

Developments in operando studies and in situ characterization of heterogeneous catalysts

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Received 13 August 2002; revised 6 November 2002; accepted 21 November 2002

Abstract

The development of in situ techniques and the introduction of operando studies have had a vast impact on research and developments in heterogeneous catalysis. Over the past 40 years, we have gone from a situation where only limited knowledge existed about the state of the active catalyst to a situation where atomic-scale insight about the catalyst and intermediates can routinely be acquired. In fact, it has recently been shown that atomic-resolved images may be obtained in situ for most catalyst systems. Operando studies have shown that catalysts may undergo dynamic structural transformations upon small changes in the reaction conditions and such transformations have a strong impact on the performance of the catalysts. The fact that, strictly speaking, the active state of a catalyst only exists during the catalysis further emphasizes the need for performing operando studies under relevant reaction conditions. The fundamental insight which can be obtained from in situ and operando studies has been important in catalyst developments since it has made more rational catalyst design strategies possible. The progress in in situ characterization and operando studies is illustrated by examples taken mainly from research on hydrodesulfurization and methanol synthesis catalysis. Some of the present major limitations and likely future developments will also be discussed.

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Keywords: In situ characterization; Operando studies; Structure–activity relationships; Dynamics; Hydrosulfurization; Methanol; Catalysis; Cobalt; Molybdenum; Copper

1. Introduction

Forty years ago, researchers in catalysis had very limited access to atomic-scale information about the state of the catalysts while the catalysis was taking place. This situation was related to the fact that very few techniques were available at the time that both allowed studies of the catalyst under reaction conditions and at the same time could provide detailed chemical and structural information. Thus, the reactor itself was often treated as a “black box” and catalysis research was to a large extent built on post-mortem ex situ analysis of the catalysts and deductions based on different types of separate kinetic experiments. This gave ample room for interpretations and speculations, which often led to situations where many conflicting models were proposed for the same reaction over the same catalyst. A key problem was the lack of surface-sensitive techniques that could provide spectroscopic information at pressures rele-

vant to the catalysis. Another problem was the difficulty of providing detailed structural insight into the complex nanostructures often present in heterogeneous catalysts. The many advances which occurred in surface science did not solve these problems, since surface science experiments were typically performed on single-crystal materials and under ultrahigh-vacuum (UHV) conditions. These difficulties have been termed the “materials gap” and the “pressure gap” in catalysis and significant efforts have been devoted to bridging these gaps.

The situation in catalyst characterization has changed dramatically and today researchers have a large variety of techniques available that may provide detailed atomic-scale structural and chemical insight into complex heterogeneous catalysts exposed to controlled environments. This type of investigations have been termed in situ studies. The term in situ is used very broadly and may have many different meanings. It has, for example, been used to describe studies of individual adsorption/desorption processes, studies of catalysts in a controlled environment after quenching of the reaction, or studies performed during catalysis under high

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pressure. In order to highlight the last type of in situ studies, they have been termed in situ on-line catalysis studies or operando studies. It is evident that such operando studies are especially important since they provide direct insight into the active state of a catalyst. Nevertheless, many other types of in situ experiments may provide very important insights.

Some major developments have been the introduction of in situ methodologies for performing infrared spectroscopy, Raman spectroscopy, X-ray diffraction, X-ray absorption spectroscopy, Mössbauer spectroscopy, nuclear magnetic resonance, and high-resolution electron microscopy (see, e.g., [1–14]). In parallel with these developments, catalysis research has also benefitted greatly from the atomic-scale insight obtained from surface science studies of single crystals (see, e.g., [5,15,16]) and the extension of such studies to model catalyst systems (see, e.g., [5,17–23]).

The fact that very complex and relevant systems can now be treated theoretically by, e.g., density functional theory (DFT) calculations (see, e.g., [24–28]) has made it highly attractive to combine such studies with in situ investigations (see, e.g., [29,30]). Furthermore, today there are improved possibilities for linking the fundamental insights obtained from operando and in situ studies to the catalysis using the microkinetic formalism [31,32].

As discussed above, many in situ studies reported in the literature are not performed as operando studies under the conditions of the catalytic reaction but are studies recorded under controlled conditions of, for example, adsorption, desorption, or surface reaction. Although these studies provide valuable insight, this may not relate directly to the catalysis, since the structure of a heterogeneous catalyst is dynamic and depends intimately on the reaction conditions. Such dynamic changes have, for example, been observed in studies of heterogeneous catalysts containing metal nanoparticles [13,14,33–35]. The changes are typically related to adsorbate-induced reconstructions and even small changes in the environment may result in large changes in the catalyst surface structure. For heterogeneous catalysts, the surface reconstructions may also result in complete morphology changes [14,34,35]. The consequence of such dynamic effects is that, strictly speaking, the active state of a catalyst only exists during the process of catalysis. This further emphasizes the need for operando characterizations. Together with the simultaneous recording of activity data, such studies allow the establishment of direct links between the catalytic activity and the surface chemistry/surface structure. These so-called structure–activity relationships are very valuable since they provide both a fundamental understanding of the catalysis and provide the basis for rational design of improved catalysts.

Section 2 discusses some of the most important experimental considerations that have to be taken into account in performing operando and in situ studies. Some major advances in methodology are also included. Sections 3 and 4 present some examples where improved fundamental understanding of catalysts has been obtained through the applica-

tion of operando and in situ techniques. The focus here will be on hydrotreating and methanol synthesis catalysis, which are both fields where the new insight has contributed dramatically to the understanding of the catalysis. It is interesting that the need to understand these catalysts has in fact stimulated the development of several new in situ techniques and methodologies. Despite the developments in methodology, it is still not always possible to perform the characterization during the conditions of high pressure catalysis. Some of the remaining challenges are discussed in Section 5, together with some of the developments we can anticipate in the future.

