# Catalyst dynamics: consequences for classical kinetic descriptions of reactors

Tue Johannessen [a,*], Jane H. Larsen [a], Ib Chorkendorff [a], Hans Livbjerg [a], Henrik Topsøe [b]

[a] *Department of Chemical Engineering and Department of Physics, Interdisciplinary Research Center for Catalysis (ICAT),*
*Technical University of Denmark, Building 229, DK-2800 Lyngby, Denmark*
[b] *Haldor Topsøe Research Laboratories, Nymøllevej 55, Dk-2800 Lyngby, Denmark*

## Abstract

The modelling of catalytic reactions/reactors has undergone great improvements since the introduction of empirical power-law kinetics in chemical reaction engineering and micro-kinetic models based on insight into the nature of elementary steps have appeared for many reactions. However, recent in situ studies and surface science investigations has brought added attention to the fact that catalysts may behave in a dynamic manner and reconstruct depending on the reaction conditions. This feature severely limits traditional kinetic descriptions.

In the present paper, we present examples of the dynamical behaviour of some catalytic systems and discuss the corresponding limitations in existing models for catalytic reactions and reactors.

Catalytic reactors operated in non-steady-state are becoming more frequent in industry. The additional efforts needed to accurately simulate these types of reactors are discussed. Finally, we discuss the role of computational fluid dynamics (CFD) as a tool for detailed simulation of catalytic reactors. © 2001 Elsevier Science B.V. All rights reserved.

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## 1. Introduction

A fundamental basis for designing industrial catalytic reactors is the knowledge of the kinetics of the catalysed reaction. In addition, one must have detailed insight in the transport phenomena in the reactor in order to couple the local reaction rate with transport of matter and heat. The applicability of model simulation of kinetics and transport phenomena in catalytic reactors has greatly improved with the increased computational power of modern computers. Furthermore, the developments in surface science and in in situ characterisation methods have brought along new knowledge about the processes occurring at the surfaces of the catalysts allowing a far more detailed description of the kinetics for the catalysed reactions. Nevertheless, the dynamic phenomena are often neglected.

The aim of this paper is to give a brief overview of the developments in kinetics and reactor design and point out possible limitations of some of the approaches. Particularly, emphasis will be given to the role of dynamic surface reconstructions. Finally, with a focus on the kinetics of $SO_2$ oxidation, we discuss to what extent the kinetic information must be expanded in order to carry out transient simulations compared to that needed for steady state simulations.

## 2. The history of kinetics in reactor design

The theory of catalytic reaction engineering, i.e. the combination of reaction kinetics and reactor design was founded in the 1950s and 1960s and has gone through many changes and developments to reach today's level.

An early approach was to use a purely empirical, algebraic expression, e.g. a power-law, to describe the rate of the catalysed reaction. The exponents in power-law expressions were fitted to experimental data and the resulting equation was applied to explore the effect of changes in reactor operation on, e.g. conversion. Rate equations of the type

$$r = k p_A^\alpha p_B^\beta p_C^\gamma \cdots \tag{1}$$

are still used widely and may give satisfactory descriptions of the reactions in limited regimes. Nevertheless, such models typically fail to model non-steady-state operations and they give little insight into the details of a complex catalytic mechanism.

* Corresponding author. Tel.: +45-45252800; fax: +45-45932906.
*E-mail address:* tj@kt.dtu.dk (T. Johannessen).

To introduce chemical insight, different developments have taken place over the years [1] which employs the use of Langmuir–Hinselwood type mechanisms based on information regarding the elementary steps occurring in the reaction (adsorption, dissociation, reaction between adsorbed molecules, desorption). If the system has only one slow, i.e. rate-determining, step, one can easily write an equation, which describes the overall reaction rate. Typically, the resulting rate equation is of the form

$$r = \frac{[\text{rate constant}][\text{driving force}]}{[\text{adsorption term}]} \qquad (2)$$

The adsorption term could also be considered a resistance term. When most sites are occupied by either reaction intermediates or catalyst poisons, the overall reaction is slow. When the surface is only sparsely covered, the adsorption resistance term becomes unity.

In a Langmuir–Hinselwood type mechanism, one can always eliminate the concentrations of the intermediate species and derive a rate expression for the catalysed reaction, based only on the steady-state assumption, but such rate expressions have often been considered too cumbersome for practical use. Often a simplified kinetic expression can be derived if one can identify or assume the most abundant surface intermediate (*masi*). Along with the *masi*, there has to be either a rate-determining step or two irreversible steps [1]. In fact sometimes, the expression for the overall reaction rate based on either one rate-determining step or two irreversible reactions might even be identical.

This sustains the statement, which cannot be repeated too often: a rate-equation that fits well to experimental data for the kinetics of the steady-state catalysed reaction does not prove a postulated mechanism. Two different mechanisms might lead to rate equations that equally can describe experimental data, i.e. the model is not representing a unique solution.

In typical approaches to reactor calculations, the structure of the surface is assumed to remain constant throughout the reactor and only the coverages of different species changes.

Normally applied assumptions are

- the surface is uniform,
- a surface reaction can be described by the mean field assumption,

$$r_{\text{surface}} = k\Theta_A\Theta_B \qquad (3)$$

i.e. the rate of the surface reaction is a function of the individual average coverages,

- Adsorbate–adsorbate interactions are neglected (except from blocking effects).

These assumptions often result in the following types of errors:

- Wrong behaviour (e.g. reaction order) in different parameter regimes.

- Loss of influence of structure sensitivity.
- Lack of coupling between surface composition/structure and the gas-composition.

Although the Langmuir–Hinselwood mechanism describes the micro-kinetics of a reaction, it is normally used to consider only the steady-state kinetics of the catalysed reaction, and the assumptions that follow the analysis often limit the applicability of the outcome.

The goal of *micro-kinetic analysis* is to estimate independently the rates of elementary steps and surface coverages [2], thereby, surpassing the pitfalls of the usual Langmuir–Hinselwood approach, and move one step closer to reality.

Micro-kinetic modelling employs data from various fields: ultra-high-vacuum (UHV) studies (e.g. sticking coefficients), thermodynamic data (e.g. equilibrium constants), spectroscopic characterisation of surface species, calculation of bond-energies and activation energies based on the theory of electronic structure.

