G} C_{Z,tot} k (1 - \Theta)^2, \quad (4.6) \]

where \( m_{cat} \) (\( g \)) is the catalyst mass, and \( V_G \) \( m^3 \) is the void volume in the catalytic zone.

Defining the modified apparent constant \( \kappa \) (\( m^3/mol/s \)) as

\[ \kappa = \frac{k_{app} V_G}{m_{cat} C_{Z,tot}} \quad (4.7) \]

and taking the square root of kinetic relation (4.6), we obtain

\[ \sqrt{\kappa} = \sqrt{k} (1 - \Theta). \quad (4.8) \]
Figure 4.2 plots the square root of modified apparent constants $\sqrt{\kappa}$ as a function of the mean surface coverage $\Theta$. During the first 14 pulses in the sequence, the conversion was 100% and the signal was too small for kinetic analysis. For the rest of the sequence, Figure 4.2 indicates that $\sqrt{\kappa}$ decreased linearly as $\Theta$ increased up to 0.8. This linear region was followed by a slower decay, as the coverage increased from 0.8 to one. The presence of these kinetically distinct regions can be attributed to the microscopic surface non-uniformity induced by adsorbate-adsorbate interactions at higher coverages (Zambelli et al., 1997; Zaera, 2002a). It may also be explained by the presence of two different catalytic sites, similarly to those conjectured for CO oxidation over the $Pt/CeO_2$ catalyst in (Shekhtman et al., 2008). While these data cannot substantiate either hypothesis, they do confirm that a simple dissociative adsorption model is valid up to 0.8 coverage.

According to kinetic relation (4.8), the slope of the first linear segment in Figure 4.2 can be used to determine the intrinsic adsorption constant, while the x-intercept indicates which fraction of catalytic sites is kinetically important in the relevant coverage range. The linear fit depicted in Figure 4.2 gives an intrinsic adsorption constant of $1.12 \cdot 10^6 \text{ (m}^3/\text{mol/s})$, and the fraction of kinetically manifested active sites as 0.83.

![Figure 4.2: The square root of the modified apparent kinetic constant $\sqrt{\kappa}$ as a function of surface coverage $\Theta$ for the multi-pulse oxygen uptake experiment](image)
Figure 4.3: The Y-Procedure results for one of the oxygen pulses This pulse is marked with a double star in Figure 4.1(a).

Next, we analyzed the same data via the Y-Procedure. Figure 4.2.2(a) presents one of the oxygen exit flow curves (marked in Figure 4.1(a) by a double star symbol). The area difference between the oxygen and inert curves indicates the conversion of 55%. Figure 4.2.2(b) shows the reconstructed gas concentration of oxygen in the thin zone for two different values of the filtering parameter $\sigma$. As far as the gas concentration is concerned, $\sigma = 1$ gives a reasonably smooth result. However, the reconstruction of the reaction rate is much more sensitive to noise, and the same smoothing is insufficient. As evident from reaction rate plots in Figure 4.2.2(c), an appropriate filtering was achieved at $\sigma = 6$. The inset of the same figure depicts the accumulation of surface oxygen within the pulse calculated from the reconstructed reaction rate as

$$C_{ZO}(t) = 2 \int_0^t R_{O_2}(t') dt'.$$ (4.9)
Experimental trajectories in the RC space are shown in Figure 4.4(a). The pulses marked with a star symbol correspond to the region of 100% conversion excluded from the kinetic analysis. It should be noted, however, that rate/concentration dependencies for these pulses appear to be very narrow when compared to the rest of the trajectories, which could be interpreted as a sign of state-defining pulses. Indeed, the adsorption of oxygen appears to be so fast that only after $2/3$ of all sites were occupied did the surface coverage affect the conversion and trajectories demonstrated a state-altering character (petal-like shape). As expected, the reaction rate descended, and the petal width increased as the coverage approached one.

Figure 4.4: (a) Experimental trajectories in the rate/composition space. The range of pulses marked with a star symbol (up to $\Theta = 2/3$) is excluded from further analysis; (b,c) The square root of the time-dependent modified apparent adsorption constant as a function of surface coverage for pulses marked in panel (a) with double and triple stars respectively. The inset shows the corresponding data range.
In terms of the reconstructed transient kinetic characteristics, the modified apparent constant $\kappa$ can be expressed as

$$\kappa(t) = \frac{R_{O_2}(t)}{C_{O_2}(t)C_{Z,tot}}. \quad (4.10)$$

Figure 4.4(b) shows the square root of $\kappa$ as a function of the transient surface coverage for the trajectory marked in Figure 3.7(a) by a double star. The inset of the same figure demonstrates the data range plotted, and the arrow points in the positive time direction. The dashed line represents the linear fit of equation (4.8) which gave the intrinsic kinetic constant of $k = 1.09 \cdot 10^6 \text{ (m}^3/\text{mol/s)}$, and the fraction of active sites of $\Theta_{act} = 0.83$. These values closely agree with the parameters estimated via the moment analysis, but, in this case, they are obtained from a single trajectory reconstructed in a kinetically ‘model-free’ manner. Figure 3.7(c) shows a similar plot for the trajectory marked with a triple star. The linear fit provides $k = 0.93 \cdot 10^6 \text{ (m}^3/\text{mol/s)}$, and $\Theta_{act} = 0.88$. The decrease in the value of the intrinsic constant and the increase of the fraction of active sites relative to the double star trajectory are consistent with the effects of high surface coverage previously seen in Figure 4.2, testifying to the validity of the Y-Procedure methodology.

### 4.3 CO oxidation on $\text{Au/SiO}_2$ catalysts

The next experimental application was CO oxidation reaction on the $\text{Au/SiO}_2$ catalysts which involved more complex interactions of oxygen with the metal. Catalysis by gold has attracted considerable attention since Haruta and co-authors discovered in 1989 that small gold nanoparticles are catalytically active in CO oxidation (Haruta et al., 1989). It was later found that supported gold catalysts and gold single crystals selectively catalyze, among other reactions, propene epoxidation, ethyne hydrochlorination, and selective hydrogenation of acrolein and crotonaldehyde (Corti et al., 2005; Min and Friend, 2007). Since many of these reactions have commercial applications, gold catalysts are evaluated as a cheaper alternative to platinum and palladium which are currently being used for similar processes. Extensive kinetic and spectroscopic studies have suggested that catalytic activity of nanosized gold, highly dependent on
the particle size, may be determined by the concentration of low-coordinated active sites on the gold surface (Schubert et al., 2001) or its interface with the support (Grunwaldt and Baiker, 1999; Fu et al., 2003). Nevertheless, the nature of gold’s catalytic properties is still an active area of research, e.g. (Baker et al., 2010; Wittstock et al., 2010), including TAP experiments, e.g. (Widmann et al., 2007; Kotobuki et al., 2009).