2. Experimental considerations and developments in in situ methodologies

In view of the dependence of the catalyst structure on the gaseous environment (see, e.g., [14]), it is often the aim to perform characterization studies under the conditions of the catalysis. In fact, it is highly desirable to perform simultaneous catalytic activity and operando characterization studies [35–38]. However, it is often not straightforward to perform such operando studies. For example, sample cells used in spectroscopy studies often have a geometry which is not ideal for operando studies [8]. Although such cells may provide good quality spectroscopy data, they may have large temperature and concentration gradients, hence poorly defined conditions at the position of the catalyst. One way to circumvent these difficulties is to have the same geometry in the in situ cell as that encountered in the reactor [37,39]. An attractive solution based on this approach is to use miniaturization in the form of capillary cells, which also serve as plug flow reactors [39]. This simple design facilitates simultaneous spectroscopy and on-line activity measurements and it is thus ideal for in situ and operando studies. The design also has the added advantage that sufficient penetration of the radiation can be achieved even during studies at high pressures. Separate experiments [35,39] have confirmed that good catalyst activity measurements can be obtained using such cells. The approach has already been adopted for operando and in situ studies using XRD [39] and combined XRD/QEXAFS experiments [40] and Raman spectroscopy. However, it can easily be adapted to other techniques as well. The small mass of the capillary reactor also makes it ideal in temperature programmed reaction and transient catalysis studies.

X-ray diffraction (XRD) is the technique for obtaining structural information most widely used in catalysis research [11]. Beside the normal angle-dispersive mode, the energy-dispersive mode (EDXRD) can also be used and this mode has certain advantages for characterizing small particles and in situ studies [41]. It is, however, important to note that XRD is not sensitive to structures where the dimension of order is less than about 2 nm. This presents a serious limitation since one of the goals in heterogeneous cataly-

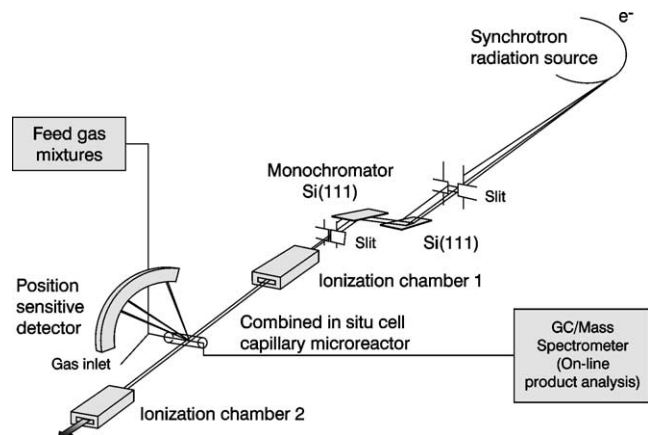


Fig. 1. Sketch of experimental setup for combined QEXAFS/XRD operando studies and simultaneous catalytic activity measurements (adapted from to Ref. [40]).

sis research often lies in the preparation of highly dispersed nanostructures with dimensions less than this value. Thus, one of the important developments in the past 40 years was the introduction of extended X-ray absorption fine structure (EXAFS), which unlike XRD does not require long-range order and can provide local structural insight (interatomic distances and coordination numbers) into complex nanostructures in heterogeneous catalysts. Some of the potential benefits of X-ray absorption techniques for the study of catalysts had already been pointed out more than 40 years ago [42], but their widespread application first took place after Sayers et al. [43] provided an understanding of the EXAFS in 1971. Several reviews have discussed the subsequent development of X-ray absorption techniques and their applications to heterogeneous catalysis [5,8–10].

In many respects, XRD and EXAFS provide complementary information, and therefore, a combination of these two methods is useful to give a more complete structural description of a catalyst. An attractive solution for performing such studies is the combined XRD/QEXAFS technique (Fig. 1) [40]. By the use of a position sensitive detector, the complete XRD pattern is recorded simultaneously and by the use of the Quick EXAFS (QEXAFS) mode, the time resolution is about 0.01 to 2 s on a routine basis. The combined XRD/QEXAFS set-up also allows operando investigations with simultaneous reactivity measurements.

As mentioned above, EXAFS has become the key technique for providing in situ structural insight into nanostructures in heterogeneous catalysts. However, the local structural information from EXAFS does not allow direct determination of the 3D structure. Thus, many details of the structure of heterogeneous catalysts have remained ambiguous. In the case of model catalyst systems, scanning tunneling microscopy (STM) may provide images of the structures (see, e.g., [21–23] and Section 4). For heterogeneous catalysts, it is difficult to apply STM and other scanning probe techniques and high-resolution transmission electron mi-

croscopy (HTREM) is the preferred technique. However, it is not trivial to perform such measurements in situ, since the gas at high pressure will interact with the electrons and decrease the possibility of achieving high-resolution images. In 1972, Baker and Harris [44] pioneered in situ microscopy and they achieved a resolution of about 2 nm. This allowed in subsequent studies the observation of many phenomena of importance to catalysis. A significant advance was made five years ago by Gai and Boyes, who demonstrated a resolution of about 0.23 nm [7]. However, in order to get detailed structural information on important metals in heterogeneous catalysis like Fe, Cu, and Ni, a resolution of at least 0.18 nm is required. Recently, this goal was reached [13,14]. Specifically, earlier this year, it was demonstrated that it is possible to use in situ HTREM to resolve 0.14-nm lattice fringes, while the catalyst was exposed to reaction gases at elevated temperatures [14].

In catalysis research it is often difficult to establish whether adsorbed species are reaction intermediates involved in the catalytic reaction or whether they are just spectator species occupying sites on the surface. Simple adsorption experiments do not allow this discrimination but temperature programmed surface reaction (TPSR) studies may be used to obtain valuable insight. Recently, in situ infrared studies of the SCR deNO_x reaction over V/TiO₂ catalysts have illustrated this point and how the use of a combination of different types of in situ and operando measurements may provide very detailed insight into the reaction mechanism [38,45–47]. The experiments show that one of the reactants, NO, does not adsorb strongly on the catalyst surface. However, NO does interact with adsorbed ammonia species and TPSR experiments (Figs. 2a and 2b) of NO reacting with catalyst surfaces predosed with ammonia gave important mechanistic insight. The in situ FTIR results show that the surface contains both Brønsted and Lewis acid sites but the results showed that it is the former sites which are of importance for the catalysis. A detailed analysis of the FTIR results revealed that redox chemistry also takes place and all the insight lead to the proposed catalytic cycle shown in Fig. 2c. A microkinetic model based on this cycle was shown to account nicely for the industrial operation [47].