The first micro-kinetic model for ammonia synthesis based on surface science insight into the nature of the elementary steps was given by Stoltze and Nørskov [3]. They bridged the "pressure gap" between UHV-experiments and industrial conditions for this catalytic system. A model with a minimum number of assumptions combined with UHV-data and parameter estimations predicts the $NH_3$ mole fraction at the reactor outlet for experimental conditions ranging from 1 to 300 atm and from 375 to 500°C.

In general, the kinetic equations have to be solved simultaneously with a model representing the flow and temperature patterns in the reactor in order to close the coupling between the kinetic equations and the macroscopic heat and species balances in the bulk flow. The influence of mass-transfer limitations has to be captured by the simulation. In addition, one has to take into account the influence of heat- and mass-transfer on the pellet efficiency.

Major difficulties arise when normal assumptions of, e.g. constant density of active sites or mean-field break down. Section 3 deals with some of these issues of dynamical changes in catalysts. Two types of dynamical behaviour are

- local coverages are changing with time,
- The surface structure is changing with time and/or with composition of the gas.

Surface reconstruction is described as a dynamic property of a catalyst. In the chemical engineering terminology, dynamic is related to "things that change in time". Therefore, we need to keep in mind whether we want to simulate a reactor in steady-state or a reactor with transient behaviour. To carry out transient simulations, the kinetic expression will have to depict the rate of the reconstruction and not just the "equilibrium" surface structure under given conditions. As we will see, novel discoveries of catalyst properties show that the catalyst surface might change with time. In a transient simulation, we need to know how fast it changes.

These aspects of reaction kinetics and transient versus steady-state simulations will be discussed throughout the paper.

## 3. Examples of dynamical changes in catalysts

In most cases, it has been difficult to identify the nature of the active surface under reaction conditions. This is a necessary input to kinetic modelling as discussed above. A major problem with simplified approaches to heterogeneous catalysis is furthermore the assumption of a uniform, non-changing surface. Often, the particle morphology and the surface composition will depend on the gas composition. Restructuring often occurs and in some cases it can be an oscillating or even chaotic process. In this section, we will discuss a few examples of the identification of reaction sites of catalysts, of structure and morphology changes during reaction conditions, and finally about the changes in the surface composition of multi-component catalyst particles.

### 3.1. Reaction sites

Information about reactivities of different crystal facets have been obtained mainly from measurements on single crystal surfaces under ultra high vacuum [4]. But can we assume equal reactivity for all sites on a given crystal facet? Such measurements have shown that catalytic reactions are often structure sensitive, i.e. the rates depend on the nature of the surfaces. Probably, the most dramatic example of structural sensitivity is that given by Dahl et al. [5], who revealed a very drastic difference in the activity of terrace sites versus step sites on the Ru($0\,0\,0\,1$) surface. The dissociative adsorption of $N_2$ is completely dominated by step-sites on the single crystal surface of Ru($0\,0\,0\,1$).

As seen on Fig. 1, the measured thermal sticking coefficients for $N_2$ are reduced by more than nine orders of magnitude when the step-sites on the Ru($0\,0\,0\,1$) surface are "removed" by blocking them with gold. Only 0.01–0.02 ML (mono-layer) of gold is deposited, but it preferentially deposits on steps.

These results show how ambiguous the concept of turn-over frequency (TOF) is, when the identity of the active sites are not clearly stated. Typically, it is difficult to answer the following types of questions. What is the number of active sites? Are all sites equally active? Do the sites on nano-particles in catalysis have similar reactivities as those on a macroscopic single crystal?

Dahl et al. [6] suggested that the reaction path of ammonia on a Ru($0\,0\,0\,1$) surface with step-sites would occur by dissociative adsorption of $N_2$ on steps and addition of H-atoms onto N-atoms that have diffused from step-sites to regular terrace sites. Clearly, such issues are difficult to represent by a normal *mean field* mechanism.

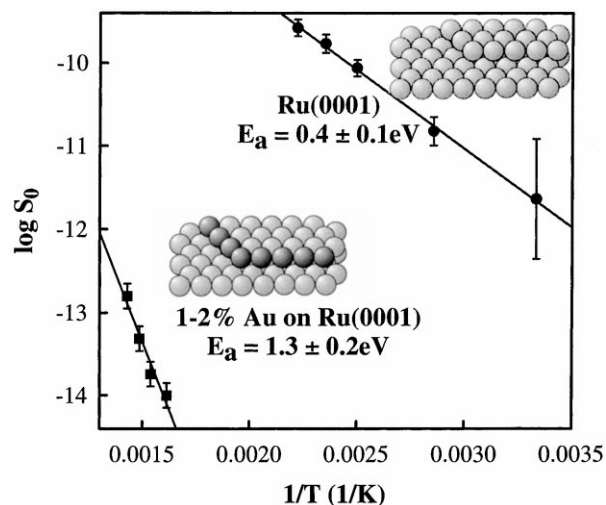By constructing a micro-kinetic model based on these fundamental observations and by assuming a realistic number



Fig. 1. Measured sticking coefficients of $N_2$ on clean Ru($0\,0\,0\,1$) surface and on Ru($0\,0\,0\,1$) with deposition of 0.001–0.002 ML of gold (reproduced from [5]).

of such active sites (B5 sites) on the small Ru particles, it was possible to describe the ammonia synthesis on Ru supported on $MgAl_2O_4$. Actually, the number of such step-like sites will naturally disappear when the particles become too small or too big meaning that there will be an optimal size distribution. The upper limit is well-known as the activity of the catalyst is decreasing by sintering. However, the other limit is less well known. In a very resent work, Jacobsen et al. [7] showed how the activity increased by increasing the particles size on the Ru/$MgAl_2O_4$ catalyst indicating that a certain particle size is necessary for the particle to accommodate the so-called B5 sites that are responsible for the high reactivity on Ru.

### 3.2. Structure and morphology

The oxidation of CO on the Pt($1\,1\,0$) surface is a well-known example of a catalytic system with dynamic behaviour of surface structure and morphology. By means of photo-emission electron microscopy (PEEM), the surface coverage was imaged at different times by Ertl [8]. The results showed that surface concentrations of reacting species vary with respect to both time and 2D-space. Phenomena like dynamical spiral patterns and nucleation and growth of a CO-front on an O-covered Pt($1\,1\,0$) surface were among the interesting results from that study. From those observations one can easily conclude that the mean-field approach here is far from reality. Concentration gradients will exist on the surface and it affects the surface structure and reactivity. Furthermore, the gradients will lead to significant transport of species by surface diffusion and complicated time dependancies.

