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In situ FTIR: A versatile tool for the study of industrial catalysts

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Abstract

Infrared spectroscopy is among the most widely used techniques for studies of industrial catalysts. Since many properties of catalysts depend intimately on the environment, it is important to carry out the studies under in situ conditions. The improved understanding obtained from such in situ IR characterizations has lead to developments of new and improved catalysts and catalytic processes. To illustrate the scope of applications, examples from three different industrial catalyst systems, i.e. $DeNO_x$, methanol synthesis and hydrotreating reactions, will be discussed.

Keywords: In situ FTIR; Industrial catalysts; $DeNO_x$; Methanol synthesis; Hydrotreating

1. Introduction

Among the various methods used in industrial catalysis research, infrared spectroscopy is among the most frequently used techniques. This is related to the great variety of important information this technique may provide ranging from characterization of supports and precursors to insight into the nature of adsorbed molecules and reaction intermediates. In the latter connection, it is noteworthy that due to its rather straightforward instrument configuration, it is relatively simple to carry out in situ IR studies. These IR studies have helped researchers move towards more rational design of industrial catalysts since in many cases it has been possible to establish correlations between observed IR parameters and the catalyst activity. There are many reviews and books published already on the application of FTIR and in situ IR [1–4] and many examples can be found of studies which combine in situ IR with measurements of catalytic activity [5–10]. Recently, it has been suggested to term in situ studies under operating conditions operando studies [9]. On line in situ measurements performed under steady state catalysis provide a picture of different adsorbed species and intermediates. However, it is difficult from such studies to determine which species participate in the catalysis and which species are merely spectator species. This distinction is aided by performing the in situ measurements during both steady state catalysis and transient reaction conditions [10].

Since the composition of a catalyst may depend critically on the temperature, pressure and the exact composition of the reaction environment, it is desirable to perform the in situ studies under a variety of well-defined conditions. Of special interest are the in situ online activity studies where one measures simultaneously the in situ IR spectra and the catalytic activities. The focus of the present paper is to illustrate how in situ and combined in situ IR and online reactivity studies have been applied in the author's laboratory and how the findings from these studies have contributed to catalyst and process developments. For this purpose, three industrial catalyst systems have been selected for the discussion, i.e. catalysts for $DeNO_x$, methanol synthesis and hydrotreating reactions.

2. $DeNO_x$ catalysts

The most commonly used SCR (Selective Catalytic Reduction) catalyst for the removal of NO_x from power plants by reduction with ammonia is based on vanadia/titania. The motivation of our initial studies is illustrated in Fig. 1, which shows the NO_x conversion over vanadia/titania based catalysts versus NH_3/NO_x ratio at two different space velocities. It is seen that NO_x conversions above 95% can be achieved at space velocities below 10,000 N m^3/m^3 h at NH_3/NO_x ratios ~ 1. However, the concentration of the unreacted ammonia (so-called NH_3 slip) increases significantly as NH_3/NO_x ratios approach 1. These curves show that in this region, a doubling of

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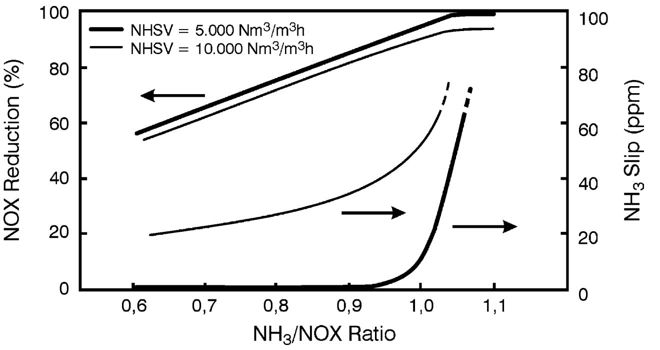


Fig. 1. NO_x conversion and NH_3 over vanadia–titania catalyst vs. NH_3/NO ratio at space velocities of 5000 and 10,000 N m^3/m^3 h (according to Ref. [11]).

the space velocity only causes a small decrease in the NO_x conversion, but the NH_3 slip is seen to increase many folds. Thus, the NH_3 slip is a very sensitive measure of the catalyst performance and in industry, the maximum allowable ammonia slip is often a decisive factor for catalyst design and also for determining the required minimum catalyst volume. In our initial studies, we found that it was impossible to model both the NO_x conversion and the NH_3 slip by traditional kinetics. The challenge was then to obtain the necessary mechanistic insight which could hopefully form the basis for the development of a satisfactory microkinetic model for the catalyst system. Several generations of such models were developed and the insight obtained from IR studies played a key role in this process. Furthermore, these results also showed that the reason that simple kinetic models did not work was related to the fact that as conditions vary, the importance of different reaction steps also changes drastically.

The first generation of microkinetic models was based on quite limited fundamental insight and it consisted of three steps as shown below. Nevertheless, it could describe the kinetic data rather well [11].