Most of the model gold catalysts are supported on reducible metal oxides (e.g. TiO$_2$, CeO$_2$, or Fe$_2$O$_3$) which often participate in catalytic reactions. Fewer studies have involved catalysts prepared using a non-reducible or inactive support such as SiO$_2$ which would provide a valuable control case for distinguishing kinetic characteristics unique to the gold nanoparticles from convoluted particle/support interactions. Here, we describe a TAP study of CO oxidation over the Au/SiO$_2$ catalyst prepared via magnetronsputtering (Veith et al., 2005, 2008). Contrary to wet chemical methods, this physical deposition technique minimizes the contamination of catalyst surface with synthesis by-products. More details on the preparation and characterization of the catalyst used in our study can be found in (Zheng et al., 2010). In summary, the catalyst contained 10.97%, $w$ of gold nanoparticles with an average size of $3.2 \pm 1.45$ (nm) which were supported on the non-porous silica. Preliminary studies indicated that significant amounts of oxygen could be introduced into the catalyst only under elevated pressures beyond TAP Knudsen regime. In this study, the introduction of oxygen under elevated pressure was followed by its titration with CO under TAP vacuum conditions in order to elucidate the role of oxygen storage in CO oxidation mechanism.

### 4.3.1 CO adsorption under vacuum TAP conditions

The interaction of CO with Au/SiO$_2$ catalyst under TAP conditions was investigated by pulsing 1 : 1 mixture of CO and argon at temperatures ranging from 323 to 643 K. The results of TAP CO adsorption experiments at different temperatures are presented in Figure 4.5(a) were CO exit flow curves are plotted in dimensionless coordinates in order to correct for the temperature dependence of Knudsen diffusion. The top curve corresponds to the dimensionless argon exit flux used as an inert transport standard. Figure 4.5(a) indicates that CO strongly adsorbs on the catalyst at low
temperature (323 K), but desorption begins to dominate as the reaction temperature is increased. The CO exit flow curves intersect the argon curve, as evident for lower temperatures, suggesting that adsorption is reversible according to the 'fingerprint' discussed in section 2.2.1. It can be concluded that at temperatures above 463 K the CO surface lifetime and surface coverage are very low.

Figure 4.5: CO adsorption on the Au/SiO₂ catalyst at different temperatures (a) Dimensionless CO exit flux compared to the standard diffusion curve (Ar); (b) The equilibrium constant $K_{eq}$ plotted as a function of reactor temperature $T$ K. The inset shows a plot of $\log(K_{eq})$ vs $1/T$ (K⁻¹) and the estimates for $\Delta H_{ads}$ and $\Delta H_{ads}$.

The exit flow data were used to estimate the heat of CO adsorption. First, an apparent equilibrium constant was calculated from exit flow moments using formulas (2.58),(2.59), and (2.60) from section 2.2.4 conveniently combined into
\[ K_{eq} = \left| \epsilon \left( \frac{\tau_{res}}{\tau_{res}^{TZ} + \epsilon \left( \frac{\Delta L_{cat}}{\Delta L_{cat}} \right)^2} - \frac{2\Delta L_{2in}}{\Delta L_{cat}} \right) \right| - 1, \]  

(4.11)

where \( \tau_{res} \) and \( \tau_{res}^{TZ} \) are the mean residence time and the TZ residence time defined by equations (2.46) and (2.49) respectively.

Figure 4.5(b) shows the equilibrium constant for CO adsorption as a function of temperature. Next, the heat and enthalpy of CO adsorption were found from these data using the Vant Hoff equation (3.12). The inset of Figure 4.5(b) shows the Vant Hoff plot of \( \log(K_{eq}) \) (natural logarithm) as a function of inverse temperature and the corresponding linear fit which gives a heat of CO adsorption of 24.39 ± 3.70 (kJ mol\(^{-1}\)) and an entropy of 32.13± 9.53 (J mol\(^{-1}\)) K\(^{-1}\) (temperature range 323-523 K). The heat of CO adsorption on the Au/TiO\(_2\) catalysts was previously measured in a TAP reactor to be 9.2 (kJ mol\(^{-1}\)) (at ambient temperature) (Olea and Iwasawa, 2004). However, according to (Hartshorn et al., 2009) the heat of CO adsorption on Au/TiO\(_2\) catalysts and Au single crystals can range from 27 to 76 (kJ mol\(^{-1}\)) (at ambient temperature) depending on weak or strong CO binding sites. Therefore, the obtained value is in the lower range of previously reported values for CO heats of adsorption on different gold catalysts.

4.3.2 CO titration of surface oxygen and pump-probe experiments

In the next set of experiments, the Au/SiO\(_2\) catalyst was pretreated with a flow of oxygen (atmospheric pressure) for 5 min at 623 K. The microreactor was then evacuated by opening the slide valve. After the evacuation, a series of CO/Ar (1 : 1 mixture) pulses were introduced into the microreactor. Figure 4.6(a) shows the pulse intensity normalized exit flow of CO as a function of pulse number. In the beginning of the titration sequence, the exit flow was very small indicating high CO conversion. As the pulse number was increased, the conversion decreased until the exit flow curves approached a plateau where the entire CO input pulse exits the microreactor unconverted. The CO\(_2\) exit flow, normalized by the CO pulse intensity, is presented
in Figure 4.6(b). Here the opposite trend is observed - the CO₂ production is high in the beginning, and then rapidly decreases approaching zero at the end of the titration sequence. These experiments clearly show that after the evacuation, oxygen adsorbed during pretreatment at atmospheric pressure is still present on the Au/SiO₂ catalyst in an active form.

**Figure 4.6:** TAP CO titration experiment after atmospheric oxygen pretreatment at 623 K (a) CO pulse intensity normalized exit flow \( F_{\text{CO}}/N_{p,\text{CO}} \) (s⁻¹) versus time \( t \) (s) as a function of pulse number. (b) CO₂ exit flow normalized by CO pulse intensity \( F_{\text{CO}_2}/N_{p,\text{CO}} \) (s⁻¹) versus time \( t \) (s) as a function of pulse number.

In TAP pump-probe experiments with oxygen pretreated catalyst, a 1 : 1 mixture of oxygen and argon was introduced into the microreactor in alternating pulses with CO/Ar 1 : 1 mixture. Oxygen was sent into the microreactor in alternating pulses with CO so that after each CO pulse the surface was exposed to oxygen for re-oxidation. Oxygen (pump-pulse A) was always pulsed first followed by the CO pulse (probe-pulse B). The pair of oxygen and CO pulses, separated by a 1.5 (s) delay,
formed a 3 (s) pump-probe cycle. Within each cycle, the amount of oxygen injected into the microreactor was approximately 6 times the amount of CO. Figure 4.7(a) shows a 3D plot of the oxygen pulse response curves obtained in the pump-probe experiment at 623 K. Oxygen exit flow curves did not change during the pump-probe sequence and their areas normalized by the pulse intensity were equal to one, indicating that under TAP conditions oxygen adsorption on the catalyst is not significant. CO$_2$ response curves plotted in Figure 4.7(b) show that CO$_2$ was produced only during the CO pulse (Pulse B). CO$_2$ production continues to decrease during the course of the multi-pulse experiment even though oxygen is continually introduced into the microreactor in alternating pulses with CO. This behavior suggests that oxygen adsorbed on the catalyst during atmospheric pretreatment is responsible for CO$_2$ production during TAP experiments and the rate of oxygen adsorption during a pump-probe sequence is not sufficient to maintain the oxygen surface coverage formed at high pressures.

