

# MODELLING OF CHEMICAL REACTION KINETICS WITH DATA FROM TEMPERATURE-PROGRAMMED EXPERIMENTS

Tuomo Keskitalo



TEKNILLINEN KORKEAKOULU  
TEKNISKA HÖGSKOLAN  
HELSINKI UNIVERSITY OF TECHNOLOGY  
TECHNISCHE UNIVERSITÄT HELSINKI  
UNIVERSITE DE TECHNOLOGIE D'HELSINKI

# MODELLING OF CHEMICAL REACTION KINETICS WITH DATA FROM TEMPERATURE-PROGRAMMED EXPERIMENTS

Tuomo Keskitalo

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Helsinki University of Technology  
Department of Chemical Technology  
Laboratory of Industrial Chemistry

Teknillinen korkeakoulu  
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Teknillisen kemian laboratorio

Distribution:

Helsinki University of Technology

Laboratory of Industrial Chemistry

P. O. Box 6100

FI-02015 TKK

FINLAND

Tel. +358-9-451 2522

Fax. +358-9-451 2622

E-Mail: [tuomo.keskitalo@tkk.fi](mailto:tuomo.keskitalo@tkk.fi)

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# Abstract

This work focused on the kinetic modelling of heterogeneously catalysed chemical reactions making use of experimental data produced by temperature-programmed methods. These methods are traditionally applied in the characterisation of gas–solid interactions. However, as is demonstrated in this thesis, the results of temperature-programmed methods are also suitable for deriving kinetic models, which describe the rates of reactions. The derived kinetic models are valuable for the design and optimisation of chemical reactors, for the study of reaction mechanisms and for catalyst development.

The methodology of kinetic modelling based on data from temperature-programmed experiments was developed through two case studies. The first study dealt with the regeneration of a ferrierite catalyst deactivated by coke formation in skeletal isomerisation of alkenes. Many industrial processes dealing with hydrocarbons suffer from the formation of relatively large carbon and hydrogen containing molecules (coke) on the catalyst, which decrease its activity. The removal of coke by heat treatment under inert gas flow was studied with temperature-programmed gasification. With the results of the experiments, kinetic models, suitable for reactor design, were derived for the evolution of light hydrocarbon fractions ranging from C<sub>2</sub> to C<sub>5</sub>. The regeneration of the catalyst by coke oxidation was studied with temperature-programmed oxidation (TPO). Several power law models and models based on assumed mechanisms successfully described the evolution of carbon oxides and water. The models that described the experimental data indicated that oxygen forms a reactive intermediate in a fast equilibrium reaction, and the formation of CO and CO<sub>2</sub> proceeds through one or more common precursors.

The second study focused on adsorption and desorption, which are fundamental steps in heterogeneously catalysed reactions. The interplay between readsorption and mass transfer in a micro-reactor were studied from the point of view of kinetic modelling. The results clearly favour the pseudohomogeneous plug-flow reactor model for the description of the reactor if intraparticle mass transfer limitations are negligible. The derived modelling methodology was applied in the study of carbon dioxide adsorption

on zirconia catalysts. Pulse adsorption followed by temperature-programmed desorption (TPD) resulted in informative experimental data for kinetic modelling. The derived kinetic models indicated that carbon dioxide adsorbs on at least three types of sites on zirconia catalysts.

In conclusion, this work shows that properly designed temperature-programmed experiments yield rich information for kinetic modelling, mainly because of the strong dependence of most reaction rates on temperature. The refined modelling methodology provides a basis for further research that utilises temperature-programmed methods for the study of kinetics of heterogeneously catalysed reactions.

**keywords:** kinetics, modelling, temperature-programmed methods, heterogeneous catalysis, temperature-programmed oxidation, temperature-programmed desorption

# Tiivistelmä

Tämä väitöskirjatyö käsittelee heterogeenisesti katalysoitujen reaktioiden kinetiikan mallinnusta hyödyntäen lämpötilaohjelmoitujen koemenetelmien tuloksia. Lämpötilaohjelmoituja menetelmiä käytetään yleisesti kaasujen ja kiinteiden aineiden vuorovaikutusten karakterisointiin. Työ osoittaa, että nämä menetelmät soveltuvat myös reaktioiden nopeuksia kuvaavien kineettisten mallien kehittämiseen. Kineettisten mallien sovelluskohteita ovat kemiallisten reaktoreiden suunnittelu ja toiminnan optimointi, reaktiomekanismien tutkimus ja katalyyttien kehitys.

Kinetiikan mallinnuksen metodologiaa kehitettiin kahden sovelluskohteen tutkimuksen puitteissa. Ensimmäinen kohde oli alkeenien skeletal-isomerointireaktiossa kokaantumisen vuoksi deaktivoituneen katalyytin regenerointi. Koksen muodostuminen katalyytille pienentää katalyytin aktiivisuutta monissa teollisissa hiilivetyjä käsittelevissä prosesseissa. Koksen poistoa inerttivirtauksessa tutkittiin lämpötilaohjelmoidun kaasutusmenetelmän avulla. Koetuloksiin pohjautuen kehitettiin kineettisiä malleja hiilivetyfraktioiden  $C_2 - C_5$  muodostumiselle kokaantuneesta katalyytistä. Katalyytin regenerointi voidaan suorittaa myös polttamalla, mitä tutkittiin lämpötilaohjelmoidun hapetuksen (TPO) avulla. Useat mekanismiin pohjautuvat kineettiset mallit kuvasivat koetuloksia hyvin. Mallien yhteiset piirteet viittavat siihen, että happi muodostaa reaktiivisen välituotteen nopeassa tasapainoreaktiossa, ja hiilen oksidit muodostuvat yhden tai useamman yhteisen välituotteen kautta.

Toinen tutkimuskohde oli kaasumaisten aineiden adsorptio ja desorptio katalyytin pinnalle. Nämä reaktioaskeleet ovat tärkeä osa katalysoituja reaktioita. Mikroreaktorissa tapahtuvien oleellisten prosessien matemaattista kuvaamista varten systeemiä tutkittiin simuloinnin avulla. Kiinnostuksen kohteena oli erityisesti takaisinadsorption vaikutus. Tulokset puoltavat pseudohomogeenisen tulppavirtausreaktorimallin käyttöä reaktorin kuvaamiseen, kun partikkelin sisäinen aineensiirto ei ole rajoittava tekijä. Työssä kehitettyä mallinnusmetologiaa hyödynnettiin hiilidioksidin adsorption ja desorption tutkimuksessa, jossa käytettiin zirkoniumoksidikatalyyttejä. Kokeet tehtiin

pulssiadsorptio- ja TPD-menetelmien mukaisesti. Mallinnustulosten perusteella hiili-dioksidi adsorboituu ainakin kolmen tyyppisille pintapaikoille tutkituille katalyyteille.

Yhteenvetona voidaan todeta, että lämpötilaohjelmoidut menetelmät tuottavat tehokkaasti suuren informaatiomäärän omaavia mittaustuloksia, jotka soveltuvat kinetiikan mallinnukseen. Tämä johtuu erityisesti siitä, että reaktionopeudet tyypillisesti riippuvat lämpötilasta erittäin paljon ja lämpötilaohjelmoitujen menetelmien tulokset kattavat laajan lämpötilavälin. Työssä kehitettyä mallinnusmetodologiaa voidaan hyödyntää edelleen heterogeenisesti katalysoitujen reaktioiden tutkimuksessa, jossa käytetään lämpötilaohjelmoitujen menetelmien tuloksia kinetiikan mallinnukseen.

**avainsanat:** kinetiikka, mallinnus, lämpötilaohjelmoidut menetelmät, heterogeeninen katalyysi, lämpötilaohjelmoitu hapetus, lämpötilaohjelmoitu desorptio

## Preface

The work presented in this thesis was carried out in the Laboratory of Industrial Chemistry, Helsinki University of Technology, between June 2002 and March 2007. The research focusing on the kinetics of regeneration of a coked catalyst and on the modelling methodology for temperature-programmed desorption was part of the projects Clean Fuels and Components / Hydrogenation of Isooctenes and Coke Oxidation Kinetics and Neste Oil Mallinnus 2005-2006. Kinetic modelling of the adsorption and desorption of CO<sub>2</sub> was carried out within the project CO<sub>2</sub>-USE. Funding of the projects by Neste Oil Corporation, The Finnish Funding Agency for Technology and Innovation (TEKES), VTT Clean World Theme and Conox is gratefully acknowledged. The Foundation of Technology (Tekniikan edistämissäätiö) provided a personal grant.

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Espoo, May 21, 2007

Tuomo Keskitalo

**model, *n.*** (quotation 8.a.)

A simplified or idealised description or conception of a particular system, situation, or process, often in mathematical terms, that is put forward as a basis for theoretical or empirical understanding, or for calculations, predictions, etc.

**modelling, *n.*** (quotation 2.c.)

The devising or use of abstract or mathematical models.

— Oxford English Dictionary, draft revision Sept. 2002

## List of Publications

This thesis is based on the following publications (Appendices I-V), which are referred to in the text by the corresponding Roman numerals:

- I Keskitalo, T.J., Korhonen, S.T. , Lipiäinen, K.J.T., Krause, A.O.I., Evolution of light hydrocarbons from a coked ferrierite catalyst during temperature-programmed gasification, *Ind. Eng. Chem. Res.* **46** (2007) 5503-5509.
- II Keskitalo, T.J., Lipiäinen, K.J.T., Krause, A.O.I., Kinetic modeling of coke oxidation of a ferrierite catalyst, *Ind. Eng. Chem. Res.* **45** (2006) 6458-6467.
- III Keskitalo, T.J., Lipiäinen, K.J.T., Krause, A.O.I., Modelling of carbon and hydrogen oxidation kinetics of a coked ferrierite catalyst, *Chem. Eng. J.* **120** (2006) 63-71.
- IV Kanervo, J.M., Keskitalo, T.J., Slioor, R.I., Krause, A.O.I., Temperature-programmed desorption as a tool to extract quantitative kinetic or energetic information for porous catalysts, *J. Catal.* **238** (2006) 382-393.
- V Keskitalo, T.J., Veringa Niemelä, M.K., Krause, A.O.I., Modeling of the adsorption and desorption of CO<sub>2</sub> on Cu/ZrO<sub>2</sub> and ZrO<sub>2</sub> catalysts, *Langmuir* **23** (2007) 7612-7619.

Tuomo Keskitalo's contribution to the appended publications:

- I            The author participated in the design of the experiments, programmed the parameter estimation software, carried out the kinetic modelling, interpreted the results of the kinetic modelling and wrote the major part of the manuscript.
  
- II, III       The author contributed to the design of the experiments, derived the kinetic models, constructed the parameter estimation program, carried out the kinetic modelling, interpreted the results and wrote the manuscript.
  