In the remaining part of this section, we will focus on recent experimental and theoretical investigations of methanol synthesis. Methanol synthesis over Cu/ZnO based catalysts

have been practised industrially for many years. Recently, it has been discovered that dynamic interactions occur between the surface structure and gas composition [9,10]. This system has been studied for quite some time and in recent years, new features of both modelling and characterisation has added significantly to the understanding of the kinetics. The results indicate that methanol is synthesised from $CO_2$ and $H_2$ and that CO is coupled to the methanol synthesis by the reverse water-gas shift reaction [11–14].

Grunwaldt et al. [9] applied in situ EXAFS with simultaneous mass-spectrometer measurements. They found that the structure of the Cu-particles (as measured by average co-ordination numbers) depend on the reduction potential of the reaction gas. Thus, the Cu-structure will depend on the conversion or the position of the catalyst in the reactor. Moreover, it was found that the reaction rate depended on the structure. Fig. 2 shows the drastic changes in the apparent co-ordination number of copper when the gas composition is switched between wet and dry synthesis gas, i.e. changing the oxidation/reduction potential. When the catalyst (Cu/ZnO) is exposed to varying gas composition, the surface structure changes and so does the methanol production rate. Clausen et al. [10] explained the differences in co-ordination numbers by a change in the copper crystallite morphology. This is illustrated on the lower part of Fig. 2, where the adhesion behaviour of the crystallite on the surface changes with the reduction potential of the gaseous environment.
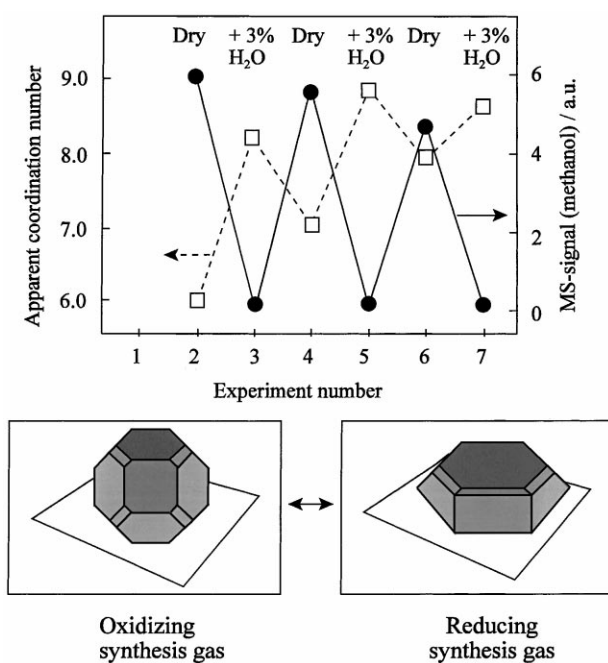


Fig. 2. (Top) Simultaneous measurements of in situ EXAFS co-ordination numbers and outlet methanol concentration (mass spectrometer). The catalyst (Cu/ZnO) is exposed to varying synthesis gasses (reproduced from [9]). (Bottom) A schematic of the restructuring from non-wetting to wetting Cu-particles on a substrate as a function of oxidising vs. reducing gas (reproduced from [10]).
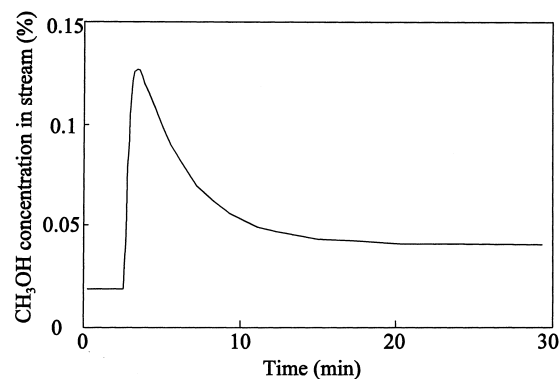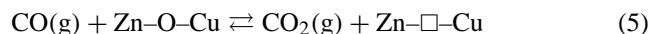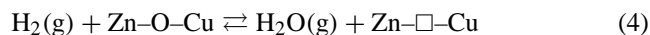


Fig. 3. Transient response of the outlet methanol concentration from a plug-flow reactor with a step-change in feed gas from 6% CO in $H_2$ to 5% CO, 5% $CO_2$ and balance $H_2$ (reproduced from [15]).

When the catalyst is exposed to reducing conditions, oxygen vacancies at the boundary between Zn and Cu are formed [15]

$$H_2(g) + Zn\text{–}O\text{–}Cu \rightleftarrows H_2O(g) + Zn\text{–}\square\text{–}Cu \qquad (4)$$

$$CO(g) + Zn\text{–}O\text{–}Cu \rightleftarrows CO_2(g) + Zn\text{–}\square\text{–}Cu \qquad (5)$$

where $\square$ denotes an oxygen vacancy. This alters the adhesion energy between copper and the ZnO substrate. The limiting situations are free Cu-particles on the ZnO substrate in one limit and a full monolayer of vacancies, $\square$, at the interface between Cu and Zn at the other limit. As a result, the copper particle "wets" the surface more effectively at reducing conditions thereby altering the ratios between exposed crystal facets of copper, and indeed exposes more of the most reactive surface. This leads to an increase in methanol production rate. As evidenced by Fig. 2 this effect is reversible.

Transient studies of methanol synthesis on Cu/ZnO [16] confirm this hypothesis.

Fig. 3 shows the exit methanol concentration as a function of time for an experiment with a step-change in the feed gas from highly reducing gas (6% CO in $H_2$) to synthesis gas (5% CO, 5% $CO_2$ and balance $H_2$).

The response of the step-change in feed gas composition is a high peak in the outlet methanol concentration, followed by a slow decay to a new steady-state level. Prior to the step change, the exposed surface area of copper is large due to the reducing synthesis gas composition. Therefore, the rate of methanol production is high immediately after the step change but gradually decays to a new steady state rate as the copper surface accommodates to the new gas composition.