4.3.3 The influence of oxygen pretreatment pressure

The next set of experiments involved pretreatment of the Au/SiO$_2$ catalyst at 573 K with different pressures, ranging from 10$^{-6}$ to 1740 (torr). To change the pressure inside the microreactor during oxygen pretreatment, the first step was to determine the total number of oxygen pulses needed to reach the maximum pressure inside the microreactor, which was approximately 35 (psia) or 1800 (Torr) due to the limitation of the pressure transducer reading. Then, while keeping the number of oxygen pulses introduced the same, the pressure was changed in the microreactor by adjusting a needle valve on the slide valve. The needle valve can be adjusted to allow a very small amount of vacuum into the microreactor to change the pressure inside the microreactor. After pretreatment with oxygen, in TAP studies the microreactor was evacuated to UHV conditions and a sequence of CO/Ar pulses (1 : 1 mixture) were introduced at the same temperature (573 K).

Figure 4.8(a) shows the amount of CO$_2$ (normalized zeroth moment) produced during the CO titration as a function of the CO pulse number for different oxygen pretreatment pressures. Two features distinguish the CO$_2$ production curves presented in
Figure 4.7: **TAP pump-probe experiment after atmospheric oxygen pretreatment at 623 K** (a) $O_2$ pulse intensity normalized exit flow $F_{O_2}/N_{p,O_2} (s^{-1})$ versus time $t (s)$ as a function of pulse number. (b) $CO_2$ exit flow normalized by CO pulse intensity $F_{CO_2}/N_{p,CO} (s^{-1})$ versus time $t (s)$ as a function of pulse number.

Figure 4.8(a): the first is an initial plateau that increases with the pretreatment pressure and the second is a decay curve that follows the plateau. At oxygen pretreatment pressures of 4.44 (psia) and above, a plateau region is observed. In this region, the rate of $CO_2$ production is the same from one pulse to the next. The plateaus height is the same for different oxygen pretreatment pressures, but the plateaus length increases with the oxygen pretreatment pressure. At the end of the plateau, the decay rate is the same for all oxygen pretreatment pressures. For oxygen pretreatment pressures lower than 4.44 (psia), there is no plateau and only the decay curve is observed. Figure 4.8(b) shows the corresponding $CO$ exit flow data (pulse intensity normalized zeroth moment) which exhibit features similar to the $CO_2$ dependences - a plateau region followed by rapidly decreasing conversion.
Figure 4.8: CO titration experiments after oxygen pretreatments at different pressures (a) Zeroth moments of CO\textsubscript{2} exit flow curves normalized by CO pulse intensity as a function of pulse number in titration sequence. (b) Zeroth moments of CO exit flow curves normalized by CO pulse intensity as a function of pulse number in titration sequence.

The integral amount of CO\textsubscript{2} produced over the entire sequence of pulses increases as a function of the oxygen pretreatment pressure. The amount of CO\textsubscript{2} produced on the Au/\textit{SiO}_2 catalyst sample pretreated with oxygen at 33.66 (\textit{psia}) is approximately 6 times the amount produced on the sample pretreated under UHV conditions. The amount of CO\textsubscript{2} produced during a titration sequence can be used to measure the oxygen capacity of the sample using the following formula

\[
U_0 = \frac{N_{a.m.u.}}{m_{cat}} \int_1^i M_0 CO_2(p)dp, \tag{4.12}
\]
where $U_O \ (mol \ O \ g_{cat}^{-1})$ is oxygen capacity per gram of catalyst (titrated oxygen), $N_{a.m.u.} = 3$ is the number of AMUs recorded by the QMS, $m_{cat} = 6 \ (mg)$ is the catalyst mass, $p$ is the pulse number in a titration sequence, and $i$ is the limit of integration which equals the last pulse number in a sequence when calculating the integral oxygen capacity. Figure 4.9 shows $U_O$ for different pretreatment pressures compared to the oxygen capacity of silica (pretreated in a hydrogen flow at 623 K) without gold nanoparticles. The amount of stored oxygen is a 'low' estimate, and it is expected that the real dependence of oxygen storage on pretreatment pressure will approach a saturation limit.

Figure 4.9: The total oxygen capacity of the catalyst $U_O \ (mol \ O \ g_{cat}^{-1})$ as a function of oxygen pretreatment pressure. The capacity of silica without gold nanoparticles is shown for comparison.

### 4.3.4 CO oxidation mechanism

As discussed in section 4.3.1, CO adsorption experiments indicate that CO surface coverage is low at reaction temperatures above 463 K. In the limit of low surface coverage of CO, the kinetics of CO oxidation can be greatly simplified by assuming that $CO_2$ is generated via one channel - the reaction between catalyst oxygen and gaseous CO. In other words, CO oxidation in this parametric domain can be described by an apparent impact mechanism. To corroborate this assumption, we performed the Y-Procedure analysis of several CO pulses over completely oxidized catalyst at 573 K. As an example, Figure 4.10(a) shows PI normalized exit flow curves of argon, CO, and $CO_2$ for the catalyst fully oxidized by oxygen pretreatment at 33.66 (psia). These curves were translated by the Y-Procedure into thin-zone reaction rates shown
in Figure 4.10(b). Despite deviations in the shoulder of the curves, CO and $CO_2$ reaction rates closely match in the beginning of the pulse and peak at the same time. This initial coherency indicates that there is no time-lag between CO adsorption and $CO_2$ release which qualitatively confirms the assumption of apparent impact mechanism for CO oxidation, as shown previously in Chapter 3 section 3.6.

Figure 4.10: The Y-Procedure analysis of CO titration pulses over fully oxidized catalyst pretreated with oxygen at 33.66 (psia) (a) PI normalized exit flow curves. (b) Reconstructed reaction rates in the catalytic zone.

4.3.5 The role of oxygen storage

Multi-pulse CO titration experiments discussed in section 4.3.3 demonstrate that $CO_2$ is produced from oxygen accumulated on gold nanoparticles during pretreatment and the total amount of oxygen stored in the catalyst increases with increasing pretreatment pressure (Figure 4.9). To understand the nature of the oxygen storage process in more detail, the apparent kinetic constant of $CO_2$ production was calculated for different catalyst states, from the most oxidized state to the lowest reduced state within the titration sequences. This constant was calculated from CO conversions using
equation (2.50), assuming the apparent impact mechanism of $CO$ oxidation. The catalyst state was characterized by the reduction degree (RD) defined as the amount of titrated oxygen, a function of CO pulse number, normalized by the maximum total oxygen storage achieved in the experiments after 33.66 (psia) pretreatment:

$$RD(p) = \frac{U_o(p)}{U_0^{[33.66]}}. \tag{4.13}$$

where $U_o(p)$ ($molO_g^{-1}cat$) is the oxygen capacity as a function of pulse number, and $U_o^{[33.66]}$ ($molO_g^{-1}cat$) is the total oxygen capacity corresponding to 33.66 (psia) pretreatment pressure.

![Figure 4.11](image)

Figure 4.11: The apparent kinetic constant of $CO$ oxidation $k_{app}$ ($s^{-1}$) as a function of catalyst reduction degree $RD$. Pulses marked with the star and double star symbols are later used for the analysis of intra-particle oxygen depletion in section 4.3.6.