- IV           The author participated in a major way in the derivation of models and the development and validation of the computer codes. He contributed significantly to the simulations, interpretation of their results and writing of the manuscript.
  
- V            The author helped in the design of experiments, developed the kinetic models and the parameter estimation software routines, carried out kinetic modelling, interpreted the results of modelling and wrote the major part of the manuscript.

# Modelling of chemical reaction kinetics with data from temperature-programmed experiments

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# 1 Temperature-programmed methods

This work focuses on the kinetic modelling of gas–solid reactions utilising experimental data produced by temperature-programmed (TP) methods. TP methods [1–4] rely on a continuously operated micro-reactor with a gas feed system and an analysis system for the outflow. “Temperature-programmed” refers to the heating (or cooling) of the reactor in a closely controlled way. TP methods are well-known thermal analysis techniques suitable for studying gas–solid interactions, and they are popular methods for catalyst characterisation. However, the results of this work show that these methods are also suitable for producing transient experimental data for kinetic modelling.

## 1.1 Types of temperature-programmed experiments

TP methods can be classified by reaction into several categories [1, 2]. Adsorption and desorption of a gas phase compound on a catalyst surface can be studied by a combination of various adsorption methods with temperature-programmed desorption (TPD). The TPD can be carried out either in vacuum or with an inert gas feed. Reduction of a catalyst surface under a reductive gas stream, such as hydrogen, can be probed by temperature-programmed reduction (TPR) [5]. Oxidation of a catalyst, or of a component on the catalyst surface, can be studied by temperature-programmed oxidation (TPO) by applying an oxidative gas stream. In general, any chemical reaction taking place on a catalyst surface under reactant flow can be studied with a temperature-programmed surface reaction (TPSR) method. Instead of the particular reaction, TP methods are sometimes classified according to the feed gas composition. For example, removal of coke from a catalyst under helium flow is referred to as temperature-programmed gasification (TPHe) [2, 6], even though the method is essentially identical with TPD.

The first part of this thesis (Chapter 3, I-III) focuses on coke regeneration studied by TPHe and TPO methods. TPO is a particularly popular method for coke characterisation [6], and the method has also been used to extract kinetic information on oxidation [7–12]. For example, the presence of several peaks in the TPO spectrum is indicative of a heterogeneity, such as chemically different species or variation in coke

morphology [8]. If these or other heterogeneities are excluded, however, multiple peaks are due to actual reaction kinetics.

The focus of the second part of the thesis (Chapter 4, IV, V) is adsorption and desorption studied by TPD [1, 2]. Ultra-high vacuum (UHV) TPD experiments have traditionally been used to study desorption kinetics [1, 13], but application of the results suffers from the difference of pressures between UHV and industrial conditions (pressure gap). While atmospheric TPD (flow TPD) is much closer to industrial conditions than UHV TPD, the simultaneous occurrence of adsorption, desorption and mass transfer in the reactor and inside the catalyst particles may make the use of these experimental data challenging [14, 15]. Some results of kinetic analyses have recently nevertheless been published [16–19]. A proper description of the reactor flow is especially important in atmospheric TPD [20]. Another feature of adsorption and desorption in atmospheric TPD is that these reactions tend to be fast compared with other processes. An equilibrium specific to the location in the reactor and to time (quasi-equilibrium) is formed, and needs to be accounted for in the kinetic modelling.

## **1.2 Kinetic modelling and temperature-programmed methods**

The aim of kinetic modelling [21–24] is to derive mathematical models that describe the rates of chemical reactions. A kinetic model can be applied to determine the reaction rate quantitatively once the values of the variables in the rate law are known. Kinetic models are essential in the design of chemical reactors, in the study of chemical reactions and in catalyst development.

Kinetic models can be tested and parameters estimated by several methods utilising data from transient TP experiments [25]. Methods based on Arrhenius plots can be used to obtain parameter estimates, but the range of applicable conditions of these methods is often limited and the methods typically include restricting assumptions on the intrinsic kinetics. In contrast, regression methods [22, 26] set no restrictions on kinetic models.

### **1.3 Aim of the work**

The aim of the work was to derive kinetic models for the regeneration of a coked ferrierite catalyst and for the adsorption and desorption of carbon dioxide on zirconia catalysts. Relevant applications of the models include reactor design and catalysis research. The experimental data needed for the modelling was obtained by temperature-programmed methods. A broader aim of the work was to show that such data can be utilised in kinetic modelling. This was demonstrated by two case studies related to catalyst regeneration, and the adsorption and desorption of carbon dioxide. The relevant methodological aspects of the modelling which emerged during the work are reported with a view to encouraging and assisting future kinetic modelling of TP experimental data.

## 2 Details of the kinetic modelling

The focus of this thesis is kinetic modelling utilising data from temperature-programmed experiments. This chapter summarises the details of the modelling relevant to the case studies described in chapters 3 and 4.

### 2.1 Design of temperature-programmed experiments

Kinetic experiments were designed so that the mathematical description of the reactor would be as simple as possible. Table 1 presents the range of variables applied in the TP experiments of this work. As far as possible the experiments were carried out under kinetically controlled conditions so that other processes besides reaction kinetics would have minimal effect on the results of measurements. For example, a small particle size of the catalyst was employed to remove mass and heat transfer limitations inside particles (IV).

Table 1: Parameters and properties in temperature-programmed experiments (I-III,V).

carrier gas	He
feed gases	O <sub>2</sub> , CO <sub>2</sub>
quantified gases	CO, CO <sub>2</sub> , H <sub>2</sub> O, C <sub>x</sub> H <sub>y</sub> (x=2 – 5)
flow rate of carrier gas, Q (cm <sup>3</sup> /min)	30 – 100
catalyst mass, W (mg)	10 – 300
catalyst particle radius, R <sub>p</sub> (cm)	0.012 – 0.035
catalyst density, ρ <sub>p</sub> (mg <sub>cat</sub> /cm <sup>3</sup> )	900 – 1300
reactor bed length, L (cm)	0.9 – 1.2
reactor diameter, d <sub>b</sub> (cm)	0.2 – 0.9
pressure (bar)	1.0 – 1.4
heating rate (°C/min)	5 – 30
temperature range (°C)	30 – 850

By design, temperature and the conversion level of the reaction are highly correlated in a TP experiment. To decrease this correlation and to thereby aid the identification of kinetic models [27, 28], TP experiments were carried out at several heating rates. The use of different heating rates may also reveal important heterogeneity. Concentration of the feed gas was also varied in several ways. In TPO experiments (II,III) the feed oxygen

concentration was constant during a single experiment and varied between experiments. The concentration of oxygen in the feed was thus accurately known. In TPD experiments (V) the pulsing technique [15] was applied in adsorption. Kinetic modelling with the results of the pulsing technique requires that the concentration-time data of the feed entering the catalyst bed is accurately known, so that the changes in concentration can be precisely simulated. The input was determined with blank experiments in an empty reactor. Axial mixing of the adsorption pulse with the carrier gas in the catalyst bed was established to be negligible in an experiment with inert material in place of the catalyst.

Various experimental errors were revealed by repetition of the TP experiments. Temperature shift of the measured thermogram (II) was attributed to a slight change in the location of the thermocouple inside the reactor. Changes in the scale of the measured thermograms (III) were due to experimental errors in the analysis of compounds (calibration vs. actual experiment). Considering the information content of TP experiments for kinetic modelling, even a few experiments with different heating rates are sufficient, and the value of numerous additional experiments is relatively small. However, with only a few experiments, the effect of errors is more pronounced than with additional experiments. The use of repetitions of experiments in the kinetic modelling added to the computational workload of the parameter estimation but decreased the biasing effect of the errors on parameter estimates.

## 2.2 Testing of kinetic models and evaluation of the results

Nonlinear regression was applied in the modelling because the dependence of some variables is nonlinear with respect to the reaction rate. For example, the temperature dependence of the rate constant ( $k$ ) in this work was often described by the Arrhenius equation presented in reparametrised form [21] as

$$k = k_{\text{ref}} \exp\left(\frac{-E}{R} \left(\frac{1}{T} - \frac{1}{T_{\text{ref}}}\right)\right), \quad (1)$$

in order to decrease the correlation between the reaction rate constant at a reference temperature ( $k_{\text{ref}}$ ) and the activation energy ( $E$ ). Even though nonlinear regression

requires somewhat more involved programming, the application of numerical methods, and a greater computational workload than for linear approximation techniques, the advantages mentioned above outweighed the downsides. In addition, nonlinear regression utilising TP experimental data has been shown to be a suitable method [25].

The derivation of the objective function, which is minimised in the estimation of parameters by nonlinear regression, was not straightforward with the applied TP experimental data. In principle, each independent point of data (i) of the variable (y) should contribute a value

$$R_i^2 = \left( \frac{y_{\text{exp},i} - y_{\text{calc},i}}{\sigma_i} \right)^2 \quad (2)$$

to the objective function, which typically is the sum over the squared residuals ( $R_i^2$ ) of all data points (residual sum of squares, RSS) [26, 29]. In equation 2,  $\sigma$  is the estimate of the standard deviation of the data point. The problem lies in how to derive the value of this estimate for all points of data, because parameter estimates depend on these values. In principle, the standard deviations should reflect the error in the measurements. However, several features of the TP experiments make it difficult to determine standard deviations. These include the interdependence of the data, the wide range of concentrations, the inclusion of several types of experiments in parameter estimation and the need simultaneously to take into account several components at several concentration levels in a number of experiments. Both the standard deviation and the scale of the variable  $y_{\text{exp}}$  affect how much the data point contributes to the objective function. As a practical solution, the standard deviations were adjusted so that the sum of  $R_i^2$  related to each variable clearly affected the value of the objective function. In the case of catalyst regeneration (II,III), the standard deviations for all points of experimental data were set to 1.0, which was sufficient for the respective data for CO, CO<sub>2</sub> and H<sub>2</sub>O to affect the value of the objective function. In the case of CO<sub>2</sub> interactions with zirconia catalysts (V), the standard deviation for the TPD data was set to one tenth of that for pulse adsorption data in order to equalise the effects of different number of data points and the scale of concentrations on the objective function.

The error estimates (confidence intervals) for the parameters (a) were evaluated by the t-test [22,23]. Accordingly, the  $100(1 - \alpha)\%$  confidence interval was calculated for each parameter  $i$  with equation

$$a_i \pm t_{\alpha/2} \sqrt{s_i^2} \quad (3)$$

in which  $t_{\alpha/2}$  is the value from Student's t-distribution with  $N-1$  degrees of freedom,  $s_i^2$  is the estimate of the variance of the parameter and  $N$  is the number of experimental data points. Equation 3 is not strictly accurate for nonlinear models, but it produces indicative estimates. Confidence region plots would give accurate information on the reliability of parameter estimates, but since the presentation of such plots with more than three parameters is not easy or efficient [22, 23], equation 3 was applied instead. Correlations between parameters were also considered, since a high correlation indicates that the parameters involved are not well identified. Parameter pairs that exhibited an absolute value of the correlation coefficient over 0.95 were reported.