Step 1 $NH_3 + M \Leftrightarrow NH_3\text{–}M$ (fast)
Step 2 $NH_3\text{–}M + S \Leftrightarrow NH_3\text{–}S + M$ (slow)
Step 3 $NO + NH_3\text{–}S \Rightarrow$ products + S (slow)

where M represents an ammonia adsorption site and S represents a reactive site on which ammonia subsequently becomes activated. Although this simple three-step mechanism could quantitatively describe both the NO_x conversion data and the NH_3 slip behaviour, it was to a large extent a semi-empirical model since no detailed knowledge of the nature of the surface sites was available at the time. Thus, a series of detailed IR studies were subsequently carried out to obtain more information about the nature of the surface structures. Fig. 2 shows one example of the IR spectra of the titania support and the vanadia/titania catalysts with increasing vanadia loadings. These series of spectra show the OH stretching band region and the first overtone band region of V=O of vanadia/titania catalysts with increasing vanadia concentration compared to that of the titania support. The results give insight into the nature of the surface structure and show that the vanadia is highly dispersed on titania and that monolayer type structures form via interaction with Ti–OH groups on the titania support. The results also show that both V–OH and V=O species are present on the catalyst surface.

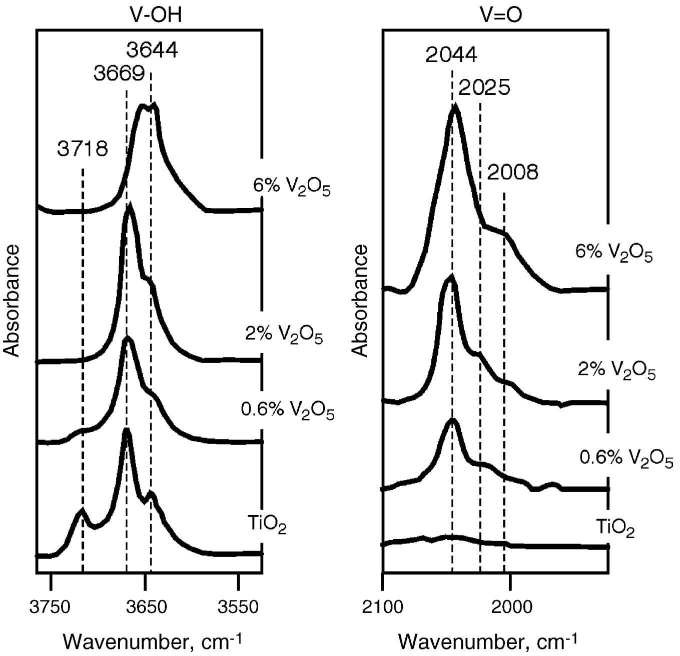


Fig. 2. IR spectra in the OH stretching region and the V=O overtone region of vanadia–titania catalysts containing 0.6, 2, and 6% V_2O_5 on TiO_2. The spectra of the TiO_2 support are included for comparison (adapted from [5]).

In order to understand the role of the different surface sites observed by IR, a series of adsorption studies of the various reactant molecules such as ammonia, nitric oxide and oxygen were carried out. It is interesting that the vanadia/titania catalyst surface itself does not contain sites capable of adsorbing one of the reactants, NO. However, the catalysts do contain strong adsorption sites for the other reactant, NH_3, and it was found that V–OH sites act as surface Brønsted acid sites capable of binding NH_3. Lewis acid sites are also present but these are mainly located on the titania support. To elucidate the importance of the different types of acid sites, the in situ IR studies were combined with on line catalyst activity measurement. A correlation between the NO_x conversion and the concentration of Brønsted acid sites was observed. On the other hand, no direct correlation was found with the concentration of Lewis acid sites (Fig. 3). Thus, these results suggest that it is the Brønsted acid sites and not the Lewis acid sites that are important for the SCR reaction.

Information about subsequent reaction steps was obtained from temperature programmed surface reaction (TPSR) studies using combined IR and on line mass spectrometry. Fig. 4 shows an example of the in situ IR results recorded during TPSR on a 6% vanadia/titania catalyst together with the corresponding mass spectrometric data [5]. The TPSR experiment was performed by pre-saturating the catalyst surface with NH_3 and subsequently exposing the surface to a flow of $NO + O_2$ while increasing temperature. This allowed one to follow the changes in the nature and concentration of the surface species as well as changes in the composition of the gas stream. This type of observation therefore provides direct information on the

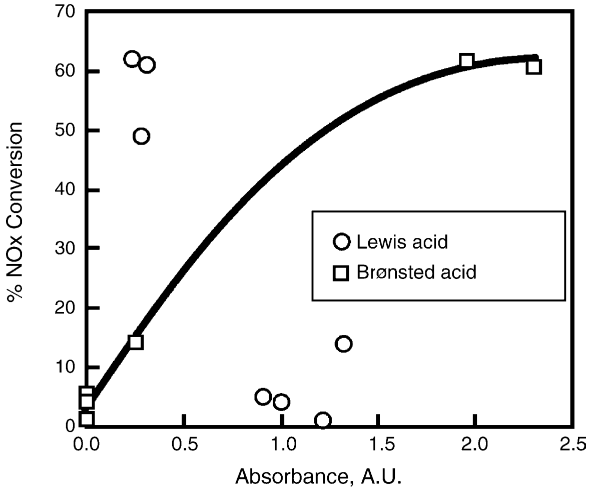


Fig. 3. Percent NO_x conversion vs. absorbance of NH_4^+ band (BA) (~1420 cm^{-1}) and band due to coordinated NH_3 (LA) (~1605 cm^{-1}).