Figure 4.11 shows the apparent kinetic constant plotted versus the reduction degree. The normalization by the maximum oxygen capacity is geometrically equivalent to shifting individual curves along the x-axis to match the end point of the reference titration curve (33.66 (psia) pretreatment). The curves corresponding to different pretreatment pressures upon normalization merge into a single combined curve which covers all experimental data. The procedure of changing the oxygen pretreatment pressure, which alters the amount of oxygen storage, only changes the initial position of the prepared catalyst on this curve.
In Figure 4.11, an initial plateau region of the apparent kinetic constant can be seen up to the reduction degree of 0.5. This behavior cannot be explained using a model with only one pool of oxygen atoms on the catalyst. Such a model assumes that adsorption occurs on equivalent surface sites, which form a 'surface reservoir', and that the apparent kinetic constant for the oxidation reaction is governed by the first-order expression

\[ k_{\text{app}} = k(1 - RD), \]  

(4.14)

where \( k \) (s\(^{-1}\)) is an oxidation constant including the absolute concentration of oxidation sites, and \( RD \) is the dimensionless reduction degree defined by equation (4.13). This expression describes an apparent kinetic constant which decreases monotonously, without a plateau, with increasing reduction degree. Clearly, the shape of the curve shown in Figure 4.11 does not comply with expression (4.14).

Instead, data in Figure 4.11 can be understood through a more complex mechanism involving an additional oxygen reservoir that exchanges oxygen with the 'surface reservoir'. According to this mechanism, during high pressure pretreatment, oxygen populates both the 'surface reservoir' and the additional reservoir. The total amount of oxygen stored in the catalyst after the pretreatment is proportional to the pretreatment pressure. During titration by \( CO \) under TAP conditions, the surface oxygen is consumed by oxidation reaction, and then partially replenished by exchange with the additional reservoir. In the course of titration, this mechanism may leads to the two regions observed in our study:

1. **Plateau.** The amount of oxygen available on the surface does not change significantly until the moment when the additional oxygen reservoir is emptied and cannot compensate surface oxygen at the same rate (end of the plateau). This is the \( CO \) controlled region where \( CO_2 \) production is limited by the amount of \( CO \) in the titration pulses.

2. **Decay region.** \( CO_2 \) production decreases after the plateau and the rate of this decrease is independent of the oxygen pretreatment pressure. The rate of \( CO_2 \)
production in this region is limited by the amount of oxygen available on the surface and is controlled by the oxygen supply from the additional reservoir.

To obtain more compelling evidence in support of the double-reservoir hypothesis, we have analyzed intra-pulse kinetic characteristics of CO oxidation during the multipulse titration which were derived from via Y-Procedure. As the next section elaborates, it was found that surface oxygen depleted by CO oxidation is indeed resupplied by the beginning of upcoming CO pulse.

4.3.6 Intra-pulse depletion of surface oxygen

Apparent kinetic constants presented in Figure 4.11 which suggested the presence of an additional oxygen reservoir were calculated via integration of exit flow curves and, therefore, represent only time-averaged characteristics. Following the methodology suggested in section 3.6, the intra-pulse evolution of kinetic properties during CO titration were examined under the assumption of impact mechanism. The apparent kinetic constant within each pulse was calculated as a ratio of the CO reaction rate and gas concentration:

\[ k_{app}(t) = \frac{R_{CO}(t)}{C_{CO}(t)}. \]  \hspace{1cm} (4.15)

Presumably, this apparent constant is determined by intrinsic kinetic parameters and the concentration of surface oxygen as

\[ k_{app}(t) = kCZO(t). \]  \hspace{1cm} (4.16)

Figure 4.12(a) shows transient apparent kinetic constants inside titration pulses 4 through 6 in the CO controlled region (plateau) for the catalyst pretreated with oxygen under 33.66 (psia). Within each pulse, the apparent kinetic constant rapidly drops indicating the initial depletion of surface oxygen by CO oxidation. Because of the noise, we were unable to reconstruct the signal for later times in each pulse represented by gray areas. However by the beginning of the next pulse, the apparent
kinetic constant indicative of the concentration of surface oxygen was restored to the same level.

This was not the case for pulses 10, 11, and 12 of the same multi-pulse sequence whose time-dependent apparent kinetics are shown in Figure 4.12(b). Here, oxygen consumption was not completely replenished by the beginning of the next pulse and initial levels of surface oxygen dropped from one pulse to the next. These intra-pulse kinetic features further substantiate the oxygen storage mechanism with an additional reservoir on the Au/SiO$_2$ catalysts and exemplify potential benefits of the Y-Procedure analysis for unraveling fast surface steps of complex catalytic reactions.

Figure 4.12: Intra-pulse apparent kinetic constants of CO oxidation $k_{\text{app}}(t)$ (s$^{-1}$) as functions of time within different titration pulses corresponding to 33.66 (psia) pretreatment (a) Pulses 4 through 6 marked in Figure 4.11 by a star symbol. (b) Pulses 10 through 12 marked in Figure 4.11 by a double star symbol. Grey areas represent the final portion of each curve which could not be analyzed because of the noise.
4.4 Concluding remarks

This chapter described the experimental part of our work which consisted of developing the PIM protocol, validating the Y-Procedure approach against the benchmark problem of oxygen uptake on polycrystalline platinum, and studying the Au/SiO$_2$ catalyst. The latter study employed a combined experimental strategy which involved high-pressure pretreatment of the catalyst with oxygen flow followed by CO titration of surface oxygen stored on the catalyst after the pretreatment, under TAP vacuum conditions. CO titration data suggested the presence of an additional oxygen reservoir on the catalyst which can re-supply surface oxidation sites during time delays between two consecutive CO pulses. The Y-Procedure analysis of intra-pulse kinetics provided compelling qualitative evidence in support of this mechanism.

It is possible that during the pretreatment procedure, dissociated oxygen atoms migrate into the bulk of gold nanoparticles. The subsurface storage formed during pretreatment supplies oxygen to the surface active sites for the oxidation reaction during TAP CO titration. Such subsurface oxygen species have been previously observed on gold. For example, (Choi et al., 1998) studied temperature programmed desorption of NO$_2$ and O$_2$ on silica-supported gold catalysts under vacuum conditions. It was found that adsorbed oxygen is present as atoms on the surface or as bulk gold oxide in the subsurface. Transition between the two species requires an activation energy which strongly depends on surface conditions; oxygen penetrates the gold surface more easily when it is already covered with oxygen atoms. (Schrader, 1977) presented a model of oxygen migration on a Au(111) from an adsorption site on which oxygen is dissociated to a less active site and diffusion of oxygen into the gold lattice. Thermal desorption experiments performed by (Gottfried et al., 2003) in which Au(110) single crystal surfaces were bombarded with oxygen ions also confirm that there are different oxidative states: chemisorbed atomic oxygen, oxygen atoms dissolved in the bulk, and gold oxide.