Evaluation of the goodness of the fit and the selection of the “best” model(s) were not straightforward. The coefficient of determination, defined as

$$R^2 = 1 - \frac{\sum_{i=1}^N (y_{\text{exp},i} - y_{\text{calc},i})^2}{\sum_{i=1}^N (y_{\text{exp},i} - \bar{y}_{\text{exp}})^2}, \quad (4)$$

is suitable for determining which model fits the experimental data best (by RSS). In this work, residual root mean square (RRMS) values, defined by

$$\text{RRMS} = \sqrt{\frac{1}{N} \sum_{i=1}^N \left( \frac{y_{\text{exp},i} - y_{\text{calc},i}}{\sigma_i} \right)^2}, \quad (5)$$

were used instead of equation 4, though the difference in the two measures of model fit is slight. Neither equation 4 or 5 is informative in regard to model complexity, however, and neither gives a measure of possible overfitting of the models to the errors in the experimental data. Several theoretical information criteria, e.g. Akaike's information criterion, are available for the evaluation of models [29]. These take into account both the model fit (by RSS) and the number of parameters in the model. However, all these criteria require an accurate estimate of the number of statistically independent experimental data

points, and the determination of this number is not easy for transient TP experiments where most of the variables are dependent, at least through time. Yet another important factor to be considered in model selection is the reliability of the parameter estimates, and this is not accounted for in the information criteria. For the above reasons, models in this work are ranked by their RRMS values, and all models that perform well, regardless of their complexity, are presented in detail.

### **2.3 Computational details**

The mathematical description and the subsequent numerical simulation of the TP experiments were somewhat involved, but still feasible through the use of well-known, reliable and suitable numerical methods. The mathematical description of the TP experiments led to a set of ordinary differential equations (ODE), partial differential equations (PDE) or differential-algebraic equations (DAE), which were calculated numerically. In publications IV and V, discussed in Chapter 4, the PDE resulting from the PFR model was transformed into a set of ODEs by discretisation of the reactor length coordinate so that numerical ODE solvers could be used. The mass matrix of the ODE system resulting from the discretisation is sparse, and therefore the calculation utilised solvers suitable for sparse systems. In addition, the fast changes in variables necessitate that the solver is suitable for the calculation of stiff ODE systems. The reasons listed above added to the computational workload, but did not make the numerical solution impractical with today's computational power. The numerical solvers applied included "rkck", an implicit embedded fourth order Runge–Kutta Cash–Karp ODE solver in the GNU scientific library [30] (II,III), "RADAU5", an implicit Runge–Kutta solver for differential-algebraic problems based on a fifth order Radau collocation formula [31] (II,III), and "ode15s", a variable order backward difference method suitable for sparse Jacobian problems in Matlab [32] (I,IV,V).

In addition to numerical ODE solvers, kinetic modelling requires numerical optimisation methods and statistical analysis tools to evaluate the results [22]. Both the polytope search (Simplex) method by Nelder and Mead [33] (I-III, V) and the Levenberg–Marquardt method [26, 34, 35] (II,III) were utilised in optimisation. The polytope algorithm was

preferred due to the robustness of the method in these cases, even though it is less efficient than the Levenberg–Marquardt method. The computations were carried out with the functions and algorithms available in the GNU scientific library [30] (II,III) or with Matlab (®MathWorks, Inc.) (I,IV,V).

A large number of iterations (more than 500 for the polytope search algorithm and more than 20 for the Levenberg-Marquardt method) and two or more restarts of the optimisation methods ensured that the minimisation of the objective function reached an optimum for the parameters. At least two different initial values were applied in the estimation of parameters in an effort to obtain globally representative values. The application of numerical algorithms involves numerical errors, which must be considered [26]. The errors were assessed by decreasing the requirements for calculation tolerances by a decade and comparing the results with those obtained with the original tolerances. If the decrease in the tolerances affected the value of the objective function by less than 0.1%, the original tolerances were considered adequate.

## 2.4 Case studies

The methodology of kinetic modelling discussed above was utilised in two case studies. The first, presented in Chapter 3, deal with coke removal (regeneration) kinetics under an inert gas stream (I) and a gas feed containing oxygen (II,III). The catalyst was a ferrierite zeolite deactivated in a pilot-scale skeletal isomerisation of alkenes. The second, presented in Chapter 4, focus on adsorption and desorption kinetics. The results of the study of mathematical description of TPD experiments (IV) formed the basis for the kinetic modelling of adsorption and desorption of CO<sub>2</sub> on zirconia catalysts (V). Modelling of the TP experimental data in all cases resulted in kinetic models suitable for design purposes and gave insight into the kinetics and overall mechanism of the reactions in question. The results confirm the suitability of TP methods for kinetic modelling.

## 3 Modelling of catalyst regeneration kinetics

### 3.1 Importance of coke formation and regeneration of catalysts

Formation of coke on a catalyst causes deactivation in many industrial catalytic processes involving hydrocarbons. The catalysts applied in fluid catalytic cracking (FCC), continuous catalytic reforming (CCR) and skeletal isomerisation all suffer from the loss of activity due to coke formation [6, 36–38]. Coke deactivates the active sites on the catalyst either by covering the sites themselves or by blocking cavities in the catalyst, which prevents the transport of molecules to the active sites. In FCC, severe deactivation occurs within just a few seconds [39] and in skeletal isomerisation in the time scale of minutes [40]. Catalyst deactivation is clearly an important aspect in such processes.

Catalysts deactivated by coke formation can be regenerated by burning off the coke. The combustion is typically carried out in diluted air, but in some cases partial coke removal is achieved with hydrogen or inert gases [6]. The exact definition of coke varies depending on the source, but the deactivating effect is an essential characteristic of the substance. In this work, coke refers to any carbon-containing compounds remaining on a deactivated catalyst after flushing the catalyst overnight with an inert gas at 285 °C (the temperature of the main reaction described below).

The most important variables affecting the composition of the coke on the catalyst are reaction temperature, feed composition and time-on-stream [37, 41]. Regardless of the exact composition, the oxidation reactions of all types of coke are highly exothermic, as indicated by the formation enthalpies of the oxidation products shown in Table 2. Exothermicity of the catalyst reactivation by coke oxidation is one of the key concerns in the design of a regenerator. If the rates of the reactions are not closely controlled, the generated heat may cause damage to the catalyst and the regeneration unit. If a safe operation is to be devised, the reaction rates occurring in the regeneration unit must be known. A kinetic model that describes the rates of regeneration reactions is therefore needed for the design of a catalyst regeneration unit.

Table 2: Enthalpies of formation of oxidation products at 298.15 K. [42]

compound	$\Delta H_{f,298.15\text{ K}}(\text{kJ} \cdot \text{mol}^{-1})$
CO(g)	-110.50
CO <sub>2</sub> (g)	-390.50
H <sub>2</sub> O(g)	-241.80

In continuous processes, regeneration of the catalyst and the main reaction can be carried out in separate units. The deactivated catalyst can be routed through a dip leg to the regenerator and returned to the reactor after removal of the coke. In this design, coke removal takes place in two steps. The first step occurs in the dip leg, where the catalyst forms a bed while being fed to the regenerator. Inert gas is fed to the dip leg, countercurrent to the catalyst flow, to desorb light hydrocarbons before the coke oxidation. However, this inert flow treatment also removes part of the coke from the catalyst. The second step is the coke oxidation in the regenerator. The reactions in these two interconnected steps of coke removal were studied by TPHe (I) and TPO (II,III).

The studied catalyst was a ferrierite zeolite, deactivated in skeletal isomerisation of C<sub>5</sub>-C<sub>7</sub> alkenes [43]. The isomerisation reaction was carried out in a pilot scale reactor, operating at 285 °C for 21 h. Before unpacking, the catalyst bed was flushed overnight with nitrogen at the reaction temperature. The coke on the catalyst was analysed (I) by in situ diffuse reflectance Fourier transform infrared spectroscopy (DRIFTS), <sup>13</sup>C cross-polarisation magic angle spinning nuclear magnetic resonance (CPMAS NMR) spectroscopy, and gas chromatography combined with mass spectrometry (GC-MS). The results of all three methods were in agreement, showing that the coke was composed of various aromatic hydrocarbons with short alkyl side-chains. The total contents of carbon (4.3 wt%) and hydrogen (0.4 wt%) on the catalyst were measured with an elemental analyser. Before the TP experiments, the catalyst sample was dried in situ in helium stream at 200 °C for 12 h.

### 3.2 Removal of coke during temperature-programmed gasification

The acid sites on ferrierite are active in skeletal isomerisation of alkenes [40] and catalytic cracking [44, 45]. Alkenes react with the acid sites and form carbenium ions, which are the reactive intermediate species. The carbenium ion reactions [44] include fast proton, double bond and alkyl-group shifts and oligomerisation. The cracking reactions, which break the C—C bonds in the intermediate species, finally result in light hydrocarbons. These catalysed reactions were assumed to be relevant for the transformation of the coke as well, since characterisation of the coke showed it to contain both alkenes and alkanes (I). Thermal cracking may play a role as well.

Temperature-programmed gasification of the coked catalyst under helium feed (TPHe) from 200 to 500 °C resulted in the evolution of C<sub>2</sub> - C<sub>5</sub> alkenes and alkanes between 300 and 500 °C (I). Propene and ethene were the main components in the outflow. The kinetic modelling was based on the results of six TPHe experiments carried out at heating rates of 5, 10 and 15 °C/min. Two power law models were derived. The models describe the rate of formation (r) of each carbon fraction from C<sub>2</sub> to C<sub>5</sub> as a function of concentration of coke carbon on the catalyst ([C]) according to

$$r_i = k_i [C]^{\beta_i}, \quad i = C_2, \dots, C_5. \quad (6)$$

Equation 6 includes an order parameter  $\beta_i$ . In model 1 (I), the order parameters ( $\beta_{C_2}$ ,  $\beta_{C_3}$ ,  $\beta_{C_4}$  and  $\beta_{C_5}$ ) were fixed to 1.0, whereas in model 2 (I) they were estimated along with the other kinetic parameters. The result was that the order parameters in model 2 were close to the value of 2.0, and model 1 did not describe the experimental data as well as model 2.