Heterogeneous catalysts are nonequilibrium solids and their structures depend critically on the choice of preparation and activation parameters. In situ studies can advantageously be used to obtain information about such parameters [12]. Fig. 3 illustrates how combined in situ XRD/QEXAFS measurements can be used to elucidate the processes occurring during the reduction of the precursors to a Cu-based methanol synthesis catalyst [40]. The EXAFS spectra (Fig. 3a) show the transformation of oxidic copper species to metallic Cu and Fig. 3b shows the XRD region corresponding to the (111) reflection from Cu metal. It is interesting that the phase transformation occurs within a very narrow temperature range and the in situ studies provide valuable information about the processes. Additional insight was obtained by simultaneous gas analysis.

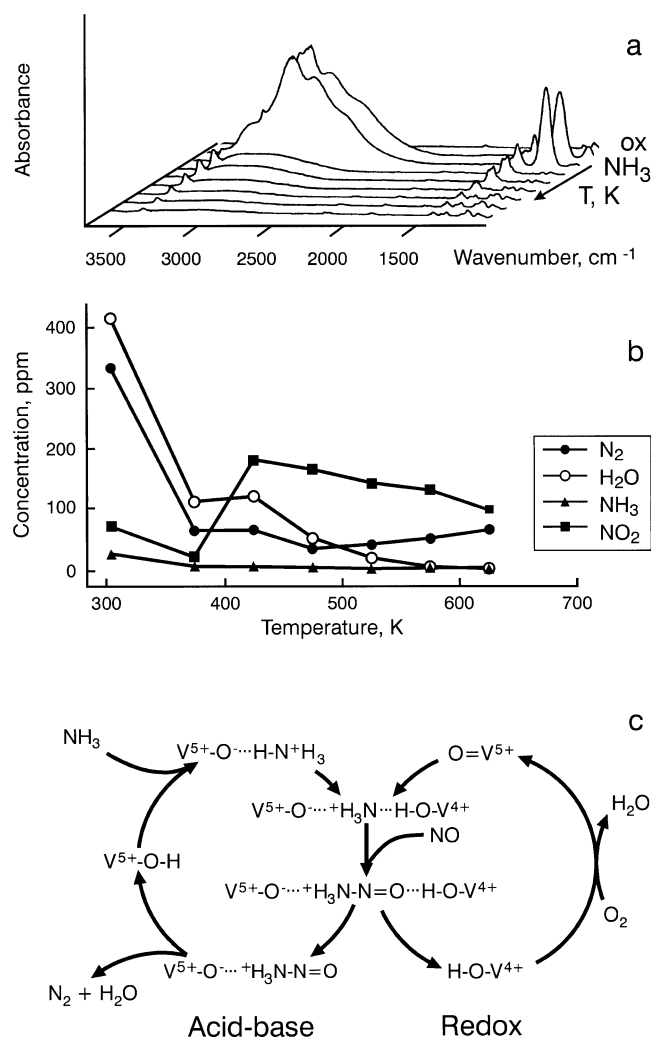


Fig. 2. Simultaneous in situ FTIR (a) and on-line product analysis (b) results obtained during TPSR DeNO_x experiments over V/TiO₂ catalysts. (c) Catalytic cycle for the SCR deNO_x reaction/TiO₂ catalysts based on the different in situ and operando studies (adapted from Refs. [38,46,47]).

3. Importance of dynamic structural changes of heterogeneous catalysts: in situ and operando studies of methanol synthesis catalysts

The nature of Cu–ZnO-based methanol synthesis catalysts has been discussed extensively in the literature and many different copper species have been proposed to be present in the active catalysts (see, e.g., [35]). Copper has, for example, been proposed to be present as Cu⁺ species dissolved in ZnO [48,49], a Cu species at the so-called Schottky junction between copper and the semiconducting ZnO support [50], or metallic copper clusters supported on the ZnO (see, e.g., [51–55]). Recently, it was considered that Cu may be alloyed with Zn [56,57], possibly only at the surface [35,58]. Zn or ZnO species on top of Cu⁰ have also been suggested [59,60]. In retrospect, the very diverging views which have been proposed for this catalyst system can also be re-

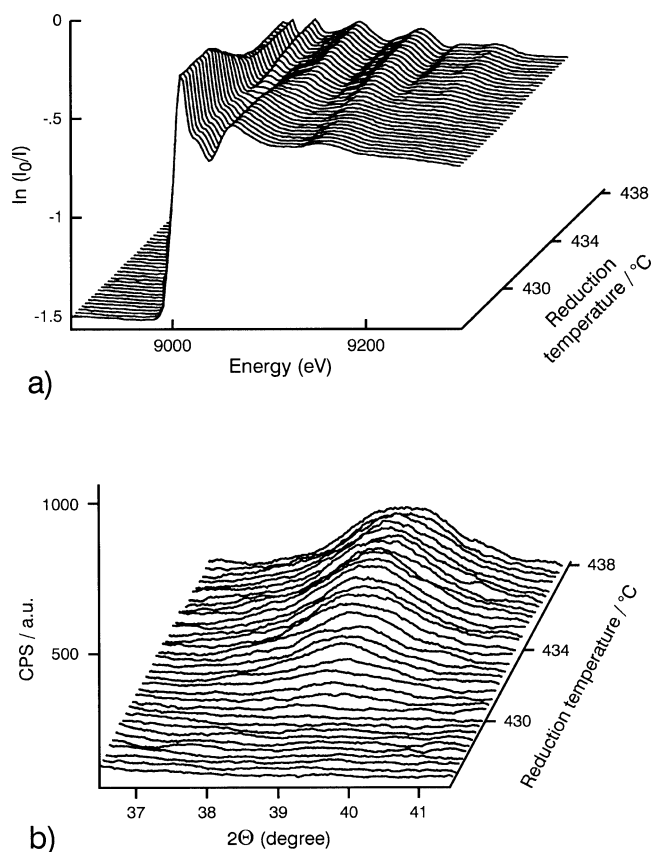


Fig. 3. (a) In situ QEXAFS data around the Cu K-edge obtained together with on-line gas analysis during the activation of a CuO/ZnO/Al₂O₃ catalyst (120 s/spectrum). (b) The corresponding XRD diffractograms of the Cu(111) reflex recorded simultaneously (adapted from Ref. [40]).

lated to the fact that for many years, only very limited in situ insight has been available.