It is also possible that the excess of oxygen manifested as the plateau region of the apparent kinetic constant dependence in Figure 4.11 represents dissociated oxygen atoms on the nanoparticle surface which slowly diffuse towards active oxidation sites. Further kinetic and spectroscopic studies are required to determine the true nature of the additional oxygen reservoir. For example, the manipulation of inter-pulse time delays
in CO titration sequences could be used to clarify whether CO$_2$ production follows variations of the surface oxygen constant on the millisecond time scale, as suggested by the proposed double-storage mechanism. In conclusion, the Y-Procedure is shown to be a promising tool for micro-kinetic analysis of complex catalytic processes. This experimental strategy combining high-pressure pretreatments with Knudsen TAP experiments can be useful for understanding the connection between vacuum and high-pressure catalytic kinetics.
Chapter 5

Conclusions and Outlook

In line with our objectives, the main results of this work are 1) the Y-Procedure was used to develop a theoretical basis for the non-steady-state high-throughput kinetic characterization of complex catalytic reactions, 2) this theoretical basis was translated into a viable data interpretation framework, and 3) the framework was applied to a novel catalytic system of considerable scientific relevance. The non-steady-state monitoring of catalytic reactions is achieved in Thin-Zone (TZ) TAP experiments which are then analyzed via the Y-Procedure to yield reaction rates, gas concentrations, and surface storages in the spatially uniform catalytic zone. These characteristics are extracted with the millisecond temporal resolution without a priori assumed kinetic models, providing a unique data set for elucidating reaction mechanisms. We have analyzed several model reactions and identified their characteristic kinetic signatures in rate-composition data which will enable an effective mechanism identification in future practical applications. Novel parameter estimation routines were also suggested and tested. This comprehensive TZ TAP data interpretation framework based on the Y-Procedure was validated experimentally and applied to study CO oxidation on the novel Au/SiO₂ catalyst. Our work employed a combination of theoretical, numerical, and experimental studies which have led to the following specific results.

Primary data acquisition and post-processing:

- The Pulse Intensity Modulation (PIM) experimental protocol was developed for collecting TAP data specifically intended for analysis using the Y-Procedure. The key idea of a pulse modulation experiment is to precisely control the catalyst composition by changing the amount of molecules sent into the microreactor and quantitatively study non-linear kinetic effects caused by increased surface
coverage. The protocol also contains instructions on how to account for a noticeable adsorption in the inert material when translating exit flow data into thin-zone kinetic characteristics.

- Instantaneous surface storage of certain molecular or atomic moieties can be calculated from intra-pulse reaction rates in the catalytic zone based on the overall transient mass balance of the catalytic surface. For a broad class of reaction mechanisms which are comprised only of elementary steps with gas-surface exchange, these moieties correspond to kinetically individual surface intermediates. Otherwise, when surface-only steps are also present, a surface storage represents combined concentrations of several intermediates.

- The progress of a pulse-response experiment can be represented and understood as a trajectory in the kinetic space spanned by reaction rates and concentrations. For an individual elementary step, such kinetic trajectories are usually three-dimensional and can be used to conveniently visualize and interpret TZ TAP data.

Analysis of model reactions:

- Numerical simulations of simple irreversible and reversible adsorption steps have demonstrated that kinetic trajectories exhibit non-linear behavior when the catalyst composition is significantly altered inside the pulse, providing a novel method for distinguishing state-defining and state-altering experiments. Procedures were also suggested for estimating intrinsic kinetic parameters including the concentration of working active sites from a small set of state-altering data. Contrary to integral methods of parameter estimation, these procedures fully utilize the transient nature of TAP data and characterize the act of catalysis in progress instead of its final outcome.

- Kinetic trajectories for reversible adsorption revealed the Momentary Equilibrium (ME) phenomenon which to the best of our knowledge has never been described in the literature. Unlike the classical chemical equilibrium in closed systems, this type of equilibrium is achieved only for an instance when a non-monotonous net reaction rate passes through zero during a pulse-response experiment. While general kinetic and thermodynamic properties of the ME are
still unknown, we have shown that the relationship between gas and surface compositions at the ME point can be used to estimate the total number of catalytic sites and the intrinsic equilibrium constant for a reversible adsorption. Hitherto, such estimations were not practiced in TAP experiments due to algebraic complexity and the integral nature of moment analysis.

- A novel concept of temporal kinetic coherency was introduced to facilitate the identification of reaction mechanisms based on intra-pulse reaction rates and concentrations reconstructed by the Y-Procedure. Kinetic characteristics are said to be coherent when their temporal evolutions are synchronized, resulting in time-independence of their ratios or matching of their peak times. The temporal kinetic coherence (or decoherence) of certain characteristics can be used as a kinetic signature in order to support or reject a specific mechanistic hypothesis. We have shown that this principle can be used to unambiguously discriminate between several possible combinations of elementary steps involved in the $CO$ oxidation reaction. In addition, we have demonstrated how kinetic decoherence can be used to reveal the presence of a hidden surface step in an irreversible isomerisation reaction.

**Experimental validation and application:**

- The first experimental validation of the Y-Procedure approach was accomplished by employing a well characterized oxygen uptake on polycrystalline platinum. The reaction followed the dissociative adsorption model up to an oxygen coverage of 0.8 and the qualitative behavior of its intra-pulse kinetics within this coverage limit was in accordance with theoretical results for irreversible processes. The intrinsic kinetic constant and the total oxygen storage capacity estimated by the Y-Procedure and the method of moments were in agreement with values previously published for this prototypical reaction.

- The Y-Procedure methodology was utilized to investigate $CO$ oxidation kinetics on the $Au/SiO_2$ catalyst prepared by the method of magnetron sputtering, a convenient model for studying catalytic properties of nanosized gold supported on a non-reducible carrier. It was found that at 573 - 623 K, $CO$ oxidation kinetics can be approximated by an apparent impact mechanism and that only
the oxygen introduced to the catalyst under elevated pressures is responsible
for CO oxidation activity under TAP vacuum conditions. Hence, kinetic data
were measured in a two-step procedure. First, the catalyst was exposed to
the flow of oxygen under an increased pressure. Second, the microreactor was
evacuated to TAP vacuum conditions and the catalyst oxygen was titrated off
with a sequence of CO pulses. Multi-pulse titration experiments suggested
that the total amount of oxygen stored on the catalyst was proportional to
the pretreatment pressure and that all CO titration data could be described
by a single curve relating apparent kinetic constants to the reduction degree.
The reduction degree was used as a common scale of the catalyst state. The
combined kinetic curve consisted of two distinct regions: 1) the plateau region
where the apparent constant did not depend on the reduction degree and 2) the
decay region where the apparent constant rapidly decreased with the reduction
degree approaching one. This kinetic behavior was explained by a mechanism
involving an additional oxygen reservoir on the catalyst that was filled during
pretreatment and from which active surface oxygen was replenished between
consecutive pulses in the plateau region of the combined kinetic curve. Once
this additional reservoir was exhausted, the apparent kinetic constant decreased
as a result of oxygen depletion. This mechanistic hypothesis was corroborated
by the intra-pulse evolution of the catalyst composition extracted from exit flow
data via the Y-Procedure.

In summary, the Y-Procedure was translated from a theoretical possibility into a
viable method of kinetic analysis, validated experimentally, and employed to obtain
strong kinetic evidence in support of the reaction mechanism for a novel catalytic
model. Potential benefits and implications of this approach in the field of kinetic
characterization of technical catalysts motivate further efforts to develop and apply
the Y-Procedure framework.

Near-term research directions:

- The Y-Procedure should be systematically applied to a variety of industrially
  relevant case studies such as selective hydrocarbon oxidation, alkane dehydro-
genation, and dry reforming of methane.
• Kinetic signatures similar to those described in Chapter 3 of this thesis for simple mechanisms should be searched for a variety of complex reaction mechanisms to guide experimental applications. An emphasis should be placed on industrially relevant cases as well as mechanistic motifs behind characteristic kinetic features, contributing to further generalization and automation of mechanism identification routines. It should also be possible to obtain rigorous theoretical or semi-empirical criteria of identifiability for reaction mechanisms and surface intermediates based on the topology of corresponding reaction networks. The analysis of reaction mechanisms discussed in (Marin and Yablonsky, 2011) can provide a good starting point for creating a library of decision trees and standardized experimental strategies for common reaction networks encountered in practice. This generalized Y-Procedure approach must utilize a diverse toolkit of TAP experiments, including multi-pulse, temperature programmed, and pump-probe experiments, to extend the range of discernible catalytic phenomena.