reactions taking place on the catalyst surface. However, despite the various advantages, transient studies have some limitations in that not all surface reactions observed during transient experiments are necessarily part of a complete catalytic cycle which contributes to the overall catalysis. It should be emphasized that on line in situ measurements performed under steady state catalyst operation also have serious limitations. Such experiments can provide information on different adsorbed species and intermediates, however, they do not allow easy differentiation between active intermediates and spectator species which cover the surfaces but do not participate in catalysis. To illustrate the above complication, one could mention that the present in situ/TPSR experiments showed that the SCR reaction can occur on pure TiO_2 which otherwise shows negligible steady state activity. It can be concluded from the combined studies that the observed reaction on TiO_2 is a simple stoichiometric reaction and under steady state is not involved in an important complete catalytic cycle which contributes to the SCR reaction. Furthermore, the steady state experiments show the presence of several spectator species. It is therefore very important to combine a variety of different types of in situ online reactivity studies. Such studies lead to the formulation of the catalytic cycle for the $DeNO_x$ reaction shown in Fig. 5 (top) [6]. In support of the model, it is interesting to note that the microkinetic model could describe a large variety of industrial data satisfactorily (Fig. 5, bottom) and this has helped both catalyst selection and process optimization.

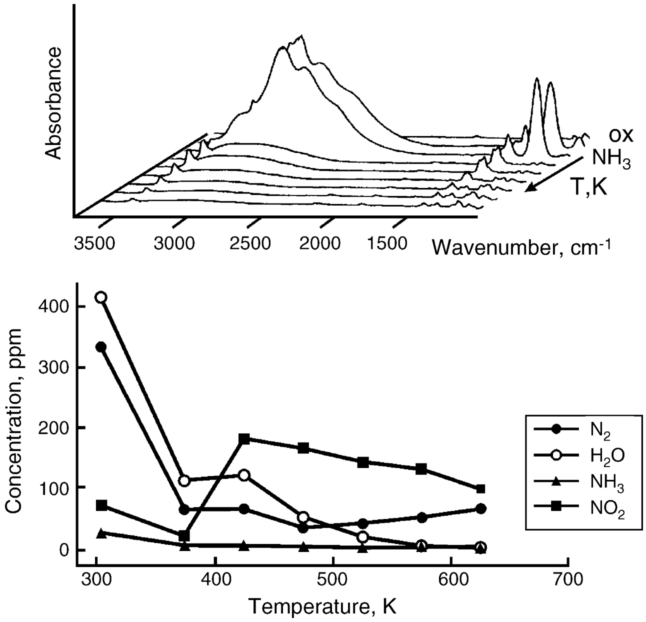


Fig. 4. (Top) In situ IR spectra of 6% V_2O_5/TiO_2 during TPSR in NO + O_2/Ar from 375 to 625 K at 50 K increments. The first and the second spectra from the back were obtained at r.t. in flowing O_2/Ar prior to adsorption and in flowing NH_3, respectively. (Bottom) Corresponding on line mass spectrometry results during the TPSR (adapted from [6]).

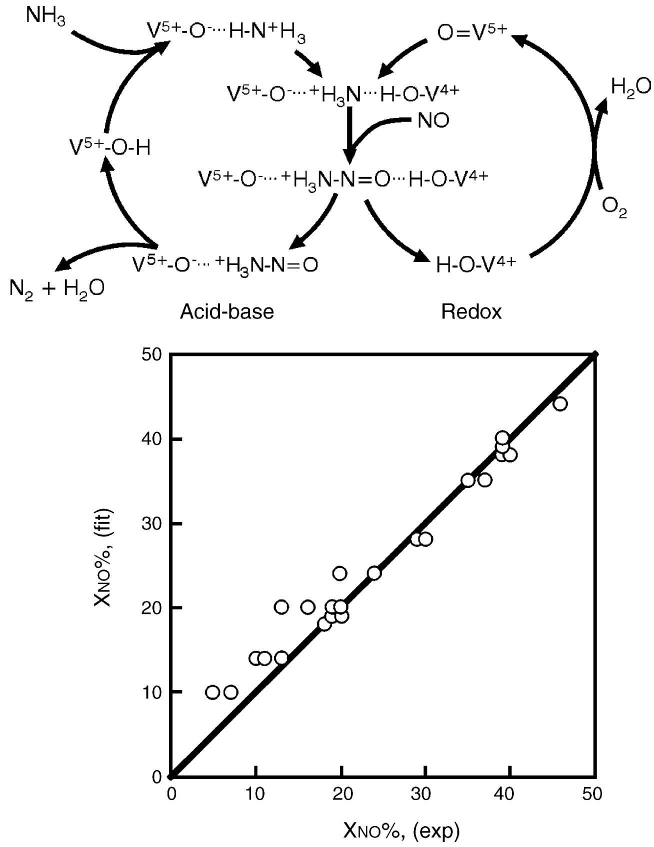


Fig. 5. (Top) Catalytic cycle for SCR reaction over vanadia–titania catalyst. (Bottom) Comparison of experimentally measured NO conversion and the calculated NO conversion based on proposed catalytic cycle (the solid line corresponds to the 1:1 correlation) (adapted from [6]).