One important development was the application of EXAFS to study such catalysts. The first study clearly showed that Cu was present in the metallic state [52]. Recent detailed XAFS studies have addressed whether Cu metal or Cu–Zn alloys may be present and to what extent this depends on the reaction conditions [34,35]. The observed spectra were compared with simulated spectra of different Cu–Zn alloys. Since Cu and Zn are neighbors in the periodic table, amplitude functions and backscattering amplitudes are quite similar and the introduction of Zn into the Cu lattice will mainly result in small changes in the interatomic distances. Thus, EXAFS has some limitations for the detection of small amounts of Cu–Zn alloys but heating a Cu/ZnO catalyst to 600 °C clearly showed the formation of Cu–Zn bulk alloys. Such temperatures are, however, much higher than those encountered industrially and EXAFS results recorded at typical reaction temperatures exclude the formation of bulk alloys with significant amounts of Zn. It is noteworthy that in situ FTIR studies [58] and DFT calculations [60] have provided evidence that Zn or ZnO species may migrate onto the Cu surfaces especially under very reducing conditions. More-

over, surface science experiments [59] have also provided evidence for enrichment of Zn at the surface.

Below we will discuss some in situ and operando studies of Cu/ZnO catalysts that we believe are of more general interest to researchers in catalysis. The studies illustrate nicely how the structure of a heterogeneous catalyst responds to changes in the reaction conditions. Such structural transformations may be reversible and may result in complete morphology changes. The consequences for the catalysis are significant and many steady state and transient kinetic phenomena cannot be understood without taking into account such structural changes.

The large structural and morphological changes in the metallic Cu particles were first observed in operando EXAFS studies [34]. Large reversible changes in the average Cu–Cu coordination numbers occurred when cycling between oxidizing and reducing synthesis gas mixtures. Since the Cu–Cu distances remained the same as in metallic copper, the results were explained by reversible changes in the morphology of the metal particles. The effects were unique for the ZnO-supported Cu catalysts and similar changes did not occur when Cu was supported on silica. It was proposed [34] that under the most reducing conditions, more oxygen vacancies are formed at the Cu–ZnO interface, and this results in an increased interaction between Cu and ZnO and a tendency for the Cu particles to spread over the ZnO to form flat structures (with decreased average Cu–Cu coordination numbers). Under more oxidizing conditions, the vacancies will be annihilated and the interaction between Cu and ZnO will diminish. Thus, more spherical equilibrium-like Cu⁰ structures are expected to result. Separate steady state and transient kinetic experiments [61,62] showed that the structural and morphological changes dramatically influence the kinetics. The catalytic consequences of the morphology changes were later [61] taken into account by developing a “dynamic” microkinetic model, and it was shown that this model allowed many controversial kinetic observations to be satisfactorily explained. Recently, the catalytic consequences of the dynamic changes were investigated directly by performing simultaneous operando EXAFS and on-line

catalytic activity measurements [35]. Fig. 4 shows the results of such operando studies.

Although the operando EXAFS studies [34,35] clearly show that morphological changes take place, the exact nature of these has remained unclear for several years. Recently, the improved possibilities for performing in situ HRTEM (see Section 2) were used to obtain direct images of the structure and morphology of Cu/ZnO catalysts in different gaseous environments [14]. The microscopy results (Fig. 5) not only confirm the previous proposals concerning dynamic structural changes, they also provide significant additional insight. In all three gas compositions (H₂, H₂:H₂O, and H₂:CO), the copper is present as metallic Cu particles. In the most reducing gas mixture (Fig. 5E), the Cu particles are, as was proposed in the operando EXAFS studies [34,35], quite flat and spread over the ZnO support, whereas in the most oxidizing gas (Fig. 5C), the Cu particles achieve a more spherical shape indicative of decreased interaction with the support. Since lattice spacings are observed for both Cu and ZnO, such studies offer new possibilities for obtaining detailed information about support interactions. Wulff constructions can also be performed and this allows quantitative determinations of the relevant surface free and interface energies in the different environments [14]. Previously such insight has not been available from in situ studies of heterogeneous catalysts and the access to such information presents many new perspectives. For example, the insight will allow a more direct incorporation of structure sensitivity into dynamic microkinetic models. In the past, such models had to be based on assumptions regarding the interfacial energies and their dependence on the gas composition [61].

The images shown in Fig. 5 represent equilibrium shapes and are recorded after long exposures to the gas mixtures. However, in situ HRTEM investigations also allow one to study in detail the dynamics of the structural transformations. Transient methanol synthesis experiments have elucidated how the catalytic activity is influenced by the structural transformation [35,62]. Fig. 6 shows the methanol produced when Cu/ZnO/Al₂O₃ and Cu/Al₂O₃ catalysts are exposed to a 5% CO-in-H₂ gas mixture and after switching to a less reducing gas (5% CO, 5% CO₂, 90% H₂) [62]. The steady-state activity for both systems is higher in the latter gas since methanol is mainly produced from CO₂. The transient behaviors for the two systems are markedly different. These can qualitatively be understood in view of the in situ microscopy [14] and operando EXAFS results [34,35]. For the ZnO containing catalyst, the exposure to the very reducing 5% CO in H₂ gas mixture gives rise to flat Cu structures with relatively high surface areas. As a result, a large increase in the methanol synthesis rate occurs after switching to the CO₂ containing gas. Subsequently, the methanol production slowly decreases since the flat structures are not stable in the more oxidizing gas (Figs. 4 and 5). For the Cu/Al₂O₃ catalyst, no large transient effects are observed since for this system, changes in the interfacial energies are