• Characterization of intra-particle diffusion should be one of the priorities for future developments of the Y-Procedure, since most technical catalysts are porous materials. Internal diffusion is also paramount to reactions in zeolites which play an increasingly important role in modern catalysis (Chal et al., 2011). The problem of estimating intra-particle diffusion parameters can be approached by relating reconstructed kinetic characteristics in the TZ to mathematical models of gas transport inside catalytic pores such as those proposed in (Zou et al., 1994; Keipert and Baerns, 1998; Colaris et al., 2002; Shekhtman, 2003; Phanawadee et al., 2005). For example, the experimentally measured TZ reaction rate and gas concentration can be treated as boundary conditions at the pore mouth. Then, the extraction of diffusion parameters can be re-casted as an inverse problem similar to the Y-Procedure itself, but formulated for the intra-particle porous domain.

• Kinetic effects of microscopic non-uniformities of catalytic surfaces, both inherent and induced by lateral interactions of adsorbates, should be studied using numerical simulations in order to estimate the potential impact of parametric variability that they introduce. If it is determined that the scale of microscopic non-uniformity effects is above the uncertainty of the TZ approximation,
then it should be possible to quantify these effects in TZ TAP experiments. Alternatively, single particle TAP experiments (Zheng et al., 2008) should be explored as an option for measuring microscopic non-uniformity because they can potentially eliminate macroscopic gradients altogether.

- Y-Procedure results are influenced by several sources of errors including uncertainty of geometric and transport reactor characteristics, high frequency noise of exit flow data, and finite non-uniformity in the thin-zone. A more formal evaluation of these errors would provide a valuable extension of the Y-Procedure methodology and would help to assess the statistical significance of estimated kinetic parameters. It would also be useful to develop guidelines for optimizing the degree of noise filtering and choosing the representative intra-pulse data range for further analysis.

- Despite the fact that data post-processing, calibration, and analysis are essential for TAP methodology, the software platform for a convenient combination of all these tasks is still not available. The development of such a platform and its integration with TAP control and data acquisition software would facilitate the use of standardized experimental and data processing protocols, thereby enhancing the reliability and quality of TAP data. Moreover, recent progress achieved in automation and internet-enabled sharing of TAP hardware (Fushimi et al.) in combination with integrated data analysis software may contribute to establishing global collaborative partnerships in advanced catalytic research.

- Last but not least, experimental and data analysis protocols should be refined by extensive experimental applications which will also guide the design of more advanced TAP systems. Special emphasis should be placed on minimizing uncertainties of experimental factors such as pulse characteristics (intensity, stability, and reproducibility), reactor packing parameters (position and thickness of the catalytic zone), and calibration coefficients.

**Long-term goals** for the TAP technique in general and Y-Procedure approach in particular lie within a broad research road-map towards bridging pressure, materials, and complexity gaps in catalytic science. Potential TAP contributions can be outlined as follows:
• **Deciphering chemical complexity.** TZ TAP experiments coupled with advanced techniques of data analysis are uniquely suited for elucidating complex reaction networks involved in catalytic mechanisms. Systematic applications of the Y-Procedure in combination with other techniques will create an extensive knowledge base of kinetic fingerprints which will further accelerate mechanism identification. What distinguishes this Interrogative Kinetic (IK) approach from conventional practices of applied catalytic kinetics is that it provides intrinsic parameters of detailed microkinetic models, rather than global descriptors (i.e. activity and selectivities) or apparent parameters of phenomenological macrokinetic models. It should be noted that mechanistic findings originating from TAP must be related to complementary methods including *in situ* spectroscopies, surface characterization techniques, and computational catalysis.

• **Establishing structure-activity relationships.** One of the grand challenges in discovering structural and compositional factors determining the catalytic activity of complex materials is to relate kinetic characteristics to a well-defined state of the catalyst. To address this challenge, detailed kinetic information available from TZ TAP experiments can be directly linked to a spatially uniform catalyst composition which, in turn, can be gradually modified by state-defining and state-altering pulses. Findings presented in this thesis enable more scrupulous control over the catalyst composition and will lead to more sophisticated experimental tactics for studying how it affects the intrinsic kinetics. Furthermore, TAP reactor systems should be integrated with other hardware modules for advanced modifications of the catalytic surface. One such example is the combined TAP-Atomic Beam Deposition instrument (Fushimi et al., 2007) which allowed transfer of catalytic samples between deposition and reaction chambers without exposing them to air. An iterative procedure may be organized in which the catalyst structure first undergoes deep modification in a deposition section of the device. Then, the catalyst is transferred to the TAP section, where its kinetics are screened over a wide range of surface coverages or oxidation degrees created by multi-pulse experiments. Such high-throughput coupled systems can potentially result in breakthrough technology for elucidating structure-activity relationships.
Another possible research direction is studying a variety of model catalysts with increasing levels of structural complexity. Model catalysts have been advanced considerably beyond single crystals; recently developed models mimic much more realistic features of technical catalysts, e.g. (Goodman, 2003; Freund et al., 2003; Libuda and Freund, 2002) and have high enough concentrations of active sites to be investigated in TAP.

- **Investigating kinetics across the pressure gap.** The operating pressure in a typical TAP Knudsen experiment ranges from $10^{-4}$ to $10^{-1}$ (Pa) which places TAP on the border between the domains of surface science and applied catalysis. However, more research is needed to address the fundamental problem of reconciling high and low pressure kinetics. In our opinion, structure insensitive reactions should provide a good starting point. Another promising research area where the pressure gap is likely to be bridged by TAP are catalysts whose composition can be scaled between two limits such as fully oxidized and fully reduced surfaces. For these catalysts, intrinsic kinetic parameters obtained via TAP on two opposite sides of the compositional scale must be quantitatively compared to kinetic parameters obtained on the same ends of the scale via atmospheric flow techniques, e.g. SSITKA. In both flow and pulse studies, kinetic parameters should be extracted by similar methods and for similar microkinetic models. It is also important to independently characterize transport processes (in gas, solid, and on the surface) specific to the pressure regime. Detailed models can then be built by coupling transport and kinetic data. These models may reveal which kinetic and/or transport parameters are affected by the increase in operating pressure, facilitating our understanding of what causes the pressure gap in each particular case. This research approach will benefit from the analysis of intra-pulse changes in catalyst composition developed in this thesis and from the experimental strategy of combining high-pressure pretreatment with low pressure titration employed in our experimental section.