Ovesen et al. [15] developed a dynamic micro-kinetic model, which took into account the structural changes mentioned above but otherwise was based on the static micro kinetic model with 13 elementary steps by Askgaard et al. [17]. All but four reaction-steps were assumed to be in equilibrium. In addition to the general derivation of a rate-expression, the model allowed for the structural

sensitivity (i.e. the different rates on different facets of the copper particle)

$$r_{obs} = (\eta r_{100} + \varepsilon r_{110} + (1 - \eta - \varepsilon) r_{111})^N \qquad (6)$$

where $\eta$ and $\varepsilon$ are the ratios (relative to $N$) of number of sites on the $(1\,0\,0)$ and $(1\,1\,0)$ surface, respectively, and $N$ the total number of sites. The rates on different facets are $r_{ijk}$.

The micro-kinetic model becomes *dynamic* in the sense that it takes into account the changes in surface morphology as a function of the gas composition. It does not deal with the rates of the morphological changes but the dynamic micro-kinetic model can explain qualitatively the transient responses (cf. Fig. 3). The morphology changes were based on so-called Wulff constructions. The stable shape of a particle is obtained when the total free surface energy is at a minimum, which leads to a unique equilibrium shape for a particle with different surface energies for the different crystal facets.

Under steady-state reaction conditions, the dynamic model fits experimental data significantly better than the static model (cf. Fig. 4).

In the upper graph on Fig. 4, the fit using the static micro-kinetic model is shown. The points above the diagonal are obtained in the most reducing regime whereas the points below the diagonal are in the most oxidising regime. This causes the break-down of the static model, which underestimates the rate in reducing environment and overestimates the rate in an oxidising environment. The dynamic model eliminates this effect and the agreement of model with the experimental data is significantly improved. Still, as mentioned above, it should be stressed that the dynamic model is a steady-state formulation of the kinetics with a coupling between surface structure and gaseous environment. The actual rates of the surface reconstructions are yet to be determined.

As we have seen, the coupling between gas composition and surface structure is very important. From inlet to outlet in a fixed-bed reactor, the change in gas-composition from reactants to products can be sufficient to change the corresponding surface structure. This can cause a normal kinetic model to break down. Even in small laboratory reactors, where powders of the catalyst is tested, this might have implications when high degrees of conversion is obtained. As always, care should be taken to fit experimental data to a model based on a constant surface area and/or structure.

### 3.3. Surface composition

Previously, it was illustrated for the methanol catalyst how the gas composition changes the area of the different single component metal particle facets and thereby the overall reactivity of the catalyst. Many catalyst particles consist, however, of several components, and in these cases, the surface composition of the catalyst particle is not always known and this may also change dynamically with gas composition.
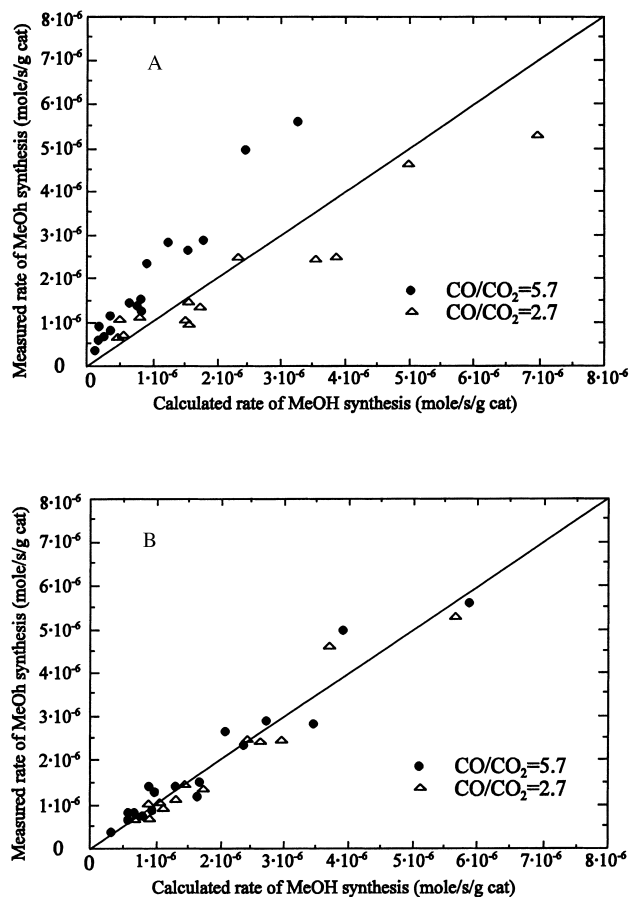


Fig. 4. Comparison of the experimental data and simulation results for methanol synthesis over Cu/ZnO/Al$_2$O$_3$ using two different approaches. (Top) Static micro-kinetic model with constant copper surface area. (Bottom) Dynamic micro-kinetic model with the surface area dynamically dependant on the gas composition (reproduced from [15]).

This is a further complication of the catalytic behaviour of such catalysts.

Considering the simplest multi-component system with only two components, the bulk structure depends on the nature of the two metals. The dependence of temperature on the thermodynamically stable bulk phases is identified and characterised in reference books [18]. The behaviour has also been described in empirical models [19], and more recently using density functional theory by Christensen et al. [20] and Ruban et al. [21], where the segregation and the mixing energy for a large number of transition metal combinations were calculated. Using these parameters, it can be predicted whether an adsorbate will stay at the surface or diffuse into the bulk, and whether there will be alloying or phase-separation between the two components [20,21]. From calculations like these, and from experimental investigations, it has been realised that stable alloys confined to the outermost atomic layer (denoted surface alloys) exist in cases where such structures are not stable in the bulk. This was for example found to be the case for gold and nickel. Below $\sim$1100 K [18], there exist no stable bulk

alloys, but theoretical and experimental investigations [22–24] have shown that the surface alloy is indeed thermodynamically stable. This discovery was recently exploited in the design of a more graphite-resistant steam reforming catalyst, where gold is alloyed into the surface of the small Ni particles [25].