3. Methanol synthesis catalysts

One phenomenon which has intrigued researchers involved in the study of Cu/ZnO based methanol catalysts is shown in Fig. 6. A sharp drop in methanol activity is observed when CO_2 is removed from the synthesis gas consisting of a mixture of CO, CO_2 and H_2. This in itself is not that surprising since methanol synthesis is generally believed to occur from CO_2. However, this was followed by an increase in the activity

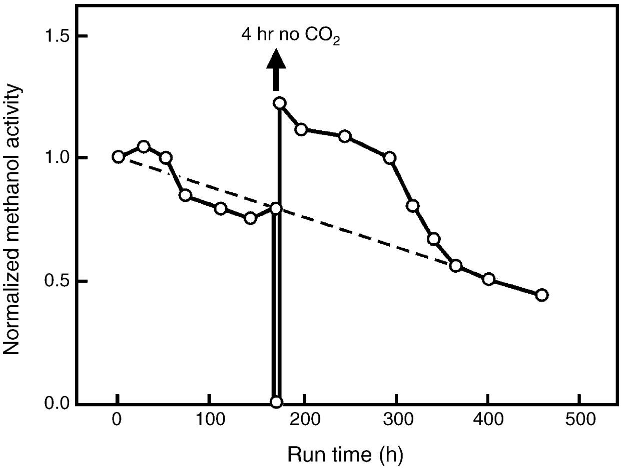


Fig. 6. Normalized methanol synthesis activity over a Cu/ZnO based catalyst as function of reaction time. CO_2 was briefly removed from the synthesis gas stream (5% CO, 5% CO_2, and 90% H_2) and added again after 4 h.

beyond the original level when CO_2 was added back again into the gas stream. After that there was a long transient period before the activity returned to the original level. Such behaviour suggests dynamic structural changes take place but the detailed nature remained unclear for a long time. EXAFS studies [12] also indicated structural changes under the different reaction conditions. The fact that similar behaviour was not observed for Cu/Al_2O_3 or Cu/SiO_2 indicates an essential role of the ZnO.

In situ IR studies of the various catalysts carried out under different reaction conditions provided detailed insight into the special changes taking place in the Cu/ZnO system. Fig. 7 shows that a large change in the IR transmittance of the ZnO occurs when the conditions are changed from an oxidizing to a reducing environment [13]. This observation can be attributed to differences in the electronic structure of ZnO. For pure ZnO and other systems, similar effects have been discussed by Taylor and Amberg [14] and Boccuzzi and Chiorino [15]. The

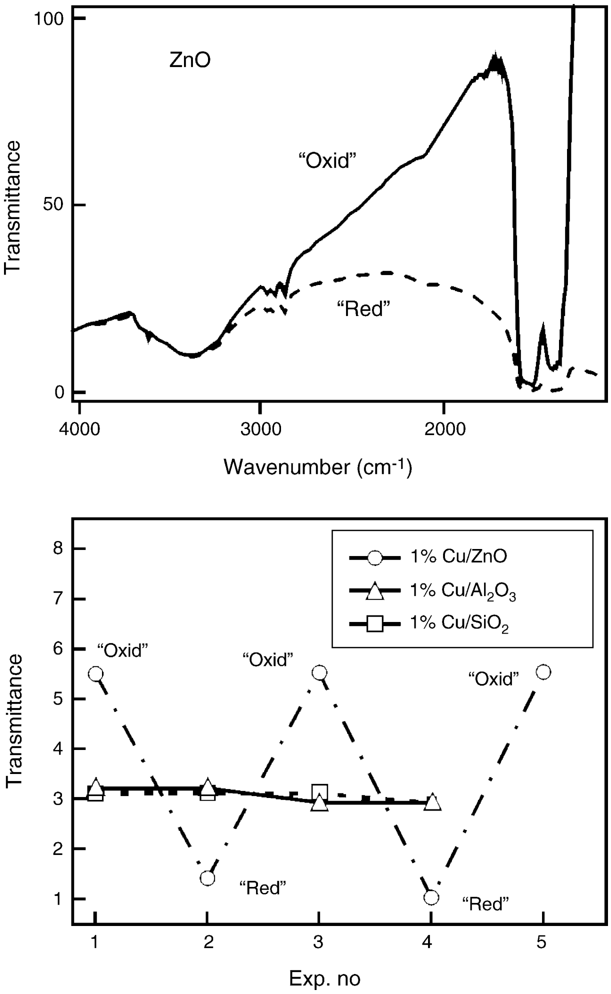


Fig. 7. The IR transmittance of ZnO after oxidation at r.t. and after reduction at 220 °C. (Bottom) The IR transmittance (measured as IR throughput in arbitrary unit) of 1% Cu supported on ZnO, Al_2O_3 and SiO_2 as function of varying oxidizing/reducing potential.