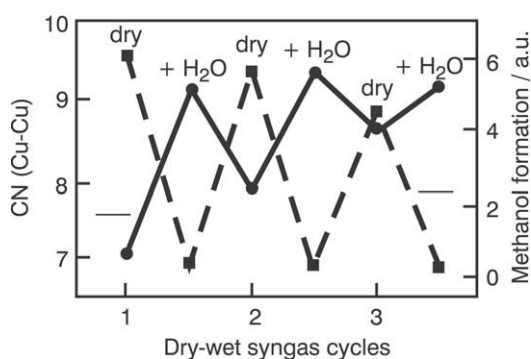


Fig. 4. Operando EXAFS experiments and on-line methanol synthesis activities for a Cu/ZnO catalyst exposed alternately to dry and wet synthesis gas mixtures. The Cu–Cu coordination numbers (CN) were determined from the EXAFS spectra (adapted from Ref. [35]).

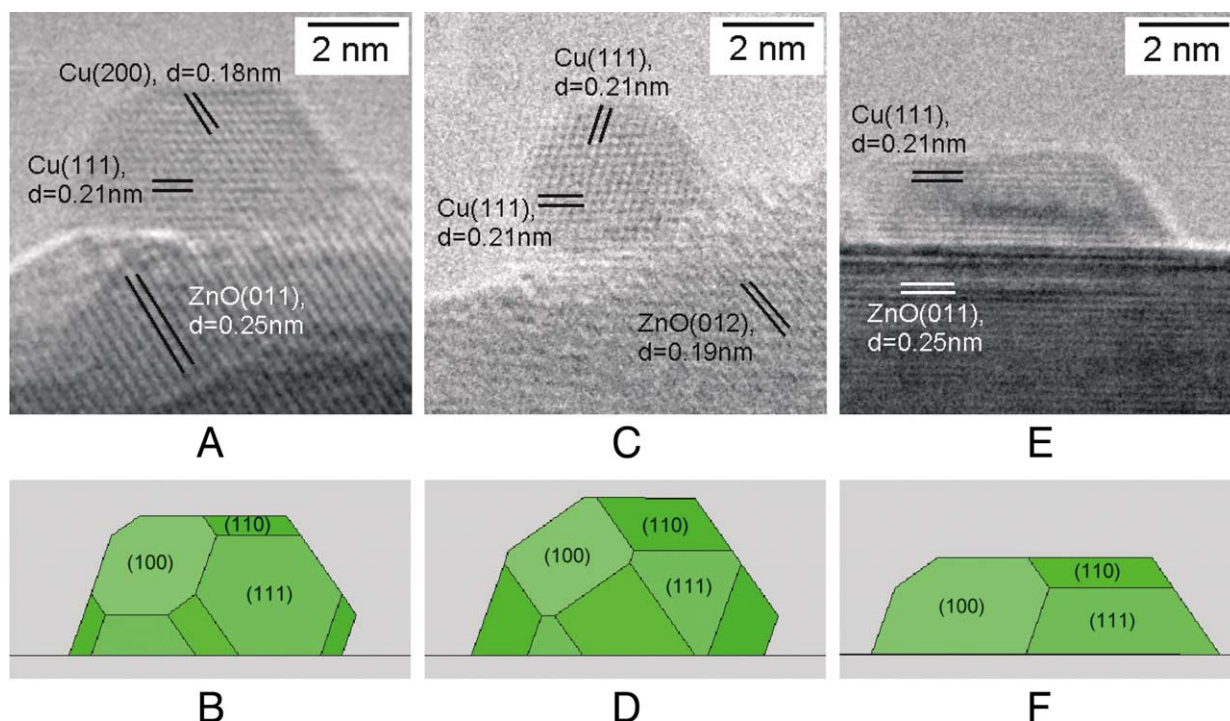


Fig. 5. In situ TEM images (A, C, and E) of a Cu/ZnO catalyst in various gas environments together with the corresponding Wulff constructions of the Cu nanocrystals (B, D, and F). (A) the image was recorded at a pressure of 1.5 mbar of H_2 at 220 °C. The electron beam is parallel to the [011] zone axis of copper. (C) Obtained in a gas mixture of H_2 and H_2O , $H_2:H_2O = 3:1$ at a total pressure of 1.5 mbar at 220 °C. (E) Obtained in a gas mixture of H_2 (95%) and CO (5%) at a total pressure of 5 mbar at 220 °C (adapted from Ref. [14]).

expected to be small. Also, surface-induced reconstructions caused by chemisorption onto the active Cu surfaces are expected to be minor in view of the low concentration of adsorbed species [61]. For other systems, the latter type of effects may be significant (see, e.g., Section 4) and will in general have to be taken into account when developing dynamic microkinetic models.

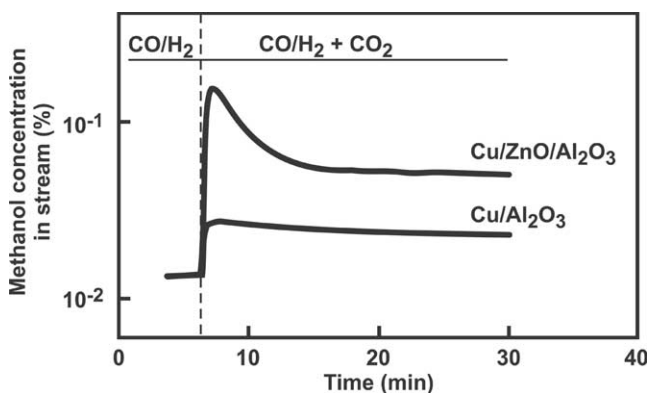


Fig. 6. Transient methanol synthesis experiments at 493 K for Cu/ZnO/ Al_2O_3 and Cu/ Al_2O_3 catalysts. The catalysts were initially exposed to a 5% CO and 95% H_2 synthesis gas and then at the time corresponding to the dotted line, CO_2 was added to the feed (5% CO, 5% CO_2 , and 90% H_2) (adapted from Ref. [62]).