When having several components at the surface, the overall reactivity may not be the simple sum of the reactivities of the different metals. There can be so-called ensemble effects and electronic effects. The changed distribution of reaction ensembles or sites is the origin of the ensemble effect, and the modified electronic structure of the metal atoms is the origin of the electronic effect. The effect of the gold–nickel surface alloy mentioned above is predominantly an ensemble effect, where the number of large nickel ensembles, which favours the formation of graphite decreases [25]. In another bimetallic system, the electronic effect was ascribed to the observed enhanced reactivity of small Co islands on the (1 1 1) facet of copper [26,27]. The cobalt in the pseudomorphic overlayer was strained by the larger lattice constant of Cu(1 1 1), giving rise to a modified electronic structure as shown by Ruban et al. [28].

In most surface science structure investigations, both theoretically and experimentally, the surface is kept free from adsorbates. This, however, is not the catalytically realistic nor relevant state of the particle surface, since adsorbates can influence the surface composition. Nerlov et al. have recently illustrated this for the Ni–Cu system [29,30] where it was observed, that the amount of nickel in the surface depends strongly on the partial pressure (surface coverage) of carbon monoxide, i.e. in situ studies like those described above are in general highly desirable. It was furthermore observed, that the presence of nickel in the surface caused a promotion of the methanol formation rate. It is interesting to speculate whether Zn from the ZnO support could play a similar role in the case of the industrial Cu/ZnO methanol catalyst. Based on experimental observations by Clausen et al. [10] and Nakamura et al. [31], it was suggested by Topsøe and Topsøe [32] that reducing conditions may cause formation of a Zn–Cu surface alloy. The exact surface composition and electronic modifications of surface atoms of the Cu/ZnO methanol catalyst still has to be clarified.

## 4. Kinetics in the simulation of catalytic reactors

### 4.1. Steady-state reactors versus transient reactors

The distinction between transient and steady-state operation is a particularly important one. Many catalytic reactors are at steady-state during their normal operation. In this case, the steady-state kinetics and the enthalpy and free energy of reaction for the catalysed reaction is all the kinetic and thermochemical information, we need for a complete description of the steady-state behaviour.

During transient operation of a reactor, the concentration of the intermediate reaction components changes with time. The simulation of the transient reactor behaviour, like e.g. the transient response of the methanol production on Fig. 3, hence, requires a knowledge, not only of the micro-kinetics of the individual steps of the catalytic mechanism, but also of the steps governing the solid-state transformation. In addition, the enthalpy and free energy of reaction for the individual steps are also needed — a vastly more complicated requirement than for a steady-state reaction. Transient models are required for the simulation of start-up and shut-down transients, for model-based process control, and, in particular, for reactors, the normal operation of which is inherently non steady-state. A comparison of the steady-state and non-steady-state catalytic oxidation of $SO_2$ discussed below serves to illustrate this point further. The example might as well have been based on the modelling of dynamic restructuring of the methanol catalyst.

### 4.2. Example: oxidation of sulphur dioxide

The alkali-promoted $V_2O_5$-catalyst for the gas-phase oxidation of $SO_2$ is doubtless, one of the most important catalysts in the chemical industry in terms of the tonnage of globally installed catalyst and produced $H_2SO_4$. Kinetically and structurally it is actually a rather complicated catalyst, and in spite of its long industrial history it is not until recent years, a full understanding of its behaviour has started to emerge. It is a prominent example of the so-called supported liquid-phase (SLP-) catalysts, in which a catalytically active liquid phase is dispersed in the pore structure of a porous support material [33]. The active phase is molten potassium pyrosulphate, $K_2S_2O_7$, with dissolved sulfo-vanadium complexes. The support is usually based on silica. The pores are only partly filled with liquid. A high gas/liquid interface penetrates the pore system, so that the interior liquid phase can be accessed by diffusion through the residual gas-filled pores.

The structural properties of the catalyst, i.e. the support pore structure and the degree of dispersion of the liquid, must be designed so as to balance optimally the rate of the catalytic reactions in the liquid with the diffusion resistance in gas and liquid phases [34,35]. The distribution of the liquid in the pore system is governed by capillary forces, which use the adhesion energy from the solid/liquid contact to expand the gas/liquid interface. Several studies have shown the existence of two different modes for the liquid phase: a uniformly and finely dispersed phase and a poorly dispersed phase forming clusters of agglomerated liquid. The latter mode usually appears at high liquid loading, when the dispersive forces of the adhesion energy vanish. Studies indicate that the support pore size distribution can be tailored to yield a favourable liquid dispersion [36].

An early attempt to formulate a mechanism for the catalytic oxidation of $SO_2$ is due to Mars and Maessen [38], who proposed a redox-mechanism of the form

$$2V^{5+} + O^{2-} + SO_2 = 2V^{4+} + SO_3,$$
$$\tfrac{1}{2}O_2 + 2V^{4+} \rightarrow 2V^{5+} + O^{2-} \tag{7}$$
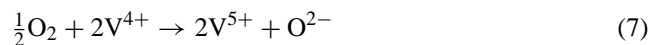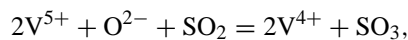
where $V^{5+}$ and $V^{4+}$ are intermediate catalyst species dissolved in the melt.

The second step, i.e. the re-oxidation of the catalyst is slow and assumed to be rate determining, while the first step is fast and approximately equilibrated under typical reaction conditions. This mechanism was set-up to explain the characteristic temperature dependence of the steady-state reaction rate, which reveals a break in the Arrhenius plot with a high value of the apparent activation energy, and thus, a high temperature sensitivity in the low temperature range (cf. Fig. 6). The mechanism provides a rate expression for the $SO_2$ oxidation rate, i.e. the Mars and Maessen expression [38], which has been extensively used for the design of steady-state reactors. However, this theory actually illustrates the fact — as stated earlier — that a completely faulty mechanism may well yield a steady-state rate expression, which can be satisfactorily fitted to measured steady-state rates. Extensive investigations of both supported and non-supported melts have lead to an identification of the precise chemical nature of several of the species present in the melt at reaction conditions, on the basis of which a detailed mechanism for the catalytic $SO_2$ oxidation has been proposed (cf. Figs. 5 and 6, [39]).