Model 3 (I) was derived to test a possible reaction network that could explain why the order parameters in model 2 (I) are close to 2.0. Model 3 describes the formation of the observed hydrocarbons with equation 6, in which  $\beta_i=1$  (as in model 1), but additionally includes a parallel reaction in which the initial coke carbon forms irreversible non-active carbon. This formation of irreversible carbon was successfully described by the second

order rate law

$$r_{\text{irrev}} = k_{\text{irrev}}[C]^2. \quad (7)$$

Model 3 described the experimental data adequately (Figure 1), and its mechanistic interpretation suggests details of the coke removal reactions. Namely, the order of carbon concentration suggests the molecularity of the reaction. Thereby, the second order of equation 7 suggests that the formation of the irreversible coke proceeds through one or more bimolecular reactions. Such a reaction might be the addition of an alkyl chain to the aromatic skeleton. Similarly, the first order in the formation of carbon fractions  $C_2 - C_5$  suggests that a monomolecular reaction, possibly the scission of carbon-carbon bond in the coke molecules, limits the formation of these compounds. In conclusion, kinetic modelling of the TPHe experiments resulted in models appropriate for design purposes and suggested aspects of the overall mechanism of coke removal under inert atmosphere.

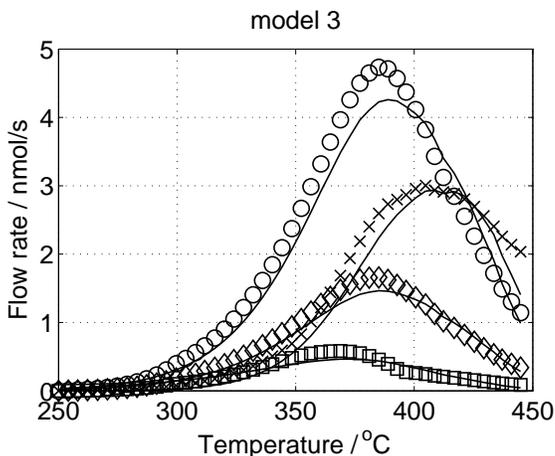


Figure 1: Fit of model 3 for the evolution of hydrocarbons during TPHe of a coked ferrierite catalyst (I). Symbols denote the experimental values and the continuous line the calculated values. (cross)  $C_2$ , (circle)  $C_3$ , (diamond)  $C_4$ , and (square)  $C_5$ .

### 3.3 Oxidation of coke during temperature-programmed oxidation

Catalyst regeneration kinetics was further studied by coke oxidation with TPO (II,III). TPO was carried out in situ, after TPHe, from 200 to 850 °C. The oxidation of the coke resulted in  $CO$ ,  $CO_2$  and  $H_2O$ . The concentrations of  $CO$  and  $CO_2$  were de-

terminated with methanation equipment (II,III) and a mass spectrometer (III) and the concentration of H<sub>2</sub>O with the mass spectrometer (III). The determinations of carbon oxides with the methanation equipment and the mass spectrometer were found to be accurate. The evolutions of CO and CO<sub>2</sub> were closely similar, and the evolution took place between 400 and 700 °C at the three heating rates tested (5, 10 and 15 °C/min).

The evolution of water continued at temperatures higher than 700 °C, even after the evolution of carbon oxides had ceased. Comparison of the results for a fresh and a deactivated ferrierite revealed that part of the water was from a source other than coke oxidation, presumably from the crystal lattice of the ferrierite. This demonstrates the importance of knowing the source of the observed products. Modelling of the oxidation reactions for coke hydrogen began with subtraction of the TPO spectra of water obtained with the fresh catalyst from the spectra obtained with the coked catalyst. The fresh and deactivated catalysts were treated in the same way in the experiments.

Power law models utilised in the description of coke oxidation reactions were

$$r_{\text{CO}_x} = k_{\text{CO}_x} c_{\text{O}_2}^{\alpha_{\text{CO}_x}} [\text{C}]^{\beta_{\text{CO}_x}}, \quad x = 1 \text{ or } 2, \quad (8)$$

$$r_{\text{H}_2\text{O}} = k_{\text{H}_2\text{O}} c_{\text{O}_2}^{\alpha_{\text{H}_2\text{O}}} [\text{H}]^{\beta_{\text{H}_2\text{O}}}. \quad (9)$$

The orders of the oxygen concentration ( $\alpha$ ) and coke concentration ( $\beta$ ) in equations 8 and 9 were either free parameters or fixed. Power law modelling is a common [8,9,46,47] and reasonable approach to kinetic modelling for design purposes. Equations 8 and 9 described the experimental data well. The fit of the model is presented in Figure 2. The order of oxygen concentration of about 0.5 in equation 8 and zero in equation 9, and the orders of coke carbon and hydrogen of 1.0 in equations 8 and 9 resulted in an adequate model fit.

The results of the kinetic modelling utilising power law models provided information on coke oxidation. First, the effectively zero order of oxygen concentration in equation 9 indicates that, within the range of oxygen feed tested (2 - 21 vol%), oxygen is in

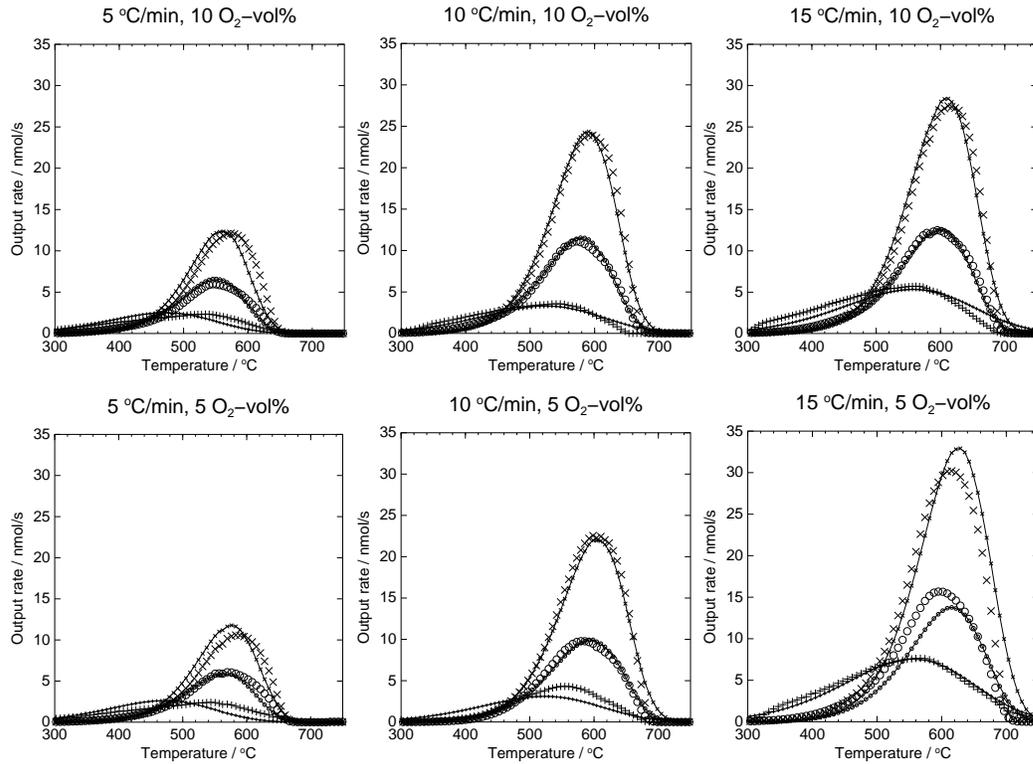
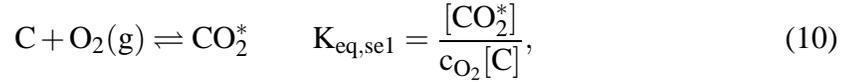


Figure 2: Experimental (large symbols) and model 2 simulation (continuous lines, small symbols) results of selected TPO experiments (III). CO response is denoted with symbol (X), CO<sub>2</sub> with (O) and H<sub>2</sub>O with (+).

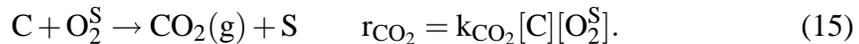
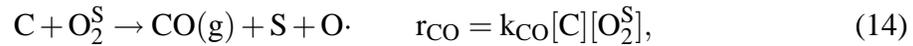
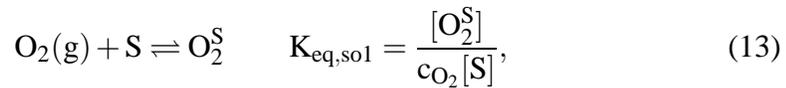
excess for the oxidation of hydrogen, so that the concentration of oxygen does not affect the rate of the reaction. Second, the differences in oxygen concentration order for the oxidation of carbon ( $\alpha_{\text{CO}_x} \approx 0.5$ ) and hydrogen ( $\alpha_{\text{H}_2\text{O}} \approx 0$ ) underline the difference in the combustion kinetics of coke carbon and hydrogen. Third, the order of 1.0 for carbon concentration suggests that the coke is present in the form of thin films.

The mechanism of coke oxidation was studied by deriving and testing kinetic models based on an assumed reaction network. As in the case of coke removal under inert flow discussed in section 3.2, the number of elementary reactions involved in coke oxidation is large [48], and therefore simplified case-specific studies are common [49]. Although the detailed picture of the elementary reactions is lost in the simplified reaction networks, the reaction steps and their rate expressions still have a physical interpretation and are useful.

Several models were tested, and three models proved suitable for the description of oxidation of coke carbon (II). The first model (model 3, II), which includes one intermediate oxide species ( $\text{CO}_2^*$ ), is described by the following reactions and equations:

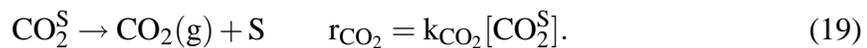
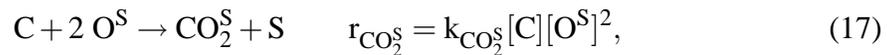
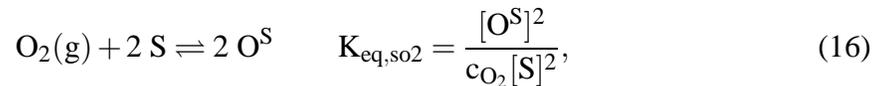


The second model (model 10, II) includes a surface-site species (S) and an associatively adsorbed oxygen species ( $\text{O}_2^{\text{S}}$ ). This model describes the oxidation reactions as



The species  $\text{O}\cdot$  in the two models above is included only to balance the stoichiometry of the reactions and has no other importance in the reaction scheme. Combination of  $\text{O}\cdot$  to gas phase dioxygen might occur, for example.