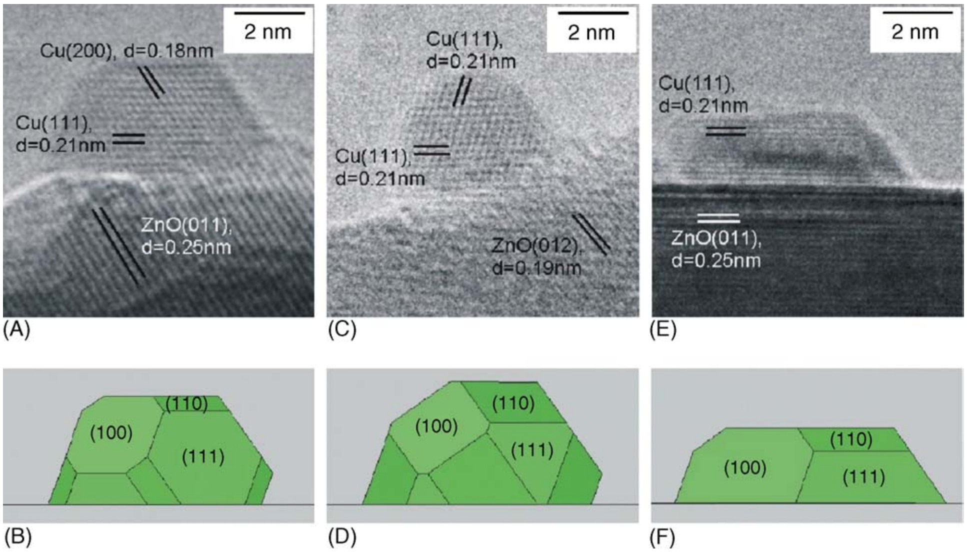


Fig. 8. In situ HRTEM images (A, C, and E) of a Cu/ZnO catalyst under various gas environments with the corresponding Wulff constructions of the Cu nanocrystals (B, D, and F). (A) was recorded under 1.5 mbar of H_2 at 220 °C. The electron beam is parallel to the [0 1 1] zone axis of Cu. (C) was recorded under 1.5 mbar of $H_2 + H_2O$ ($H_2:H_2O = 3:1$) at 220 °C. (E) was recorded in a gas mixture of H_2 (95%) and CO (5%) at a total pressure of 5 mbar at 220 °C (according to [17]).

effect was seen to be influenced by the presence of Cu indicating an importance of the Cu–ZnO interface. Furthermore, the results indicated that changes in the Cu–ZnO interface occurred depending on the redox environment. Specifically, under more reducing conditions, Cu appears to be more spread out on ZnO. Under more oxidized condition, the reverse was seen. Such phenomenon was detected only for Cu/ZnO and not for Cu/Al_2O_3 and Cu/SiO_2.This change in the Cu–ZnO interface with changing redox environment is in good agreement with results from in situ EXAFS experiments [16] on similar Cu/ZnO catalysts since these results also indicated that reversible spreading/agglomeration processes occur upon changing the reduction potential of the synthesis gas. Direct atom resolved images of the spreading/agglomeration process has recently been provided by in situ HRTEM [17] as shown in Fig. 8.

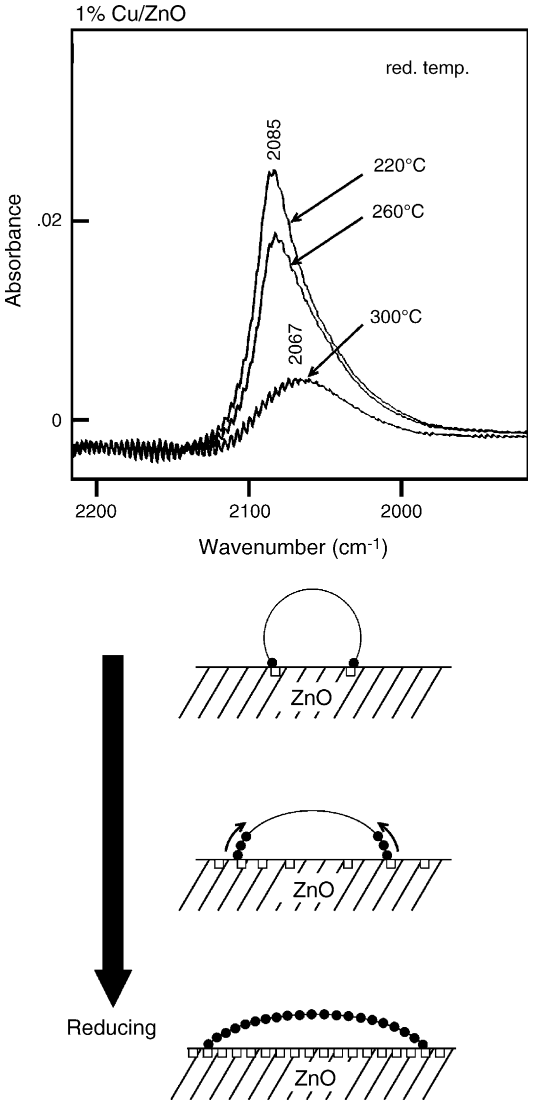


Fig. 9. IR spectra of CO adsorbed at r.t. on 1% Cu/ZnO after reduction treatment at 220 °C (top), 260 °C (middle) and 300 °C (bottom) (spectral contribution due to gas phase CO has been subtracted from all spectra). The schematic view below depicts the proposed structural changes together with the formation/destruction of Cu–Zn surface alloy.