In the central cycle of this mechanism, the net reaction: $2SO_2 + O_2 \rightarrow 2SO_3$ occurs by four steps involving intermediate sulfovanadium complex ions. It is noteworthy, that contrary to the Mars and Maessen mechanism, vanadium remains in its highest oxidation stage, +5, in this cycle. The uptake of oxygen occurs through the formation of a peroxide compound in step one. Vanadium (+4) does appear in this mechanism, but in a side-branch to the catalytic cycle, involving a phase transition by the precipitation of vanadyl sulphate crystals in the melt — an extremely important step, which it is now known to be responsible for the break in the Arrhenius plot and the rapidly vanishing steady-state rate at temperatures below $400°C$.

As we have already seen with the dissociative nitrogen adsorption and the dynamic surface reconstruction of the methanol catalyst, the $SO_2$-oxidation catalyst is also an example of the challenges involved in unravelling catalytic mechanisms. It goes through tedious identification of inter-
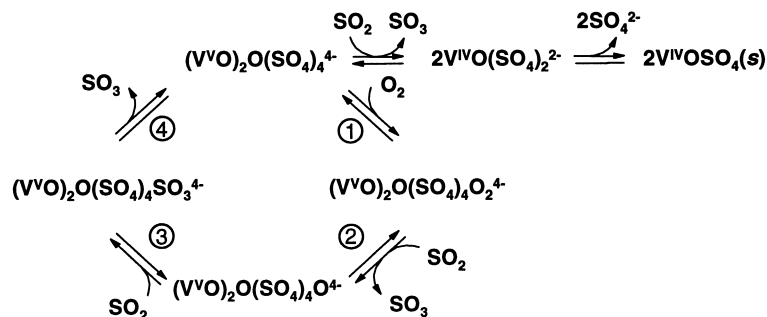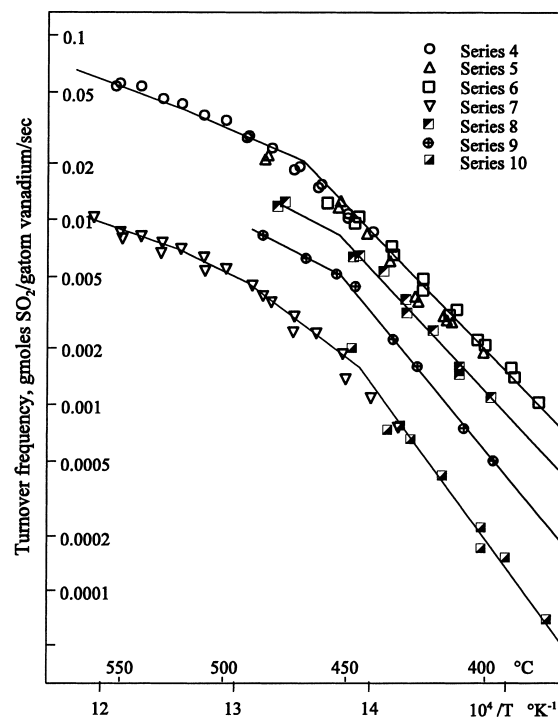


Fig. 5. Arrhenius plot of the turnover frequency for steady-state $SO_2$ oxidation. Gas composition 10.7% $O_2$, 4.4% $SO_2$, 3.6% $SO_3$. The wt.% $V_2O_5$ on silica support: series 4: 2.85; 5: 2.85; 6: 1.37; 7: 21.1; 8: 7.87; 9: 14.2; 10: 24.2. Constant potassium content: K/V = 3.5, [37]. For high catalyst loading on the support, the reaction becomes controlled by liquid diffusion resistance.

mediates and kinetic measurements and, more often than not, the true mechanism is only revealed decades after the catalyst has been introduced industrially.

In the following, we will look into the increase in complexity once the transient reactor is considered.

### 4.3. Comparison of steady-state and transient $SO_2$ oxidation

The traditional catalytic $SO_2$ converter consists of multiple adiabatic layers of catalyst pellets with intermediate cooling between the layers [40]. A mixture of air and $SO_2$ from a sulphur burner is led to the first layer. After the last



Fig. 6. Mechanism for $SO_2$ oxidation as proposed by Lapina et al. [39].

layer, the product $SO_3$ proceeds to an absorber tower, where it is converted to sulphuric acid. The required $SO_2$ conversion in modern plants can usually be obtained only by the use of an additional absorber tower to withdraw part of the $SO_3$ before the last catalyst bed, thereby increasing the equilibrium conversion. An alternative process is the reversed-flow process, which is a non-steady-state process based on periodic reversal of the direction of the gas flow through the catalyst bed. The reverse-flow principle combining chemical reaction with regenerative heat exchange was used first time by Topsøe in 1977 for VOC catalytic oxidation [41]. Later, the principle was further developed and applied for a number of other reactions, including $SO_2$-oxidation as an alternative to conventional $SO_2$-converters with recuperative heat exchange used in the sulphuric acid industry. In the Topsøe REGESOX process [42], the reverse flow principle is extended to treatment of $SO_2$-gases with an excess content of $H_2O$ and production of sulphuric acid directly in the reverse flow reactor without use of additional towers for absorption or condensation of the sulphuric acid.

The two processes, the traditional process and the reversed-flow process, might in principle apply the same catalyst. Thus, they basically differ, not with respect to the catalytic mechanism, but with respect to the steady-state condition. It is instructive to study how the different steady-state conditions affect the formulation of a reactor model for the two processes, in particular with respect to the requirement of kinetic data. It is not just that terms containing the time derivatives that appear in the equations of change for the non steady-state model. The number of necessary equations is different. In a steady-state model, the number of mole balance equations is reduced to a single equation for the key reactant, $SO_2$, for the gas phase and the catalyst phase, respectively. Due to the stoichiometric bounds, the concentrations of the overall reaction components $SO_2$, $O_2$ and $SO_3$ are linearly related at steady-state in both phases. The transient model requires three separate mole balances, i.e. for both $SO_2$, $O_2$ and $SO_3$ in the gas phase and a separate mole balance for each reaction component, including all catalyst intermediates — in total 10 species — for the catalyst phase.