Increasing the operating pressure in the TAP microreactor beyond the Knudsen regime by pulsing more molecules should also be explored as a way to narrow the pressure gap. As peak pressure increases, the gas transport mechanism is expected to transition from Knudsen diffusion, through Stefan-Maxwell diffusion, to viscous flow (Kerkhof and Geboers, 2005). Accordingly, new mathematical tools must be developed for the extraction of intrinsic kinetic characteristics
from the exit flow data corresponding to each successive transport regime. The Dusty Gas Model (DGM), for example, incorporates all three of the mentioned transport mechanisms and is widely used for modeling of porous media flow (Mason and Malinauskas, 1983). Previously, the DGM was employed to evaluate the potential influence of viscous flow on TAP experiments (Rothaemel and Baerns, 1996; Delgado et al., 2002), but hitherto no attempts have been made to use this model for a quantitative data analysis. A valuable extension to the theory of TAP experiments would be to determine the range of pulse sizes for which the DGM can be applied and validate the model experimentally. There may exist a window of experimental conditions (pulse intensity, length of the catalyst zone, temperature) within which it will be possible to maintain some level of catalyst zone uniformity and develop an algorithm for extracting intrinsic kinetics from exit flow data in a ‘model free’ manner similar to the Y-Procedure.

In conclusion, transient kinetic characterization of technical catalysts with Thin-Zone TAP experiments has a significant potential to contribute to several research avenues towards rational catalyst design and optimization of catalytic processes. On one hand, advanced data analysis based on the Y-Procedure allows faster and more sound microkinetic modeling of complex catalytic reactions which, in turn, guides catalyst synthesis. On the other hand, systematic gathering of intrinsic kinetic data over the wide pressure range from UHV, through Knudsen conditions, to atmospheric pressures and unifying these data with operando results will reveal how technical catalysts change under industrially relevant conditions. This multi-scale information will be used for engineering more economically viable, energy efficient, and safe chemical technologies, thereby increasing the likelihood for the commercialization of molecular scale discoveries.
Appendix A

Numerical simulations of TZ TAP experiments

Virtual TAP experiments presented in this thesis employed numerical methods to solve the Thin-Zone TAP reactor model outlined in Chapter 2 section 2.1.4. The numerical solution was used instead of analytical because it allowed us to study multi-step mechanisms and non-linear kinetic effects induced by state-altering experiments. First, the reactor domain was discretized into a regular computational grid of \( N_{\text{grid}} = 300 \) points separated by a small distance \( \Delta_x \). Mesh refinement beyond 300 points did not change the resulting exit flow curve. The spatial second derivative in equation (2.1) was then approximated at each point \( i \) by the second order central difference:

\[
\frac{\partial^2 C_g^{(i)}}{\partial x^2} \approx \frac{C_g^{(i-1)} - 2C_g^{(i)} + C_g^{(i+1)}}{\Delta_x^2}.
\] (A.1)

The discretized model takes the form of coupled ordinary differential equations (ODEs):

\[
\frac{dC_g^{(i)}}{dt} = \frac{D}{\epsilon \Delta_x^2} \left(C_g^{(i-1)} - 2C_g^{(i)} + C_g^{(i+1)}\right) - \frac{S_v(1 - \epsilon)}{\epsilon} R(k, C_g^{(i)}, C_s^{(i)}),
\] (A.2)

\[
\frac{dC_s^{(i)}}{dt} = R(k, C_g^{(i)}, C_s^{(i)}),
\] (A.3)

where \( i = 1, 2, ..., N_{\text{grid}} \).
Rather than using boundary condition (2.19), it was more convenient computationally to represent the inlet pulse by an initial condition of the form

$$C_g(x, t = 0) = \delta(x - 0^+) \frac{N_P}{\epsilon A},$$  \hspace{1cm} (A.4)

where $\delta(x - 0^+) \ (m^{-1})$ is now Dirac delta function localized at the reactor entrance. Although this form is physically less sound than (2.19), it was argued in (Constales et al., 2006) that mathematically they are equivalent. In practice, the delta function was approximated by assigning a large number to the concentration at the inlet boundary of the domain. The exact value of this initial pulse is grid-dependent and was adjusted by matching the model exit flow for pure diffusion with the analytical SDC. The change in model formulation led to an alternative boundary condition at the reactor entrance which represented the close pulse-valve:

$$F(x = 0, t) = -AD \frac{\partial C_g}{\partial x} (x = 0, t) = 0.$$  \hspace{1cm} (A.5)

Equation (A.2) for the first point in the reactor ($i = 1$) references a ghost point ($i = 0$) which lies outside of the domain. However, this reference was eliminated when the gradient in boundary condition (A.5) was approximated by

$$\frac{\partial C_g^{(1)}}{\partial x} \approx \frac{C_g^{(2)} - C_g^{(0)}}{2\Delta x} = 0 \quad \rightarrow \quad C_g^{(0)} = C_g^{(2)}.$$  \hspace{1cm} (A.6)

Depending on whether the catalytic zone is represented as a third zone or as a reactive interface, the model has internal boundary conditions (2.30) or (2.36) respectively. In order to implement these internal conditions, we used one-sided finite differences (Rahul and Bhattacharyya, 2006) to approximate gradients on both sides of the boundary located at $i$th point:

$$\frac{\partial C_g^{(i)}}{\partial x} \approx \mp \left( \frac{3C_g^{(i)} - 4C_g^{(i+1)} + C_g^{(i+2)}}{2\Delta x} \right).$$  \hspace{1cm} (A.7)
With this approximation, the transmission condition (2.30) can be written as

\[-AD \frac{\left(3C_g^{(i)} - 4C_g^{(i-1)} + C_g^{(i-2)}\right)}{2\Delta x} = -AD \frac{\left(3C_g^{(i)} - 4C_g^{(i+1)} + C_g^{(i+2)}\right)}{2\Delta x}, \tag{A.8}\]

from where the following explicit expression for the gas concentration at the boundary was obtained

\[C_g^{(i)} = \frac{4C_g^{(i+1)} - C_g^{(i+2)} - C_g^{(i-2)} + 4C_g^{(i-1)}}{6}. \tag{A.9}\]

This expression for the \(i\)th point was then substituted into the ODEs corresponding to the adjacent points \(i - 1\) and \(i + 1\). The differential equation for the point \(i\) itself was not solved during the simulation and the concentration value at this point was reconstructed \textit{a posteriori} using expression (A.9). For the catalyst represented as a reactive interface, discretization of the thin-zone boundary condition (2.36) leads to

\[-AD \frac{\left(3C_g^{(i)} - 4C_g^{(i-1)} + C_g^{(i-2)}\right)}{2\Delta x} + AD \frac{\left(3C_g^{(i)} - 4C_g^{(i+1)} + C_g^{(i+2)}\right)}{2\Delta x} = S_{cat} R(k, C_g^{(i)}, C_s^{(i)}). \tag{A.10}\]

An expression similar to (A.9) can be obtained for a particular rate form \(R(k, C_g^{(i)}, C_s^{(i)})\) and then substituted into ODEs for the points adjacent to the TZ interface. The resulting system of ODEs describing the evolution of model variables at every grid point was solved in time by the \texttt{odepack} solver (Hindmarsh and Stepleman, 1983) embedded in \texttt{scipy} Python libraries \url{www.scipy.org}. The exit flow curves were extracted from simulation results as

\[F_{\text{exit}}(t) \approx -AD \frac{C^{(N+1)} - C^{(N-1)}}{2\Delta x} = AD \frac{C^{(N-1)}}{2\Delta x}, \tag{A.11}\]
where the concentration at the ghost point \((N + 1)\) is equal to zero because it is located in the vacuum system.
Appendix B

The Pulse Intensity Modulation (PIM) protocol

1. **Tuning pulse-valves.** In order to organize robust and stable pulsing in the Knudsen regime, an intricate balance must be reached between tension of the pulse-valve spring, voltage applied to the magnetic coil, and pressure in the feed line. The following sequence of steps describes how to tune a pulse-valve before one proceeds with TAP experiments.