4. Hydrodesulfurization catalysts

The important hydrodesulfurization (HDS) catalysts have, especially in the period preceding the mid 1980s, been one of the most controversial group of catalysts (see, e.g., [63–65]). In retrospect, the controversies can be related to the lack of adequate in situ characterization tools which could provide insight into the very complex structures under relevant sulfiding conditions. Typical HDS catalysts are Co (or Ni)-promoted Mo/Al_2O_3 . The catalytic behavior of Co-Mo/ Al_2O_3 catalysts may be very complex (Fig. 7) and catalysts with similar overall composition may exhibit very different promotional behaviors. Many models were proposed to explain such behaviors and the origin of promotion. However, these proposals remained speculative in the absence of direct in situ insight. The introduction of in situ Mössbauer emission spectroscopy (MES) provided the first detailed insight into the nature of the promoter atoms in the active sulfided state of the catalysts [66,67]. It was found that typical catalysts may contain many different promoter phases. By performing quantitative in situ MES phase analysis of many catalysts with different activities, it was revealed that the HDS activity is dominated by the fraction of the promoter atoms present in a structure called Co–Mo–S (Fig. 7). Thus, the in situ insight allows the establishment of important fundamental structure–activity relationships. Furthermore, the in situ studies revealed that the reason catalysts with similar overall composition may

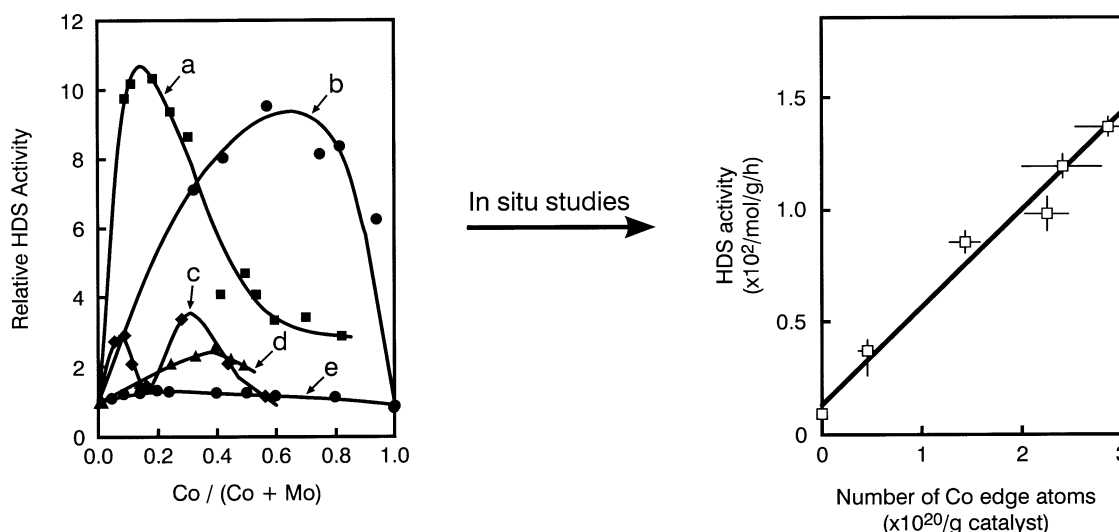


Fig. 7. Illustration of the complex promotional behaviors encountered in Co–Mo/Al₂O₃ hydrodesulfurization catalysts (left panel) and the simple fundamental structure-activity relationships (right panel) which have resulted from the in situ studies (adapted from Refs. [63,67]).

have very different catalytic activities is related to the fact that not all the promoter atoms after activation may end up in the desired Co–Mo–S structures. In fact, the phase composition of such catalysts is very dependent on the choice of preparation and activation parameters and the in situ studies have allowed detailed insight into these very important parameters.

In the early in situ MES studies, it was proposed that the Co–Mo–S structure could be considered as Co located at the edges of small nanoclusters of MoS₂ (see, e.g., [63]). The introduction of in situ EXAFS had a significant impact on the further understanding of the molybdenum and cobalt structures. Such studies directly showed the presence of small MoS₂ clusters (see, e.g., [63,68]). The possibility of studying the highly adsorbing sulfided HDS catalysts by in situ FTIR [69] has also greatly contributed to our understanding of these catalysts. In fact, FTIR studies were the first to show that the MoS₂ and the Co–Mo–S structures are typically present as monolayers (single MoS₂ sheets) and that the promoter atoms in Co–Mo–S occupy MoS₂ edge positions [69,70]. Important insight into these structures has subsequently been obtained by combining the in situ MES studies with in situ studies using many other techniques (see, e.g., [63]).

The in situ insight into the nature of the active structures and the preparation parameters leading to their formation has had a large impact on the developments of improved industrial hydrotreating catalysts [71]. Before the application of such techniques, catalyst developments in this field were done mainly by trial-and-error approaches and around 1980, the catalyst manufacturers and the refining industry regarded these catalysts as nearly optimized (Fig. 8). This has turned out not to be the case; the fundamental insight obtained from the application of in situ techniques has resulted in several novel molecular design strategies and many improved catalysts have been introduced to the industry (Fig. 8).

The in situ studies show that the catalytic activity is related to the presence of the Co–Mo–S edge structures in promoted catalysts and to the MoS₂ edge structures in unpromoted catalysts. In order to understand why these structures are important, more detailed atomic-scale insight into the structures has been sought after. This has been difficult to obtain experimentally since, for example, the important in situ structural technique EXAFS does not provide a unique 3D structure. In fact this limitation has led to different interpretations and proposals for the detailed structure of the Co–Mo–S and MoS₂ nanoclusters (see, e.g., [63,64]).