Finally, the third model (model 14, II) incorporates a surface-site species (S), a dissociatively adsorbed oxygen species ( $\text{O}^{\text{S}}$ ) and a carbon dioxide complex ( $\text{CO}_2^{\text{S}}$ ). The model reactions are



Unfortunately there was no experimental information on the intermediate species in coke oxidation and no model could be favoured over the other two. It was possible,

nevertheless, to draw conclusions on the basis of the common properties of the models and thereby gain insight into the overall mechanism of coke oxidation.

One property shared by all three models (3, 10 and 14, II) is that they include a fast equilibrium reaction between gas phase oxygen and an active intermediate species. Six other models that did not include such a reaction step did not fit the experimental data. The results suggest that coke oxidation includes an active form of oxygen, which in the studied temperature range is essentially in equilibrium with the gas phase oxygen.

Another shared feature of the three models is that the formation of the two oxides occurs through the same precursors, resulting in mathematically similar reaction rate expressions. Three other models included a different mathematical rate expression for the formation of CO and CO<sub>2</sub>, but none of them described the experimental data. The results of the modelling suggest that the formation of both carbon oxides occurs through common intermediate species.

The parameter estimates of model 3 (II) were all reliable (no large confidence intervals), but some in models 10 and 14 could not be identified. Only model 3 is suitable, therefore, for process design purposes. The mechanisms of models 10 and 14 cannot, however, be ruled out simply because some of the parameters were not well-identified. The mechanisms of models 10 and 14 may, in fact, have a recommending feature. Namely, the surface-site species in these models may represent the acid sites of the zeolite, as suggested by the carbocation mechanism for coke oxidation proposed by Dong et al. [50] (Figure 3). Other authors also report a correlation between the strength of the acid sites and coke oxidation [51–53].

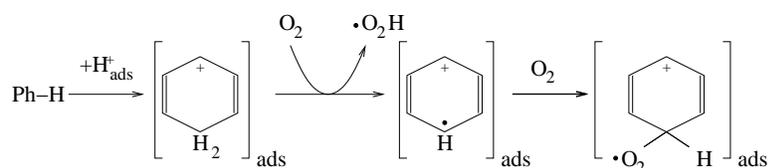
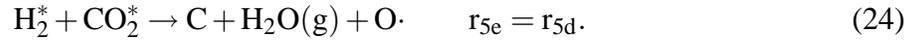
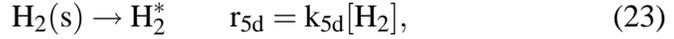
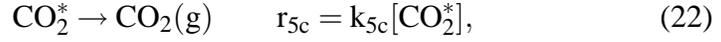
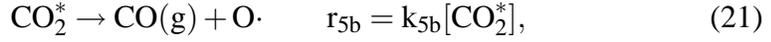
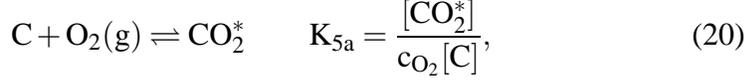


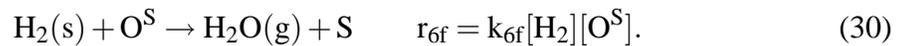
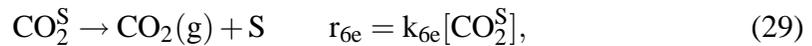
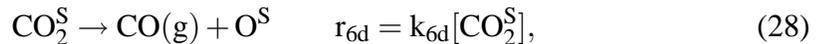
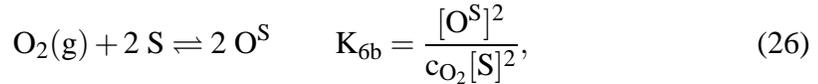
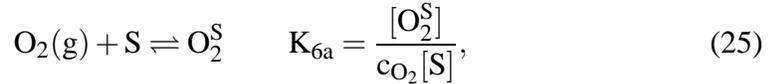
Figure 3: Carbocation mechanism for the reaction of oxygen with an adsorbed coke molecule presented by Dong et al. [50].

The models described above were extended (III) to include the oxidation of coke hydrogen ( $H_2(s)$ ). Two models that describe the oxidation as a whole were derived. The first model (model 5, III) is an extension of model 3 (II) and is described by reactions



An active coke hydrogen species ( $H_2^*$ ) is formed in reaction 23. Reaction 24 is assumed to be fast in comparison with reaction 23, and therefore the rate of water formation in reaction 24 is equal to the rate of reaction 23.

The second model (model 6, III) includes both associative and dissociative adsorption of oxygen on a site (S). The associatively adsorbed oxygen contributes to the oxidation of carbon, and the dissociatively adsorbed oxygen to the oxidation of hydrogen. The model reactions were



Both of the above models described the experimental data nearly as well as the power law model (model 2, III). The parameter estimates of models 2 and 5 (III) were reliable,

but some parameters of model 6 were poorly identified. Either model 2 or model 5 could be used for purposes of designing a catalyst regeneration unit.

In summary, models based on assumed reaction mechanisms were derived to study the oxidation reactions in more detail, and several such models described the experimental data nearly as well as the power law model. Although no single model proved superior, the common features of those models that described the experimental data adequately suggested two properties for the mechanism of oxidation of coke carbon. First, gas-phase oxygen forms a reactive intermediate in a fast equilibrium reaction before the production of carbon oxides, and second, the formation of the two carbon oxides occurs through common intermediate species. Although the actual number of elementary reactions in coke oxidation is large, this work shows that some kinetic models based on simplified reaction networks capture the essential dynamics of the coke oxidation reactions.

For the future, in situ coke formation and regeneration might provide a useful experimental setup for the study of coke removal kinetics. In such a configuration the fresh catalyst would be pretreated, deactivated, and studied by TPHe and TPO. This setup would make it possible to obtain variation in the coke composition and quality, which would assist the kinetic analysis. Study of the reaction intermediates by in situ spectroscopy might also prove beneficial. In general, a combination of results from several analysis techniques increases the information available for kinetic modelling [54].

## **4 Modelling of adsorption and desorption kinetics**

Since adsorption and desorption are elementary steps in any catalysed reaction cycle, their study is a step towards fundamental understanding of a catalysed surface reaction. TPD is an efficient method to that end. Publication IV, discussed in Section 4.1, deals with the simultaneous processes relevant in the study of adsorption and desorption kinetics by atmospheric TPD. The results were utilised in a case study (V) which deals with the adsorption and desorption of CO<sub>2</sub> on two zirconia catalysts, as summarised in Section 4.2.

### **4.1 Kinetic modelling of atmospheric temperature-programmed desorption data**

To obtain practical guidelines for kinetic modelling with atmospheric TPD data, the interplay of intrinsic kinetics and mass transfer in the reactor and inside the catalyst particles was studied by simulation (IV). The work utilised first order adsorption and desorption kinetics, with parameters in agreement with transition state theory [55]. A wide range of values for the rate constants and activation energy provided both fast and slow adsorption and desorption steps, so that the results can be considered valid for the typical range of parameters and conditions that was specified. Many of the results in this work rely on comparisons between the results of different models. The basic principle was that if a simplified model gives essentially the same results as a complete model, then the process that was not described in detail is insignificant from the practical point of view and can be simplified.

The system including the relevant processes (kinetics, intraparticle mass transfer, flow in the reactor) was studied with a heterogeneous model, which included the PFR model, radial mass transfer in the catalyst modelled by the effective diffusion model, and first order intrinsic kinetics. In addition, adsorption and desorption at the reactor inlet, where the changes in conditions are most severe, were investigated by simulations of a single catalyst particle with the assumption of infinite external mass transfer. By way of example, Figure 4 presents a typical TPD spectrum calculated with the heterogeneous

model and the gas phase concentrations at three different temperatures during the calculation. The figure shows that concentration gradients exist along the reactor length coordinate, while only minimal variations exist inside the particle.

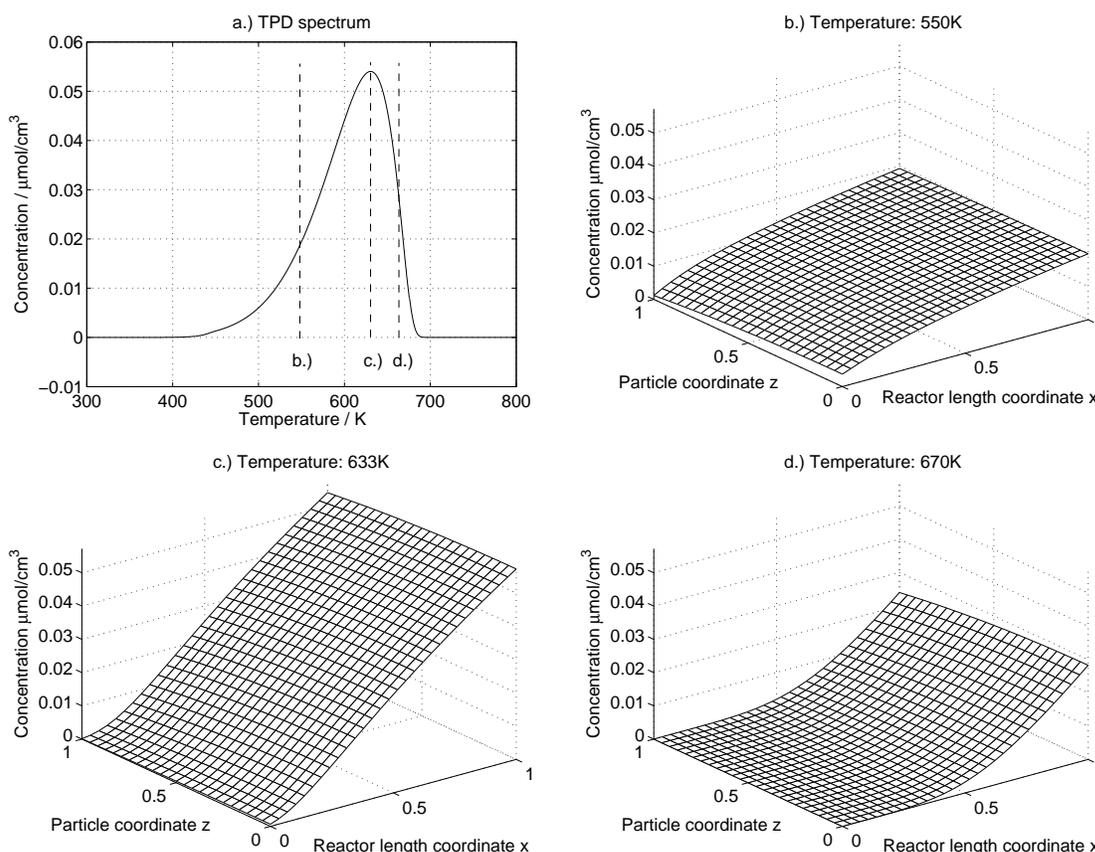


Figure 4: (a) TPD response simulated with a heterogeneous model including intraparticle mass transfer and PFR model. The figure shows the gas phase concentrations in the reactor at (b) 550 K, (c) 633 K and (d) 670 K. Values of parameters used in simulation:  $W=100$  mg,  $Q=100$  ml/min,  $L=0.4$  cm,  $d_b=0.4$  cm,  $D_e=0.01$   $\text{cm}^2/\text{s}$ ,  $R_p=0.01$  cm,  $N_{\text{tot}}=0.5$   $\mu\text{mol}/\text{mg}$ ,  $k_a=10^7$   $\text{cm}^3/(\mu\text{mol s})$ ,  $k_d=10^{16} \exp(-125 \text{ kJ}/\text{mol}/(RT))$  1/s.