- Set the argon feed pressure at $30 - 35\, (\text{psi})$, voltage at $7 - 8\, (V)$, and pulse width at $135\, (\mu\text{s})$.
- Start with the pulse-valve spring fully released. Screw in the nut controlling the spring tension so that it barely holds onto the valve. This will ensure that pulses are very small and will not damage the mass spectrometer. Special care should be taken in order to prevent possible damage to the valve tip caused by over-tightening the spring.
- With the manifold in the raised position, set the distance between the wire coil and the magnetic disc attached to the pulse-valve stem at around $1\, (\text{mm})$. Engage the pulse generator and attain large noticeable pulses (with loud ”clicking” noise) by adjusting the distance between the coil and the magnetic disc. Once the optimum distance is found, fix the coil position by tightening the back-nut.
- Stop pulsing, lower the manifold, evacuate the microreactor, and open the slide-valve.
• Turn on the QMS and let it warm up for few minutes. Automation software should not be in any of the collection modes at this point.

• Enter the vacuum scan mode. Background signals corresponding to water (several peaks around 18 a.m.u.), nitrogen (28 a.m.u.), and oxygen (32 a.m.u.) may be present, but they should not be significant on gain 7. Leaks of air into the vacuum chamber can be diagnosed if the nitrogen peak is larger than the water peak.

• Enter the scope mode. Engage the pulse generator and carefully adjust the spring tension until pulses appear in the mid range of gain 7. The tension should not be decreased more then necessary for reproducible pulses. Spring tension, feed pressure, and voltage may be further adjusted in order to achieve stable smooth pulses with high signal-to-noise ratio on gain 7. It is important to keep signal peaks within the gain range in order to prolong the life-span of the QMS. Tighten the nut controlling the spring tension.

• After proper pulse size and shape are reached in scope mode, confirm the reproducibility of pulses by comparing their sizes within a long sequence (hundreds of pulses). The spring tension should not be changed further until all necessary data are collected and relevant pulse intensities are measured.

2. Establishing the Largest Knudsen Pulse (LKnP). Robust pulses established at this point may still not be in the Knudsen transport regime. For a constant spring tension, find the largest pulse (LKnP) for which the exit flow closely matches the SDC by gradually decreasing the feed pressure and/or voltage. Sufficiently small pulse intensity should eliminate non-Knudsen transport mechanisms which may deform the exit flow shape. The shape may also deviate from the SDC due to dead volumes between the pulse valve and the microreactor, packing irregularities, pulse-valve malfunctioning, or significant gas-solid interactions. While determining a proper combination of experimental parameters for the LKnP, these imperfections must be diagnosed and alleviated if found. The best performance is usually achieved at the highest allowable pressure, voltage, and spring tension. Nevertheless, the pressure and voltage during
future pulse-response experiments should never exceed their values for the LKnP to remain in the Knudsen regime required for data analysis.

3. **Adjusting the gas mixture composition.** Prepare gas mixtures anticipated to be used during catalytic experiments and pulse them over inert in order to determine the gain on which every gas will be monitored in future experiments. In our experience, gain affects calibration coefficients relating QMS readings to exit flows and conversion factors between adjacent gains. Therefore, signals should preferably be monitored on the same gain in order to avoid introducing the uncertainty of inter-gain conversions. In the absence of other requirements, mixture compositions should be found which will allow collecting reactants and inert signals within the same QMS gain. Products signals, on the other hand, often require increased sensitivity and may be detected at higher gains (up to 9).

4. **Control experiments over inert.** Condition the inert packing according to the same pretreatment routine that will be used for the catalyst. Then, interactions of individual gases with inert packing in the absence of the catalyst must be assessed. For each gas, record a series of pulses with variable gas-to-argon ratios and temperatures and extract the following information these control pulses:

   - Individual calibration coefficients for converting raw signals into exit flow curves.
   - Effective diffusion coefficients which must comply with equation (2.48) if the Knudsen regime is established properly.
   - Apparent adsorption and desorption constants (using the one-zone model) for those gases which clearly interact with inert packing. The variation of these constants in the experimental temperature range should also be established and used to calculate corresponding activation energies.

5. **Catalytic experiments.** Pack the microreactor with a catalyst sample in the Thin-Zone configuration and execute the pretreatment routine. Perform planned pulse-response experiments for relevant temperatures and pulse intensities. As an example, consider the experiment suggested in section 3.4.1 for measuring the concentration of active sites reversibly adsorbing gas A. The
goal of pulse modulation, in this case, is to shift the position of Momentary Equilibria (ME) in the rate-composition space. Record a sequence of 10 to 20 pulses for at least six pulse intensities, ranging from the LKnP to the smallest pulse with acceptable signal-to-noise ratio on gain 8. The pulse intensity can be gradually decreased by using more diluted gas mixtures or by lowering the pulse-valve voltage. We found that a combination of these two approaches is more convenient than either of them separately. Specifically, we recommend using only two or three mixtures ranging in gas A concentration. For each mixture, the pulse intensity should be changed in a broad window by adjusting the voltage. Pulse sequences collected for different mixtures will provide a combined overlapping set of widely ranging intensities for further analysis. Repeat all measurements for at least six temperatures in order to extract statistically significant activation parameters. Similar procedures should be followed for irreversible reactions, but after each multi-pulse sequence irreversibly adsorbed molecules must be removed by titration.

6. **Measuring pulse intensities.** Disconnect the feed line of the pulse-valve $PV$ from the mixing tank and connect it to a device for pulse intensity calibrations whose scheme is shown in Figure B.1. A small known volume $V_0$ is connected to a sensitive pressure gauge $PG$ through a valve 1. The device is connected to the gas supply through valve 2 and needle valve 3. First, measure the feed volume $V_{feed}$ in the following sequence of steps:

- Evacuate the device through valve 2 with valve 1 open.
- Fill the device with argon through valve 2 with valve 1 open. The pressure can be controlled by needle-valve 3.
- Record the reading from the pressure gauge $P_0$, close valve 1, and evacuate the rest of the device through valve 2.
- Close valve 2 and record the background pressure $P_1$ of the feed volume $V_{feed}$.
- Open valve 1 and record the pressure reading $P_2$ after the argon has expanded.
- Repeat for several values of $P_0$.
- Calculate the feed volume as
where all quantities are expressed in SI units.

Then, fill the feed volume with argon through the needle-valve up to the total pressure used for all experiments plus 0.2 (psi). Record the initial pressure \( P_{init} \) and close valve 2. Set the pulse-valve voltage to one of the values used for experiments. Start pulsing and record exit flow data until the feed pressure drops at least 0.4 (psi). Repeat several times for each pulse-valve voltage used in pulse-response experiments. Next, calculate the corresponding average pulse intensities from pressure drop measurements using the following formula

\[
N_P = \frac{N}{N_z} = \frac{\Delta PV_{feed}}{RT},
\]

where \( \Delta P \) is the pressure drop (in SI units) and \( N_z \) is the number of recorded pulses. It may be more convenient for further data analysis to estimate the absolute calibration coefficient of argon (mol/a.u.) by adjusting the total area under exit flow curves recorded during the pressure drop to match the total amount of pulsed molecules \( \Delta N \).
References