Recently, it was possible for the first time to obtain direct atomic-resolved STM images of the MoS₂ nanostructures [22,23]. By choosing the herringbone reconstructed Au(111) surface as a template, Helveg et al. [22] succeeded in prepar-

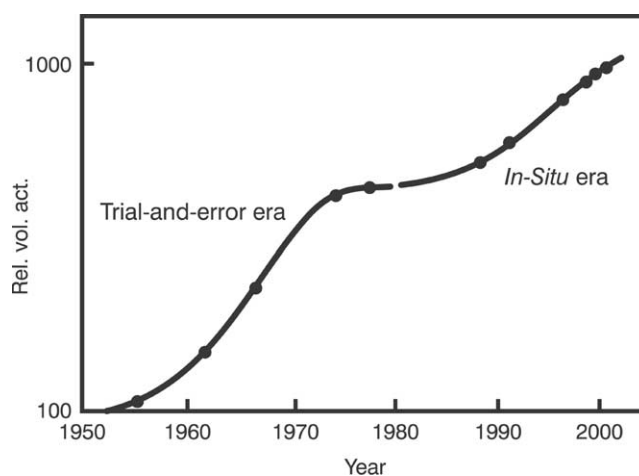


Fig. 8. Developments in the catalytic activity of industrial HDS catalysts during the past 50 years. The figure illustrates how the in situ insight has resulted in improved catalysts based on new molecular design strategies (adapted from Ref. [71]).

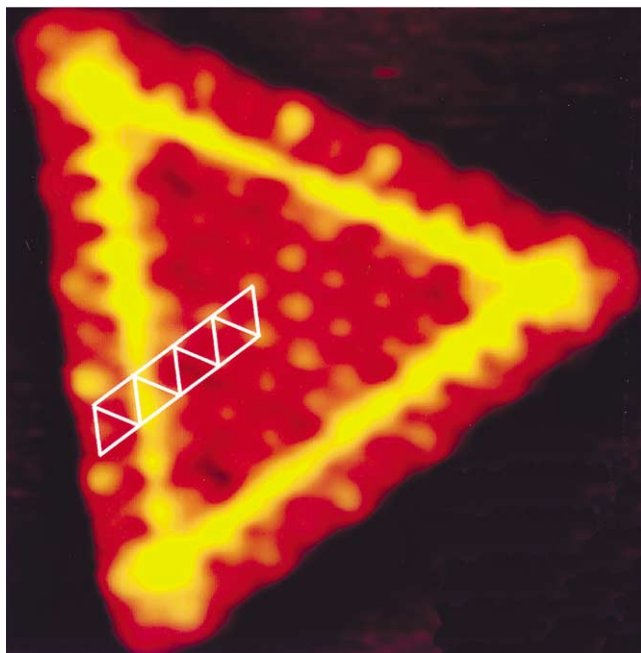


Fig. 9. An atom-resolved STM image ($41 \text{ \AA} \times 42 \text{ \AA}$) of a single-layer MoS_2 nanocluster. The grid shows the registry of the edge atoms relative to those in the basal plane of the MoS_2 triangle (adapted from Ref. [22]).

ing small nanocrystals of MoS_2 (Fig. 9). The nanocrystals are one-layer thick and this allows the recording of atom-resolved STM images of the active edge structures of MoS_2 . It is apparent from the images that the structure of the edges is reconstructed with respect to that of the bulk. This new insight implies that the edge structures may be quite different from those typically proposed in earlier studies (see, e.g., [63,64]).

Under the sulfiding conditions used in the above study, the MoS_2 structures are triangular and expose only the so-called Mo-terminated edges. This was not always observed to be the case [72], and DFT calculations show that the type of termination is expected to depend on the sulfiding/reaction environment [73,74]. Thus, as is observed for Cu/ZnO catalysts (Section 3), hydrotreating catalysts may also be expected to undergo dynamic structural rearrangements. For example, as the $P_{\text{H}_2}/P_{\text{H}_2\text{S}}$ ratio changes through a reactor, the structure of the hydrotreating catalyst may change and such changes should ideally be included in the kinetics analysis. The fact that today we have insight into these phenomena will make such dynamic microkinetic treatments possible.

It should be stressed that the STM studies reported so far are performed on Au supported MoS_2 model systems and although Au is expected to be rather inert, it has been questioned whether such triangular structures may also be observed for MoS_2 structures on more industrially relevant supports [75]. Recent microscopy investigations have investigated this issue and shown that the structures in the model catalysts may indeed also be observed in

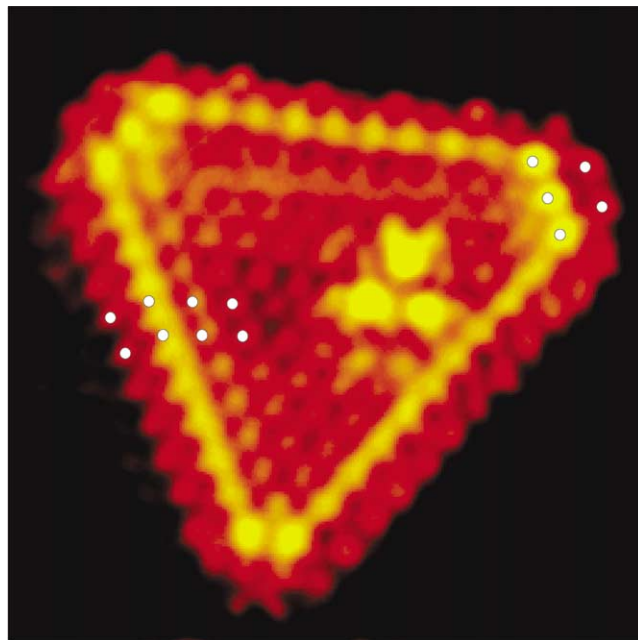


Fig. 10. An atom-resolved STM image ($48 \text{ \AA} \times 53 \text{ \AA}$) of a single-layer Co–Mo–S nanocluster. The small white dots illustrate the position of the protrusions (adapted from Ref. [23]).

alumina-supported catalysts (Carlson, Brorson, and Topsøe, unpublished results).