In the description of atmospheric TPD, the results clearly supported the PFR model over both CSTR and the convection-axial dispersion reactor (C-ADR) model. Significant concentration gradients may occur in the packed-bed micro-reactor, as depicted in Figure 4. The choice of the reactor model was often found to affect the calculated TPD spectrum and the choice is therefore very important in modelling. The limiting values of the reactor Peclet number ( $Pe_r$ ) for PFR and CSTR operation were derived by comparing the results

of the C-ADR model with the results of PFR and CSTR models. Typical values of  $Pe_T$  for conditions in TPD given in several published correlations clearly supported the PFR model. A pulse tracer experiment with a large amount of catalyst suggested the same (IV). In some cases, such as TPO (II,III), however, where there is a lack of readsorption and only nominal consumption of reactive gases, it is possible to treat the reactor as a CSTR.

The calculations showed that the adsorption and desorption rates were so fast that locally species adsorbed on the surface and species in gas phase essentially reached equilibrium. This finding means that, if the kinetics follows the transition state theory, modelling must take this quasi-equilibrium into account. In this case it is not possible to identify the adsorption and desorption rate constants from the experimental data, but only the equilibrium constant between adsorption and desorption can be determined.

A significant simplification of the TPD system was achieved by decreasing the size of the catalyst particles so that intraparticle diffusion gradients became insignificant. The criterion

$$\frac{1/\tau}{D_e/R_p^2} = \frac{QR_p^2\rho_p(1-\epsilon_b)}{D_eW\epsilon_b} < 0.16, \quad (31)$$

which is appropriate in the tested range of conditions and variables, was derived for the determination of insignificant mass transfer limitations in the catalyst particle. If no intraparticle limitations are present, the derived pseudohomogeneous PFR model equation

$$\frac{dc_{A,x}}{dt} = -\frac{U}{L\epsilon_b} \frac{dc_{A,x}}{dx} + \frac{(1-\epsilon_b)\rho_p r_{A,x}}{\epsilon_b} \quad (32)$$

can be applied. Equation 32 describes the change in concentration of component A at an axial point x in the packed-bed.

For practical computation of equation 32, the reactor length coordinate x was discretised with an equidistant grid. As a result of the discretisation, the use of numerical ODE solvers designed for sparse mass matrices could be used to speed up the calculations. Concerning the evaluation of  $dc_{A,x}/dx$ , it was noted that a three-point central difference

formula resulted in numerical fluctuations, probably due to the characteristics of the PFR model. A three point backward difference formula, on the other hand, was stable and appropriate for the application.

The most important conclusion of this work is that kinetic modelling of atmospheric TPD data is valid as long as the experiments are properly designed and the relevant processes occurring in the TPD system are adequately described. By adjusting the particle size of the catalyst it is possible to obtain purely kinetic data that includes no interference from intraparticle mass transfer limitations. The pseudohomogeneous PFR model (equation 32) can then be applied in the description of the packed-bed micro-reactor.

## **4.2 Adsorption and desorption of carbon dioxide on zirconia catalysts**

Adsorption of carbon dioxide on a catalyst is required before reaction of the carbon dioxide with hydrogen to methanol. The synthesis of methanol from carbon oxides and hydrogen is an industrially important production route [56, 57]. The use of CO<sub>2</sub> is interesting from the environmental point of view, too, since carbon dioxide is a greenhouse gas. Knowledge of the adsorption and desorption of CO<sub>2</sub> on a catalyst and of the rates of these steps is important to understand how the catalyst works and to optimise the reaction conditions for the synthesis of methanol.

Traditional catalysts for the low pressure synthesis of methanol include copper on zinc oxide and/or alumina [56, 57]. During the last ten years, increasing attention has been paid to zirconia-based catalysts [58–70]. CO<sub>2</sub> adsorption on zirconia has been actively studied, and the CO<sub>2</sub> is known to adsorb as bicarbonates as well as carbonates. On Cu/ZrO<sub>2</sub>, virtually all of the CO<sub>2</sub> adsorption takes place on the zirconia [65, 66], while hydrogen is adsorbed on copper and then reacts with the adsorbed carbon dioxide species.

This work (V) focused on the adsorption and desorption of carbon dioxide on Cu/ZrO<sub>2</sub> and ZrO<sub>2</sub> catalysts. DRIFTS analysis of CO<sub>2</sub> adsorption on ZrO<sub>2</sub> suggested, as expected,

that adsorption of carbon dioxide involves the hydroxyl groups on the catalyst. The kinetic experiments were carried out with use of pulse adsorption and TPD methods. After the in situ pretreatment of about 300 mg of the catalyst, CO<sub>2</sub> was adsorbed by introducing ten 1-ml CO<sub>2</sub> pulses at 30 °C, followed by an inert flush at 30 °C and subsequent TPD at a heating rate of 15, 20, 25 or 30 °C/min.

The results of the pulse adsorption experiments showed that the catalysts adsorb the first pulse almost completely, and the pulses stabilise after 4-6 pulses. Comparison of the feed input pulse (averaged pulses measured through an empty reactor tube) with the stabilised pulse response revealed a difference due to adsorption and desorption. The height of the input pulse decreased while the peak width increased indicating that some sites on the catalysts adsorb and release CO<sub>2</sub> quickly at 30 °C (weak interaction). Since little carbon dioxide was detected during the inert flush, it was assumed that a part of the adsorbed CO<sub>2</sub> is bound to the catalyst surface. These strongly bound species then desorb during TPD.

The study showed that pulse adsorption combined with TPD gives rich information for kinetic modelling of adsorption and desorption. The kinetic modelling revealed that both Cu/ZrO<sub>2</sub> and ZrO<sub>2</sub> catalysts adsorb CO<sub>2</sub> on at least three distinct types of sites. The sites of type 1 adsorbed carbon dioxide reversibly at 30 °C. The adsorbed species desorbed quickly from these sites during the inert flush following the adsorption pulse. Possibly the adsorption on sites of type 1 was physisorption. The sites of types 2 and 3, however, adsorbed CO<sub>2</sub> irreversibly during the pulsing, and released the adsorbent during TPD (Figure 5).

The kinetic modelling also showed that the adsorption of CO<sub>2</sub> could be described by first order kinetics if the model includes a Freundlich-type [71] logarithmic dependence of adsorption enthalpy on coverage for sites of type 2 (model 1). The need of such dependence suggests that the catalyst contains a distribution of different adsorption sites, which seems likely considering the heterogeneity of zirconia [60]. Another model, in which the kinetics of desorption were of second order, described the experimental

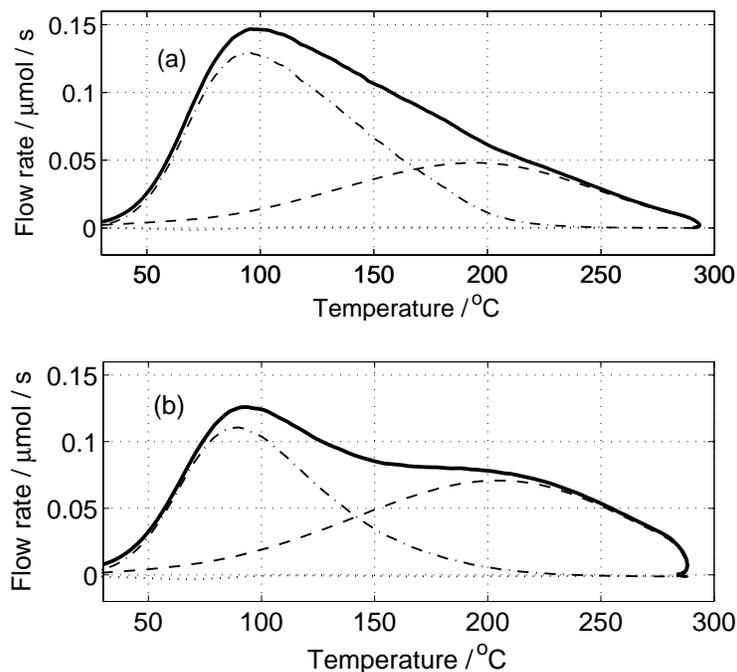


Figure 5: Interactions of the three types of sites according to model 1 (V) during a TPD experiment carried out at 20  $^{\circ}\text{C}/\text{min}$  with (a) Cu/ZrO<sub>2</sub> and (b) ZrO<sub>2</sub> as catalysts. The bold line denotes the simulated total flow rate of carbon dioxide (values on left y-axis) and the broken lines the average of the derivatives of the surface coverages (A.U.) of site 1 (dotted line), site 2 (dot-dashed line) and site 3 (dashed line).

data as well as model 1. However, since there is no experimental evidence in favour of bimolecular desorption, model 1 was concluded to be physically more realistic.

Comparison of the estimated parameters for Cu/ZrO<sub>2</sub> and ZrO<sub>2</sub> showed that the addition of copper to zirconia affected the sites of type 3 least. The adsorption capacity of type 3 sites was decreased slightly, but the kinetics remained unaffected. Changes in the values of the kinetic parameters showed that addition of copper to the catalyst affect the sites of type 2 most, and the sites of type 1 only slightly. In summary, kinetic modelling utilising experimental pulse adsorption and TP data proved to be a useful tool, providing insight into the kinetics of carbon dioxide adsorption on the tested zirconia catalysts.

The results of the present work revealed two additional parameters appropriate for the design of TP experiments. First, the duration of the inert flush between adsorption and

the beginning of TPD should be varied to test for the existence of slow desorption of the species from the catalyst. The start of TPD after a fast (or no) inert flush exposes a catalyst with high coverage of adsorbent to high temperatures, whereas after a long inert flush all but the irreversibly adsorbed component will have been removed. Second, the adsorption temperature in experiments should be varied because exposure of the catalyst to a wide range of concentrations at many adsorption temperatures would give more information for kinetic modelling. These two variations in the design of experiments would likely aid identification of the temperature-dependent parameters of all relevant sites and could prove especially advantageous if the adsorption occurs through several parallel reactions.