It is, however, with respect to the kinetics that the deviation between the two models is really crucial. In the steady-state model, all we need to know is the steady-state rate expression, $R$, and the reaction enthalpy, $\Delta H_R$, for the overall reaction: $2SO_2 + O_2 \rightleftarrows 2SO_3$. The rate expression, $R$, only depends of the concentration of the overall reaction components $SO_2$, $O_2$ and $SO_3$ and the temperature. The catalyst components so to speak vanish from the model and only appear indirectly in the algebraic form of the steady-state rate expression, which is either based on an assumed mechanism for the reaction or a completely empirical expression.

For the transient model, we must know, for all six reactions constituting the mechanism of Fig. 6, an expression for the rate as a function of temperature and concentrations of the reaction components in these reactions. This is true, not only for the four reactions in the central catalytic cycle, but also for the two side reactions. In addition to the rate expressions, we must also know the reaction enthalpy for each of the six reactions.

With respect to the numerical solution of a non-steady-state model, e.g. [43], the complexity of the model is hardly a matter of real concern today due to the availability of efficient computer capacity and software. However, the amount of additional kinetic and thermo-chemical data required for the transient model certainly presents a challenge to the catalytic reaction engineer, since for most catalytic reactions these data are not available. He, therefore, must make decisions of model simplifications to adjust the model to available data, with the risk of introducing model errors, or devise costly and time consuming experimental investigations to acquire the desired data.

### 4.4. Catalyst dynamics and computational fluid dynamics

Computational fluid dynamics (CFD) is becoming widely used within the field of chemical engineering. In general, CFD is applicable for simulating a wide range of physical systems, e.g. a chemical reactor, by solving the fundamental equations for mass, momentum and energy transfer in a computational domain similar to the actual geometry of the real system. Contrary to normal plug-flow simulations, the geometry is not limited to, e.g. tubes.

The principal governing equations, which form the basis for the calculations can be found in the text books by Bird et al. [44] or Fletcher [45].

The complete system of equations is solved using a control-volume-based technique (e.g. [45]). This technique is based on

- division of the physical domain into discrete control volumes, i.e. the computational grid;
- integration of the governing differential equations on the individual control volumes, which results in algebraic finite difference equations for the discrete unknowns, like velocity, pressure, species concentrations, etc.;
- solving the discretised equations and obtaining a solution, where the residuals are "suitably" low.

Solution accuracy and CPU time both increase with the size (number of cells) of the grid and the number of dependant variables (e.g. species).

Fig. 7 outlines the complexity of catalytic reactor simulation where the level of detail ranges from bulk flow of gasses to surface structure and reaction kinetics. The different elements to be included in a "complete" reactor model are

- Fluid phase equations of change
  - Equation of motion:
    - additional equations for turbulence models;
    - equation of continuity for all components;
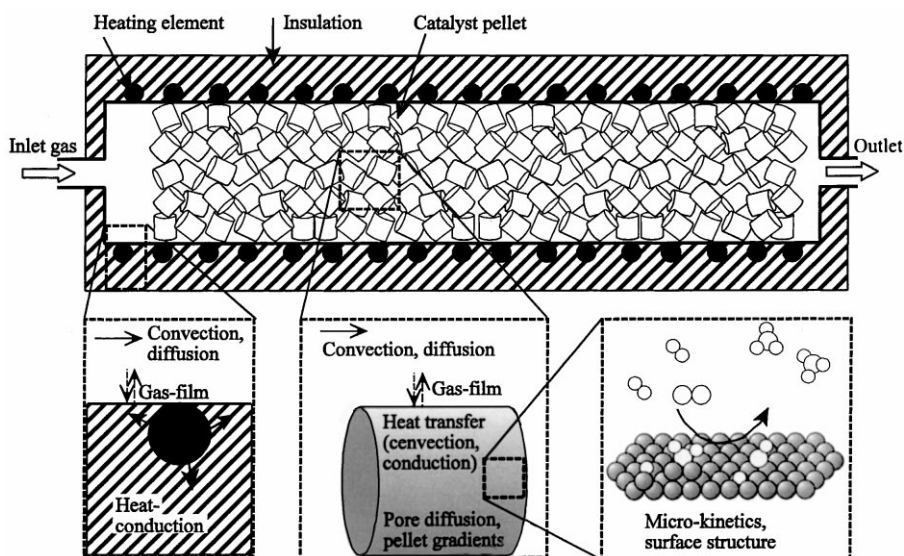    - equation of energy.

Fig. 7. A schematic of the different levels of detail in a complete reactor simulation.

- Solid phase equations of change
  - Equation of continuity:
    - diffusion and chemical reactions in porous solid;
    - *for steady-state*: one rate expression for each net reaction;
    - *for transient operation*: one rate expression for each step in the mechanism;
    - *catalyst structure*: equations describing, e.g. the rate of surface reconstruction.
  - Equation of energy:
    - heat conduction and chemical reaction on/inside a porous solid.
- Boundary conditions
  - Statement of conditions along reactor walls and at the inlet and outlet.

The important coupling between catalyst dynamics and reactor simulation is highlighted as *italic* in the list above. For a transient simulation, we have to define an appropriate number of species to represent the proposed mechanism. Furthermore, we have to introduce additional scalars describing the nature of the surface in cases where it changes with time or with process conditions. If we have proper data for the solid transformation in the methanol catalyst, the model could easily be implemented in the CFD-code (or any other reactor simulation) and the transient response of Fig. 2 would be captured. As a first approach, one could propose a simple empirical model including a time constant for the rate of surface restructuring, which could be fitted to experimental data. However, as in the case of the reaction kinetics, a simple model subjected to fitting is not always the proper choice. For $SO_2$ oxidation, the transient deactivation is automatically captured if the rate of the side-branch is included in the model.

It is obvious that one has to stop at a certain level of detail in the reactor simulation to obtain a result within a reasonable amount of computational time. However, the advent of very strong CFD packages for the simulation of non-isothermal, reacting flow systems has expanded these limits much further.

For reactions in porous materials, the diffusion rates in bulk gas and inside a porous catalyst are entirely different. At this point, we reach the maximal level of detail in the simulation. Employing a mathematical grid for the description of the pore system is prohibitive for any kind of simulation. A more appropriate method is to use an effective diffusion coefficient for the porous material. Haugaard and Livbjerg [46] compared different pore diffusion models to experimental data with a 30-fold pressure range and with different gas-pairs. They concluded that the simple cross-linked pore model [47,48] gave good predictions of pore diffusion fluxes solely from pore size distribution input. This is a suitable approach for implementation in CFD. In the bulk gas, a normal diffusion coefficient is computed but in the porous zones, only the effective diffusion coefficient is employed.