Despite the vast structural information provided by in situ EXAFS and HRTEM, no direct information could be obtained on possible changes in surface chemistry. In order to follow this, IR studies of CO adsorption were carried out on the various catalysts as function of reduction temperature. Fig. 9 shows that the CO stretching frequency on a 1% Cu/ZnO catalyst shifts downwards from 2085 to 2067 cm^{-1} when the reduction temperature was increased from 220 to 300 °C. Such a frequency shift was not observed for Cu/Al_2O_3 under similar conditions. The results from these in situ IR studies lead to the proposal of the formation of Cu–Zn surface structures under more severe reduction conditions [18]. In agreement with the IR findings, theoretical calculations using density functional theory also showed downward frequency shift for CO on Cu(1 1 1) with ZnO adspecies, suggesting that Zn and/or ZnO species may be present on the surface of copper or at sites close to the metal–support interface under highly reducing conditions [19]. The formation/destruction of the Cu–Zn surface alloy like structures was found to be reversible and was believed to be the origin of the unique transient kinetic behaviours observed for the Cu/ZnO catalysts. Although the IR studies have provided important insight, it is clear from the above discussion that it is advantageous to employ a variety of experimental and theoretical methods to solve complex catalytic phenomena.

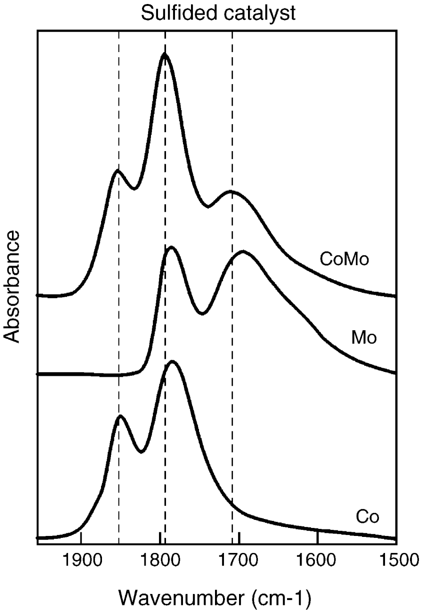
4. Hydrotreating catalysts

Hydrotreating catalysts consist generally of Mo supported on alumina promoted by either Co or Ni. Before the availability of in situ techniques, which were introduced mainly in the early 1980s, very little was known about this complex catalyst system. Thus, most catalyst developments prior to that time had to rely heavily on trial-and-error approaches. IR was one of the first in situ techniques applied to the studies of the active sulfided catalysts [20]. The first studies revealed that the active structures are present as very highly dispersed single layer molybdenum sulfide structures and subsequent studies have supplied a wealth of information on the nature of the promoter structures and the important surface sites.

By studying the IR spectra of the OH structure of the alumina support with increasing amount of Mo added, information on support interactions and the nature of Mo phases could be obtained. The gradual disappearance of the different Al–OH bands with the addition of molybdena to the alumina support indicates that Mo interacts strongly with the Al–OH groups on the alumina surface. A quantitative analysis of the different OH bands showed that there is a preferential interaction of Mo with the most basic Al–OH group which gives rise to the OH band at the highest frequency (3771 cm^{-1}). The analysis revealed that there is a strong tendency for Mo to form single-layer structures on the support surface [21]. After activation via sulfiding, the IR spectra in the OH region showed reappearance of some of the original Al–OH bands indicating that Mo–O–Al bonds are broken. Despite this, the conclusion from these results was that the monolayer coverage can be retained but the single slab Mo sulfide structures may be more randomly distributed over the Al_2O_3 surface [21]. About the same time as the early in situ IR studies, in situ EXAFS showed that the Mo structures are present as small MoS_2 clusters [22]. The presence of small single slab MoS_2 structures has also been observed by HRTEM [23] and more recently by high-angle annular dark field scanning transmission electron microscopy (HAADF-STEM) [24]. Detailed atomic resolved insight into the structure of MoS_2 nanoclusters have been obtained in the case of MoS_2/Au (1 1 1) model system by means of STM [25].

In order to gain insight into the nature of the surface sites, we found that IR studies of the adsorption of NO probe molecule can be a useful method [26,27]. Other molecules such as CO may also provide interesting information [28,29]. The results show that the adsorption exclusively takes place at the edge sites of MoS_2 [30]. Thus, measuring the amount of NO adsorbed can provide information on the number of Mo edge sites in the small MoS_2 nanocrystals. Moreover, the adsorption of NO on Mo could be easily distinguished from that on the promoter atoms (Co or Ni) as reflected by the different NO-IR band frequencies (Fig. 10, top). Such studies are therefore able to contribute to the understanding of the origin of promotion and they have been important in the development of industrial catalysts. IR studies of NO adsorption on a series of sulfided promoted catalysts with similar Mo edge dispersion are shown in Fig. 10. It is seen that Co addition results in a decrease in the number of available Mo edge atoms (Fig. 10, bottom). The results provided direct evidence that Co is atomically dispersed at the MoS_2 edges in the important Co–Mo–S type structures. These were originally observed by in situ Mössbauer emission spectroscopy [31] but the exact location could not be revealed by this technique.