## 5 Conclusions

The case studies in this work showed that TP methods are suitable for generating experimental data for kinetic modelling of gas–solid interactions. Modelling of coke removal utilising data from TPHe (I) and TPO (II,III) experiments provided kinetic models suitable for the design and optimisation of catalyst regeneration units. Furthermore, models based on reaction mechanisms provided information on the overall mechanisms involved in coke removal. The results suggest that oxygen and coke form an active intermediate species in a fast equilibrium reaction, and that a common intermediate or intermediates are involved in the formation of CO and CO<sub>2</sub>. The results of the modelling show that relatively simple models can describe the overall dynamics of the complex reaction network of coke oxidation.

The simulation study on adsorption and desorption kinetics (IV) resulted in a general methodology for kinetic modelling utilising results from TPD experiments. The results showed the importance of taking into account readsorption and the reactor flow model in the modelling of TPD data. The developed methodology was utilised in a study of adsorption and desorption of CO<sub>2</sub> on zirconia catalysts (V). The results of the modelling indicated that CO<sub>2</sub> adsorbs on at least three different types of sites on zirconia. Successful modelling assuming monomolecular adsorption and desorption required the incorporation of a Freundlich-type logarithmic dependence of adsorption enthalpy on coverage. This kind of dependence suggests that there is a distribution of different adsorption sites on the catalyst, which is reasonable considering the heterogeneous nature of zirconia.

To sum up, TP methods are attractive for kinetic modelling for several reasons. The micro-reactor can often be treated as a continuously stirred tank reactor (CSTR) or an ideal plug-flow reactor (PFR). The experimental equipment is relatively simple to design. Owing to their transient nature, TP methods produce hundreds of experimental data points in a comparatively short time. The large number of measurements produces good reliability of the parameter estimates. Temperature, which is a key variable for most reaction rates, is varied and closely controlled. During a TP experiment the catalyst is

subjected to a wide range of reactant concentrations, and this facilitates the identification of the dependence of reaction rate on concentration. Use of adsorption techniques and TPD together extends the probed range of concentrations.

Generally speaking, TP methods involve some restrictions. At least today, study is limited to gas–solid interactions. Moreover, owing to the complexity of the underlying chemistry and physics, only rarely can an existing approach (program codes, processing of experimental data, kinetic models) be utilised in a new case as such. Nonetheless, the need for reliable and accurate kinetic models continues, for the design of reactors, for fundamental research on surface reactions and for catalyst development. In this work, kinetic modelling utilising the results of TP methods was found to be a suitable approach to that end. It can be expected that, as more cases are studied, the methodology related to the kinetic modelling with TP experimental data will become better established, and the similarities of the different cases will speed up the modelling process. In addition, developments in the relevant areas of computational science will likely reduce the time required for the modelling.

# Notation

## Symbols

- [i] concentration of intermediate or surface species i ( $\text{mol} \cdot \text{g}_{\text{cat}}^{-1}$ )
- a parameter
- $c_i$  concentration of gas phase component i ( $\text{mol} \cdot \text{dm}^{-3}$ )
- $d_b$  diameter of tubular reactor (m)
- $D_e$  effective diffusion coefficient ( $\text{m}^2 \cdot \text{s}^{-1}$ )
- E activation energy ( $\text{J} \cdot \text{mol}^{-1}$ )
- F molar flow rate ( $\text{mol} \cdot \text{s}^{-1}$ )
- $\Delta H_f$  enthalpy of formation ( $\text{J} \cdot \text{mol}^{-1}$ )
- k reaction rate constant ( $\text{s}^{-1}$ ,  $\text{dm}^3 \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$  or  $\text{g}_{\text{cat}} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$ )
- $k_a$  rate constant of adsorption ( $\text{m}^3 \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$ )
- $k_d$  rate constant of desorption ( $\text{s}^{-1}$ )
- K equilibrium constant ( $\text{dm}^3 \cdot \text{mol}^{-1}$  or no unit)
- L reactor bed length (m)
- n molar amount (mol)
- N number of data points or degrees of freedom
- $N_{\text{TOT}}$  number of active sites on catalyst ( $\text{mol} \cdot \text{g}_{\text{cat}}^{-1}$ )
- $Pe_r$  reactor Peclet number
- Q volumetric flow rate ( $\text{dm}^3 \cdot \text{min}^{-1}$ )
- r reaction rate ( $\text{mol} \cdot \text{g}_{\text{cat}}^{-1} \cdot \text{s}^{-1}$ )
- R universal gas constant ( $\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ )
- $R^2$  coefficient of determination (the  $R^2$  value)
- $R_i$  residual of data point i
- $R_p$  particle radius (m)
- $s_i^2$  estimate of variance
- t time (s)
- $t_{\alpha/2}$  value from Student's t-distribution

T temperature ( $^{\circ}\text{C}$  or K)  
 $T_{\text{ref}}$  reference temperature (K)  
U superficial velocity ( $\text{m} \cdot \text{s}^{-1}$ )  
W mass of catalyst ( $\text{g}_{\text{cat}}$ )  
x dimensionless reactor length coordinate  
y state variable  
z dimensionless particle radius coordinate

### **Greek letters**

$\alpha$  reaction order for oxygen concentration  
 $\beta$  reaction order for carbon or hydrogen concentration  
 $\varepsilon_{\text{b}}$  bed porosity  
 $\varepsilon_{\text{p}}$  particle porosity  
 $\rho_{\text{p}}$  catalyst density ( $\text{g}_{\text{cat}} \cdot \text{dm}^{-3}$ )  
 $\tau$  space-time of packed bed reactor (s)

### **Superscripts**

\* intermediate active compound  
S compound adsorbed to a surface site

### **Abbreviations**

C-ADR convection-axial dispersion reactor  
CSTR continuously-stirred tank reactor  
DRIFTS diffuse reflectance Fourier transform infrared spectroscopy  
FCC fluid catalytic cracking  
FID flame-ionisation detector  
ODE ordinary differential equation  
PFR plug-flow reactor  
PDE partial differential equation  
RSS residual sum of squares

RRMS residual root mean square

TP temperature-programmed

TPD temperature-programmed desorption

TPHe temperature-programmed gasification under helium flow

TPO temperature-programmed oxidation

UHV ultra-high vacuum

## References

- [1] Schwarz, J. A. and Falconer, J. L., Application of transient techniques. Methanation on supported nickel catalysts, *Catal. Today* **7** (1990) 1–92.
- [2] Bhatia, S., Beltramini, J. and Do, D. D., Temperature programmed analysis and its applications in catalytic systems, *Catal. Today* **7** (1990) 309–438.
- [3] Boaro, M., Vicario, M., de Leitenburg, C., Dolcetti, G. and Trovarelli, A., The use of temperature-programmed and dynamic/transient methods in catalysis: Characterization of ceria-based, model three-way catalysts, *Catal. Today* **77** (2003) 407–417.
- [4] Falconer, J. L. and Schwarz, J. A., Temperature-programmed desorption and reaction: Applications to supported catalysts, *Catal. Rev.—Sci. Eng.* **25** (1983) 141–227.
- [5] Kapteijn, F., Moulijn, J. A. and Tarfaoui, A., Catalyst characterization and mimicking pretreatment procedures by temperature-programmed techniques, *Stud. Surf. Sci. Catal.* **123** (1999) 525–541.
- [6] Querini, C. A., Coke characterization, *Catal.* **17** (2004) 166–209.
- [7] Gayubo, A. G., Arandes, J. M., Aguayo, A. T., Olazar, M. and Bilbao, J., Calculation of the kinetics of catalyst regeneration by burning coke following a temperature ramp, *Chem. Eng. J.* **54** (1994) 35–40.
- [8] Querini, C. A. and Fung, S. C., Temperature-programmed oxidation technique: Kinetics of coke-O<sub>2</sub> reaction on supported metal catalysts, *Appl. Catal., A* **117** (1994) 53–74.
- [9] Kanervo, J. M., Krause, A. O. I., Aittamaa, J. R., Hagelberg, P. H., Lipiäinen, K. J. T., Eilos, I. H., Hiltunen, J. S. and Niemi, V. M., Kinetics of the regeneration of a cracking catalyst derived from TPO measurements, *Chem. Eng. Sci.* **56** (2001) 1221–1227.
- [10] Li, C., Minh, C. L. and Brown, T. C., Kinetics of CO and CO<sub>2</sub> evolution during the temperature-programmed oxidation of coke deposited on cracking catalysts, *J. Catal.* **178** (1998) 275–283.

- [11] Li, C. and Brown, T. C., Temperature-programmed oxidation of coke deposited by 1-octene on cracking catalysts, *Energy Fuels* **13** (1999) 888–894.
- [12] Li, C. and Brown, T. C., Carbon oxidation kinetics from evolved carbon oxide analysis during temperature-programmed oxidation, *Carbon* **39** (2001) 725–732.
- [13] Cvetanovic, R. J. and Amenomiya, Y., Temperature programmed desorption technique for investigation of practical catalysts, *Catal. Rev.* **6** (1972) 21–48.
- [14] Gorte, R. J., Temperature-programmed desorption for the characterization of oxide catalysts, *Catal. Today* **28** (1996) 405–414.
- [15] Bennett, C. O., Experiments and processes in the transient regime for heterogeneous catalysis, *Adv. Catal.* **44** (2000) 329–416.
- [16] Makowski, W., Quasi-equilibrated temperature programmed desorption and adsorption: A new method for determination of the isosteric adsorption heat, *Thermochim. Acta* **454** (2007) 26–32.
- [17] Strunk, J., d’Alnoncourt, R. N., Bergmann, M., Litvinov, S., Xia, X., Hinrichsen, O. and Muhler, M., Microkinetic modeling of CO TPD spectra using coverage dependent microcalorimetric heats of adsorption, *Phys. Chem. Chem. Phys.* **8** (2006) 1556–1565.
- [18] Kanervo, J. M., Reinikainen, K. M. and Krause, A. O. I., Kinetic analysis of temperature-programmed desorption, *Appl. Catal., A* **258** (2004) 135–144.
- [19] Olsson, L., Westerberg, B., Persson, H., Fridell, E., Skoglundh, M. and Andersson, B., A kinetic study of oxygen adsorption/desorption and NO oxidation over Pt/Al<sub>2</sub>O<sub>3</sub> catalysts, *J. Phys. Chem. B* **103** (1999) 10433–10439.
- [20] Hinrichsen, O., Rosowski, F., Muhler, M. and Ertl, G., Microkinetic analysis of temperature-programmed experiments in a microreactor flow system, *Stud. Surf. Sci. Catal.* **109** (1997) 389–400.
- [21] Berger, R. J., Stitt, E. H., Marin, G. B., Kapteijn, F. and Moulijn, J. A., Chemical reaction kinetics in practice, *CATTECH* **5** (2001) 30–60.