STM studies have also provided insight into the structure of Co–Mo–S [23]. It is observed that Co gives rise to the

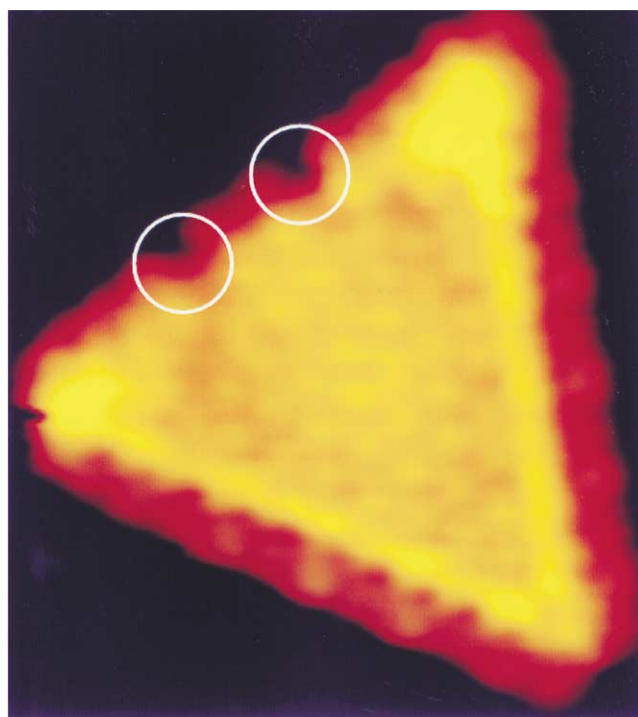


Fig. 11. An atom-resolved STM image of a MoS_2 nanocluster exposed to atomic hydrogen at 600 K. This resulted in the formation of S vacancies at the edges as indicated by the white circles (adapted from Ref. [22]).

presence of truncated hexagonal structures (Fig. 10). Such structures are somewhat different from those proposed previously based on in situ spectroscopic measurements [63]. However, it is noteworthy that the structures are in accord with recent DFT calculations [26] since these show that Co prefers to be located at the so-called S-terminated edges that are not present in the triangular MoS₂ clusters.

In order to get further information about the nature of the active sites, the sulfided nanocrystals were also treated with atomic hydrogen and this resulted in the creation of vacancies at the MoS₂ edges (Fig. 11) [22]. The observation of such sites is interesting, since it has often been assumed [63] that vacancies are the active sites for hydrodesulfurization, but no direct evidence for such sites has been given previously. In the future, it should also be possible to follow adsorption and reactions with STM and this may provide mechanistic insight. Moreover, it should also be possible to extend the studies to higher temperatures and pressures as well as to perform studies with more realistic supports. In the latter connection, Højrup Hansen et al. [21] have recently been able to record atomic-resolved STM images for Pd clusters deposited on thin Al₂O₃ films.

5. Conclusions and outlook

The studies discussed in the present article illustrate how the introduction of in situ techniques and operando studies has completely revolutionized research in heterogeneous catalysis. Over a few decades, we have seen a change from a situation where virtually no direct insight was available for the active catalysts to a situation today where a large variety of techniques may provide fundamental atomic-scale information under relevant conditions. The fact that the in situ insight can be obtained for complex heterogeneous catalyst systems under reaction conditions (i.e., operando studies) is very important since it has facilitated the establishment of direct links to the catalysis. Operando studies with simultaneous recording of catalytic activities have been especially useful in this connection.

It is noteworthy that relevant fundamental information about heterogeneous catalysts may also be gained from surface science studies of model systems. However, a clear advantage of the operando studies of heterogeneous catalysts performed during the catalysis is that possible complications associated with crossing both the “pressure gap” and the “materials gap” are eliminated [12].

In the past, it has been difficult to obtain information on the 3D structure of complex heterogeneous catalysts in the presence of reactive gases. Progress made within the last few years, has shown that such information may now be obtained by in situ HRTEM [7,13,14]. With recent improvements in resolution [14], the perspectives for performing such studies have further increased. Although such studies are performed at quite modest pressures at the present time, it is expected that in the future we will have relevant atomic

resolved real space images available for most heterogeneous catalysts. It is also likely that in situ HRTEM studies will provide new fundamental understanding into many dynamic processes of importance in catalysis. There has also been significant improvements with respect to the time resolution of many other in situ techniques. Such progress is expected to continue, and this will provide new possibilities for further understanding the dynamic behavior of catalytic processes.

Many of the examples of in situ and operando studies discussed here have shown that the structure and morphology of heterogeneous catalysts behave much more dynamically than previously anticipated. And not surprisingly, the studies do show that the dynamic changes have a direct impact on the catalysis. Thus, in order to develop kinetic models of catalytic reactions, it is in general not adequate to make the typical assumption that the total number of active sites in a reactor remains constant under different reaction conditions. Instead, it will be necessary to construct dynamic microkinetic models which take the structural changes into account [61,62]. Thus, an important goal for in situ and operando studies in the future is to provide the necessary information for the development of dynamic models for the catalysis.

It should be mentioned that despite progress in in situ methodologies, there still is a need for developing many more methods which will allow spectroscopy and other measurements to be performed under conditions of high pressure catalysis. Also, in order to establish direct links between the characterization and the catalysis, such operando studies should ideally be combined with on-line measurements of catalytic activities. However, it may be difficult to establish the direct links if the in situ cells used for the measurements do not satisfy stringent reactor criteria (Section 2).

Finally, the examples discussed here have also demonstrate that in order to fully understand catalysis, it is desirable to employ a combination of several in situ techniques and in addition to combine these studies with theoretical calculations as well as surface science experiments on model systems. In view of the rapid advancement occurring in the latter fields, multidisciplinary approaches are expected to play an increasingly important role in the future.

Acknowledgments

The author is grateful to B.S. Clausen, Nan-Yu Topsøe, J.K. Nørskov, F. Besenbacher, S. Mørup, J.A. Dumesic, P.L. Hansen, S. Helveg, J.V. Lauritsen, J.-D. Grunwaldt, J.B. Wagner, C.J.H. Jacobsen, Haldor Topsøe, E. Törnqvist, and C.V. Ovesen for fruitful discussions on the research included in this manuscript.

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