The IR studies also provided understanding into the role of the promoter sites. This was obtained by comparing the in situ IR-NO adsorption results with the corresponding HDS activities. A direct correlation was observed between the activity and the number of Co_{edge} sites in the sulfided catalyst determined from in situ IR studies (Fig. 11) [30]. It is important that the IR studies were able to show that among the many types of Co species, the Co_{edge} sites were the most important ones for HDS reaction [30]. Furthermore, FTIR also revealed the existence of similar Ni–Mo–S type structures [30]. In fact, it is



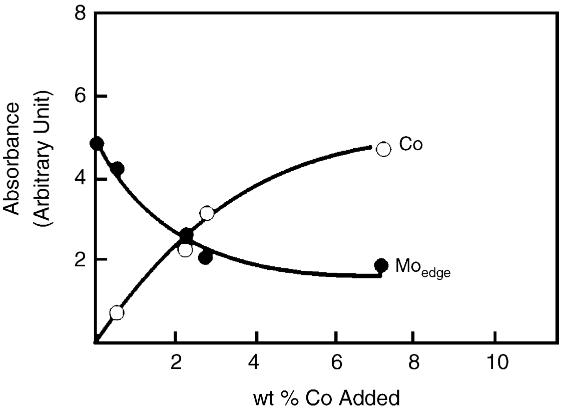


Fig. 10. (Top) IR spectra of NO adsorbed on sulfided 2% Co/Al_2O_3, 8% Mo/Al_2O_3, 2% Co and 8% Mo/Al_2O_3. (Bottom) Absorbance of IR bands of NO adsorbed on Co (1850 cm^{-1}) and Mo (1690 cm^{-1}) plotted as function of Co/Mo ratio at constant Mo loading.

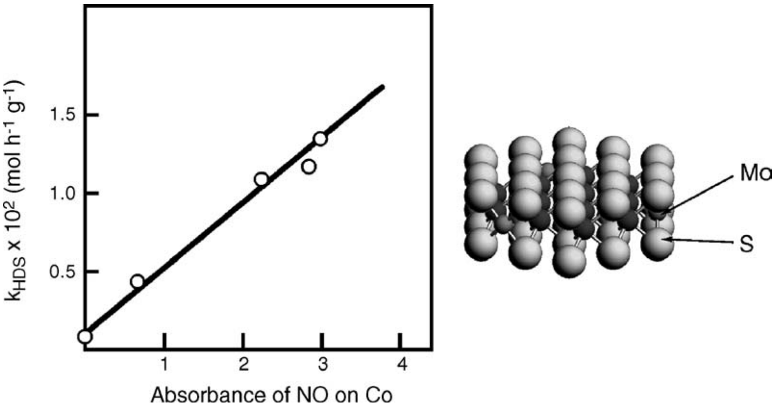


Fig. 11. Thiophene HDS activities vs. absorbance of IR band of NO adsorbed on Co. Bottom figure shows a schematic view of single slab MoS_2 structure showing the Mo edge sites.

one of the key techniques to study Ni–Mo catalysts which for example cannot be studied by Mössbauer emission spectroscopy. It is noteworthy that unlike Mössbauer emission spectroscopy which requires radioactive isotopes, FTIR studies do not require special catalyst preparations and can provide information on both fresh and used catalysts. The information on the structure–activity relationships has proven to be very important in catalyst developments.

In situ IR studies of the $CoMo/Al_2O_3$ catalysts subjected to sulfidation treatment at different temperatures have also shed some light on the nature of the active sites. For example, by comparing the changes in the surface structure upon increasing the sulfiding temperature from 673 to 873 K, we found evidence for the existence of different types of Co–Mo–S structures as well as information on the nature of these structures. Specifically, the Type II Co–Mo–S structure, which was formed at the higher sulfiding temperature, has none or very few bonds to the alumina support. This structure was found to have a significantly higher activity than the Type I Co–Mo–S structure which was formed at the lower temperatures and has some Mo–O–Al linkages between the MoS_2 and the alumina support [32]. The results further indicated that the lower activity for the Type I Co–Mo–S structure is due to the presence of Mo–O–Al linkages which decrease the tendency to form active sites (vacancies).

The above examples illustrate some of the direct impact that in situ IR has had on the understanding and development of hydrotreating catalysts. The intimate relationship of support properties and their interaction with the metal atoms and the correlation of the subsequent surface structures with catalytic activity found from these studies have contributed to our understanding of these catalysts. Numerous subsequent investigations using a variety of techniques have given additional detailed insight. For example, recently the surface OH structure and the properties of alumina have been elucidated by theoretical tools [33–35]. Also, density functional theory calculations have further explored the origin of the activity difference between the Type I and Type II MoS_2 structures and provided information on the nature of the transition between the two types of structures [36].

5. Conclusions

Among the many in situ methods available today, IR spectroscopy has been one of the most widely used techniques for the studies of catalysts. This undoubtedly is due to the vast information one can obtain with IR together with the rather straightforward and affordable experimental setups. In industrial research, it is important not only to study the structure and properties of different support materials, metal-support interaction, catalyst precursors, and aged catalyst but also to obtain information on the nature of adsorption and reactivity of the catalysts. The capability of FTIR and in situ IR, which allows one to follow adsorption and reaction on catalyst surfaces, makes it possible to examine the effect of various preparations, activation and deactivation parameters. Furthermore, it is seen that a variety of in situ on line IR studies can provide important insight into reaction mechanism and the dynamic behaviour of catalysts under different reaction environments. Such information has been valuable for the development of improved catalysts and optimized processes. It should, however, be mentioned that although IR can provide a large variety of information, it is often advantageous to combine with studies using other techniques.