As an example of applying CFD in the field of catalysis, McKenna et al. [49] computed heat transfer from catalyst pellets under different flow conditions. They report that the most common correlations for heat-transfer from particles do not apply for densely packed reactors. Particle interaction, i.e. solid–solid conduction is important for the distribution of heat. In some cases, the simulated temperature rise of packed reactors are overestimated because of lack of this effect.

From these results, we can conclude that detailed simulation of small regimes in a packed bed can provide valuable insight in the transport phenomena and catalyst dynamics.
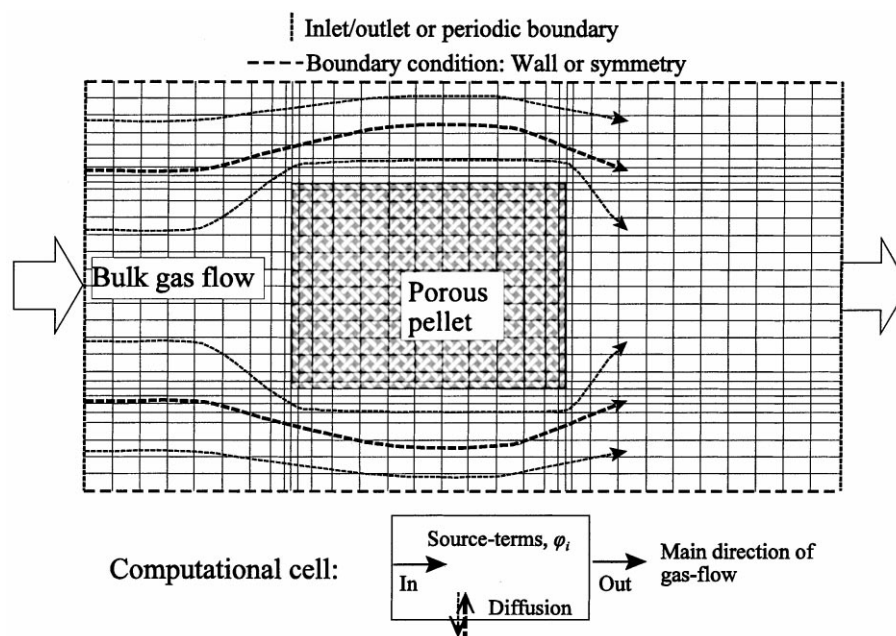
Fig. 8. A schematic of applying computational fluid dynamics (CFD) for the detailed simulation of single catalyst pellets. In addition to the normal CFD-variables, e.g. velocity, mole fractions and temperature, we must introduce user-defined scalars to describe surface coverages in the porous pellet. Therefore, the computational grid includes the interior of the pellet. Properties such as reaction rates and enthalpy of reaction are represented in the source terms. The computational grid must be carefully designed to capture steep gradients in certain regions of the domain.

We believe that valuable information can be extracted from simulations like the one outlined in Fig. 8. The fluid dynamics surrounding the single pellet is coupled to the diffusional transport of species inside the porous pellet. This can provide information on effects such as mass-transfer induced selectivity. However, this type of simulation calls for additional scalars in the CFD-formulation of the system. As mentioned above, the diffusional transport of species in the pellet can be modelled by effective diffusion coefficients. The composition of the gas-phase is described by mole-fractions, obviously, while new scalars must be introduced to describe surface coverages of adsorbed species along with kinetic description of the homogeneous and heterogeneous reactions.

With respect to the packed bed, we reach the limit of detail in a CFD-simulation. The simulation of an entire catalytic reactor consisting of chaotically packed pellets is impossible to implement in CFD on the pellet-level. A computational grid cannot be created for such a system.

In this case, we must employ the more simple plug flow model with certain improvements with respect to catalyst dynamics. Throughout the reactor, a possible method would be to describe the transport of

- bulk fluid through the channels of the pellets defined by a macro-porous system;
- energy and species through a gas-film covering the pellets;
- species and energy through the pellet by effective diffusion coefficients and thermal conductivity coefficients in a micro-porous zone.

Usually, the pellet efficiency is obtained by solving the diffusion-reaction problem in the pellet by, e.g. orthogonal collocation [50]. This has to be implemented in the plug-flow model, which in the case of non-adiabatic reactors will require a 2D model with axial and radial variations throughout the reactor. This system of equations can be solved as algebraic equations for steady-state solutions or by integration in time for a transient system of coupled differential equations.

If the goal is a reliable model taking into account the novel discoveries of catalyst dynamics, the catalytic packed bed remains a challenging task. As a consequence, we might have to settle with less detailed simulations of the bulk flow in the system. However, that does not exclude the implementation of accurate kinetic models that capture transient behaviour and surface reconstruction.

## 5. Summary

The understanding of catalyst micro-kinetics has improved greatly in the past couple of decades, and the increased possibilities for in-situ characterisation has revealed interesting properties of catalysed reactions. Surface reconstructions in changing gaseous environments has significant effects on the catalytic performance and the influence of surface structure on the reaction rate are in some cases tremendous. But the step from recognising these effects to developing accurate models is difficult. Until that point

is reached, we are somewhat limited by our traditional modelling of catalytic reactors.

Simulation of transient reactors requires a much higher level of detail for the kinetic description than reactors operated at steady-state. At steady-state, the reactor can be described by simple, even purely empirical kinetics, but once one needs to explore the effect of making changes in the operating conditions or modifying the catalyst, a much more detailed description comes into play. For simulation of start-up or shut-down of reactors, i.e. also transient phenomena, the same degree of detail is indeed needed.

The CFD is as a possible integrated simulation tool for future modelling of catalytic reactors. Current use of plug-flow assumptions and correlations for mass- and heat-transfer can be avoided with a more detailed description of variations in axial and radial directions in a complex reactor. Still, randomly packed reactors are very complex in terms of detailed modelling of the fluid flow between the catalyst pellets and the introduction of plug-flow assumption and correlations for, e.g. mass-transfer is unavoidable.

## Acknowledgements

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