- [22] van der Linde, S. C., Nijhuis, T. A., Dekker, F. H. M., Kapteijn, F. and Moulijn, J. A., Mathematical treatment of transient kinetic data: Combination of parameter estimation with solving the related partial differential equations, *Appl. Catal., A* **151** (1997) 27–57.
- [23] Kittrell, J. R., Mathematical modeling of chemical reactions, *Adv. Chem. Eng.* **8** (1970) 97–183.
- [24] Stoltze, P., Microkinetic simulation of catalytic reactions, *Prog. Surf. Sci.* **65** (2000) 65–150.
- [25] Kanervo, J. M. *Kinetic analysis of temperature-programmed reactions*. Ph.D. thesis, Helsinki University of Technology, Laboratory of Industrial Chemistry, 2003.
- [26] Press, W. H., Teukolsky, S. A., Vetterling, W. T. and Flannery, B. P., *Numerical recipes in Fortran 77 — The art of scientific computing*, 2nd Edition, Cambridge University Press, Cambridge 2001.
- [27] Maciejewski, M., Computational aspects of kinetic analysis. Part B: The ICTAC kinetics project — the decomposition kinetics of calcium carbonate revisited, or some tips on survival in the kinetic minefield, *Thermochim. Acta* **355** (2000) 145–154.
- [28] Burnham, A. K., Computational aspects of kinetic analysis. Part D: The ICTAC kinetics project — multi-thermal–history model-fitting methods and their relation to isoconversional methods, *Thermochim. Acta* **355** (2000) 165–170.
- [29] Ljung, L. and Glad, T., *Modeling of dynamic systems*, Prentice Hall, New Jersey 1994.
- [30] Galassi, M., Davies, J., Theiler, J., Gough, B., Jungman, G., Booth, M. and Rossi, F., *GNU scientific library reference manual*, 2nd Edition, Network Theory Limited, Bristol 2003.
- [31] Hairer, E. and Wanner, G., *Solving ordinary differential equations II — Stiff and differential-algebraic problems*, Springer, Berlin 1996.

- [32] Shampine, L. F. and Reichelt, M. W., The Matlab ODE suite, *SIAM J. Sci. Comput.* **18** (1997) 1–22.
- [33] Nelder, J. A. and Mead, R., A simplex method for function minimization, *Comput. J.* **7** (1965) 308–313.
- [34] Marquardt, D. W., An algorithm for least-squares estimation of nonlinear parameters, *J. Soc. Ind. Appl. Math.* **11** (1963) 431–441.
- [35] Moré, J. J., The Levenberg-Marquardt algorithm: Implementation and theory, *Lecture Notes in Mathematics* **630** (1978) 105–116.
- [36] Tomita, A., Catalysis of carbon-gas reactions, *Catal. Surveys from Japan* **5** (2001) 17–24.
- [37] van Donk, S., Bitter, J. H. and de Jong, K. P., Deactivation of solid acid catalysts for butene skeletal isomerisation: On the beneficial and harmful effects of carbonaceous deposits, *Appl. Catal., A* **212** (2001) 97–116.
- [38] Bhatia, S., Beltramini, J. and Do, D. D., Deactivation of zeolite catalysts, *Catal. Rev.—Sci. Eng.* **31** (1989) 431–480.
- [39] den Hollander, M., Makkee, M. and Moulijn, J., Fluid catalytic cracking (FCC): Activity in the (milli)seconds range in an entrained flow reactor, *Appl. Catal., A* **187** (1999) 3–12.
- [40] Meriaudeau, P. and Naccache, C., Skeletal isomerization of n-butenes catalyzed by medium-pore zeolites and aluminophosphates, *Adv. Catal.* **44** (2000) 505–543.
- [41] Guisnet, M. and Magnoux, P., Organic chemistry of coke formation, *Appl. Catal., A* **212** (2001) 83–96.
- [42] Yaws, C. L., *Chemical properties handbook*, McGraw-Hill, New York 1999.
- [43] Sandelin, F., Eilos, I., Harlin, E., Hiltunen, J., Jakkula, J., Makkonen, J. and Tiitta, M., A CFB unit for skeletal isomerization of linear C<sub>4</sub>–C<sub>6</sub> olefins on ferrierite catalysts, *Proc. 14th Int. Zeol. Conf.*, Eds. E. van Steen, L. Callanan, M. Claeys and C. O’Connor, 2004, pp. 2157–2162.

- [44] Kissin, Y. V., Chemical mechanisms of catalytic cracking over solid acid catalysts: Alkanes and alkenes, *Catal. Rev.* **43** (2001) 85–146.
- [45] Corma, A. and Orchillés, A. V., Current views on the mechanism of catalytic cracking, *Microporous and Mesoporous Materials* **35-36** (2000) 21–30.
- [46] Tang, D., Kern, C. and Jess, A., Influence of chemical reaction rate, diffusion and pore structure on the regeneration of a coked Al<sub>2</sub>O<sub>3</sub>-catalyst, *Appl. Catal., A* **272** (2004) 187–199.
- [47] Kern, C. and Jess, A., Regeneration of coked catalysts — modelling and verification of coke burn-off in single particles and fixed bed reactors, *Chem. Eng. Sci.* **60** (2005) 4249–4264.
- [48] Miller, J. A., Pilling, M. J. and Troe, J., Unravelling combustion mechanisms through a quantitative understanding of elementary reactions, *Proc. Comb. Inst.* **30** (2005) 43–88.
- [49] Hayhurst, A. N. and Parmar, M. S., Does solid carbon burn in oxygen to give the gaseous intermediate CO or produce CO<sub>2</sub> directly? Some experiments in a hot bed of sand fluidized by air, *Chem. Eng. Sci.* **53** (1998) 427–438.
- [50] Dong, Q.-N., Anderson, J. R., Mole, T., Chang, Y.-F. and Western, R. J., Reaction of benzene and toluene in the presence of oxygen over H-ZSM5 zeolite. Aromatic oxygenates in the product, *Appl. Catal.* **72** (1991) 99–107.
- [51] Moljord, K., Magnoux, P. and Guisnet, M., Coking, aging and regeneration of zeolites XVI. Influence of the composition of HY zeolites on the removal of coke through oxidative treatment, *Appl. Catal., A* **121** (1995) 245–259.
- [52] Cavani, F., Giordano, G., Pedatella, M. and Trifirò, F., The effect of zeolitic textural properties on the catalytic activity in hydrocarbon oxidation, *Stud. Surf. Sci. Catal.* **84** (1994) 1425–1432.
- [53] Jong, S.-J., Pradhan, A. R., Wu, J.-F., Tsai, T.-C. and Liu, S.-B., On the regeneration of coked H-ZSM-5 catalysts, *J. Catal.* **174** (1998) 210–218.

- [54] Brückner, A., Looking on heterogeneous catalytic systems from different perspectives: Multitechnique approaches as a new challenge for in situ studies, *Catal. Rev.* **45** (2003) 97–150.
- [55] Dumesic, J. A., Rudd, D. F., Aparicio, L. M., Rekoske, J. E. and Treviño, A. A., *The Microkinetics of heterogeneous catalysis*, American Chemical Society, Washington, DC 1993.
- [56] Weissermel, K. and Arpe, H.-J., *Industrial organic chemistry*, 4th Edition, VCH Verlagsgesellschaft mbH, Weinheim 1997.
- [57] Waugh, K. C., Methanol synthesis, *Catal. Today* **15** (1992) 51–75.
- [58] Jung, K. T. and Bell, A. T., The effects of synthesis and pretreatment conditions on the bulk structure and surface properties of zirconia, *J. Mol. Catal., A* **163** (2000) 27–42.
- [59] Montoya, J. A., Romero-Pascual, E., Gimón, C., Angel, P. D. and Monzón, A., Methane reforming with CO<sub>2</sub> over Ni/ZrO<sub>2</sub> – CeO<sub>2</sub> catalyst prepared by sol-gel, *Catal. Today* **63** (2000) 71–85.
- [60] Pokrovski, K., Jung, K. T. and Bell, A. T., Investigation of CO and CO<sub>2</sub> adsorption on tetragonal and monoclinic zirconia, *Langmuir* **17** (2001) 4297–4303.
- [61] Zhao, Y., Tao, K. and Wan, H. L., Effect of zirconia phase on the reduction behaviour of highly dispersed zirconia-supported copper oxide, *Catal. Comm.* **5** (2004) 249–252.
- [62] He, M.-Y. and Ekerdt, J. G., Infrared studies of the adsorption of synthesis gas on zirconium dioxide, *J. Catal.* **87** (1984) 318–388.
- [63] He, M.-Y. and Ekerdt, J. G., Methanol formation on zirconium dioxide, *J. Catal.* **90** (1984) 17–23.
- [64] Nitta, Y., Suwata, O., Ikeda, Y., Okamoto, Y. and Imanaka, T., Copper-zirconia catalyst for methanol synthesis from carbon dioxide: Effect of ZnO addition to Cu/ZrO<sub>2</sub> catalysts, *Catal. Lett.* **26** (1994) 345–354.

- [65] Fisher, I. A. and Bell, A. T., In-situ infrared study of methanol synthesis from  $\text{H}_2/\text{CO}_2$  over  $\text{Cu}/\text{SiO}_2$  and  $\text{Cu}/\text{ZrO}_2/\text{SiO}_2$ , *J. Catal.* **172** (1997) 222–237.
- [66] Jung, K.-D. and Bell, A. T., Role of hydrogen spillover in methanol synthesis over  $\text{Cu}/\text{ZrO}_2$ , *J. Catal.* **193** (2000) 207–223.
- [67] Schilke, T. C., Fisher, I. A. and Bell, A. T., Influence of titania on zirconia promoted  $\text{Cu}/\text{SiO}_2$  catalysts for methanol synthesis from  $\text{CO}/\text{H}_2$  and  $\text{CO}_2/\text{H}_2$ , *Catal. Lett.* **54** (1998) 105–111.
- [68] Schilke, T. C., Fisher, I. A. and Bell, A. T., In situ infrared study of methanol synthesis from  $\text{CO}_2/\text{H}_2$  on titania and zirconia promoted  $\text{Cu}/\text{SiO}_2$ , *J. Catal.* **184** (1999) 144–156.
- [69] Jung, K. T. and Bell, A. T., Effects of zirconia phase on the synthesis of methanol over zirconia-supported copper, *Catal. Lett.* **80** (2002) 63–68.
- [70] Rhodes, M. D. and Bell, A. T., The effects of zirconia morphology on methanol synthesis from  $\text{CO}$  and  $\text{H}_2$  over  $\text{Cu}/\text{ZrO}_2$  catalysts part I. Steady-state studies, *J. Catal.* **233** (2005) 198–209.
- [71] Vannice, M. A., *Kinetics of catalytic reactions*, Springer, New York 2005.