References

[1] G. Ertl, H. Knözinger, J. Weitkamp (Eds.), Handbook of Heterogeneous Catalysis, VCH, Weinheim, 1997.
[2] J.W. Niemantsverdriet, Spectroscopy in Catalysis, 2nd ed., Wiley–VCH, Weinheim, 2000.
[3] J. Ryczkowski, Catal. Today. 68 (2001) 263.
[4] J.F. Haw, In situ Spectroscopy in Heterogeneous Catalysis, Wiley–VCH, Weinheim, 2002.
[5] N.-Y. Topsøe, H. Topsøe, J.A. Dumesic, J. Catal. 151 (1995) 226.
[6] N.-Y. Topsøe, J.A. Dumesic, H. Topsøe, J. Catal. 151 (1995) 241.
[7] I.A. Fischer, A.T. Bell, J. Catal. 172 (1997) 222.
[8] J.A. Lercher, V. Veefkind, K. Fajerwerg, Vib. Spectrosc. 19 (1999) 107.
[9] B.M. Weckhuysen, Chem. Commun. (2002) 97.
[10] J. Saussey, F. Thibault-Starzyk, in: B.M. Weckhuysen (Ed.), In situ Spectroscopy of Catalysis, ASP, 2004, p. 15.
[11] J.A. Dumesic, N.-Y. Topsøe, T. Slabiak, P. Morsing, B.S. Clausen, E. Törnqvist, H. Topsøe, in: Proceedings of the 10th International Congress of Catalysis, Budapest, 1993), p. 1325.
[12] B.S. Clausen, J. Schiøtz, L. Gråbæk, C.V. Ovesen, K.W. Jacobsen, J.K. Nørskov, H. Topsøe, Top. Catal. 1 (1994) 367.
[13] N.-Y. Topsøe, H. Topsøe, J. Mol. Catal. A: Chem. 141 (1999) 95.
[14] J.H. Taylor, C.H. Amberg, Can. J. Chem. 39 (1961) 535.
[15] F. Boccuzzi, A. Chiorino, J. Phys. Chem. 100 (1996) 3617.
[16] J.-D. Grunwaldt, A.M. Molenbrock, N.-Y. Topsøe, H. Topsøe, B.S. Clausen, J. Catal. 194 (2000) 452.
[17] P.L. Hansen, J.B. Wagner, S. Helveg, J.R. Rostrup-Nielsen, B.S. Clausen, H. Topsøe, Science 295 (2002) 2053.
[18] N.-Y. Topsøe, H. Topsøe, Top. Catal. 8 (1999) 267.
[19] J. Greeley, A.A. Gokhale, J. Kreuser, J.A. Dumesic, H. Topsøe, N.-Y. Topsøe, M. Mavrikakis, J. Catal. 213 (2003) 63.
[20] N.-Y. Topsøe, J. Catal. 64 (1980) 235.
[21] N.-Y. Topsøe, H. Topsøe, J. Catal. 139 (1993) 631.
[22] B.S. Clausen, H. Topsøe, R. Candia, J. Villadsen, B. Lengeler, J. Als-Nielsen, F. Christensen, J. Phys. Chem. 85 (1981) 3868.
[23] H. Topsøe, B.S. Clausen, F.E. Massoth, in: J.R. Anderson, M. Boudart (Eds.), Hydrotreating Catalysis, Science and Technology, vol. 11, Springer, Berlin, 1996.
[24] A. Carlsson, M. Brorson, H. Topsøe, J. Catal. 227 (2004) 530.
[25] S. Helveg, J.V. Lauritsen, E. Lægsgaard, I. Stensgard, B.S. Clausen, H. Topsøe, F. Besenbacher, J. Catal. 197 (2001) 1.
[26] N.-Y. Topsøe, H. Topsøe, Bull. Soc. Chim. Belg. 90 (1981) 1311.
[27] N.-Y. Topsøe, H. Topsøe, J. Catal. 75 (1982) 354.
[28] J. Bachelier, M.J. Tilliette, J.C. Duchet, D. Cornet, J. Catal. 87 (1984) 292.
[29] F. Maugé, J.C. Duchet, J.C. Lavalley, S. Houssenbay, E. Payen, J. Grimblot, Catal. Today 10 (1991) 561.
[30] N.-Y. Topsøe, H. Topsøe, J. Catal. 84 (1983) 381.
[31] H. Topsøe, B.S. Clausen, R. Candia, C. Wivel, S. Mørup, J. Catal. 68 (1981) 433.
[32] R. Candia, J. Villadsen, N.-Y. Topsøe, B.S. Clausen, H. Topsøe, Bull. Soc. Chim. Belg. 93 (1984) 763.
[33] Z. Łodziana, N.-Y. Topsøe, J.K. Nørskov, Nat. Mater. 3 (2004) 289.
[34] M. Digne, P. Sautet, P. Raybaud, P. Euzen, H. Toulhoat, J. Catal. 211 (2002) 1.
[35] M. Digne, P. Sautet, P. Raybaud, P. Euzen, H. Toulhoat, J. Catal. 226 (2004) 54.
[36] B. Hinnemann, J.K. Nørskov, H. Topsøe, J. Phys. Chem. B 109 (2005) 2245.