Snapshots of a working catalyst: possibilities and limitations of *in situ* spectroscopy in the field of heterogeneous catalysis

Bert M. Weckhuysen

Department of Inorganic Chemistry and Catalysis, Debye Institute, Utrecht University, Sorbonnelaan 16, 3508 TB Utrecht, The Netherlands. E-mail: b.m.weckhuysen@chem.uu.nl

Probing events taking place in a heterogeneous catalyst under reaction conditions has attracted a lot of attention in recent years. It requires the development of characterization techniques and the construction of *in situ* spectroscopic–reaction cells, which allow the identification of reaction intermediates and active sites in a working catalyst. The ultimate goals are the development of quantitative structure/composition–activity/ selectivity relationships and the gathering of fundamental insight in short- and/or long-term deactivation mechanisms of heterogeneous catalysts. The use of *in situ* infrared, Raman, UV–VIS, electron paramagnetic resonance, nuclear magnetic resonance, X-ray absorption and Mössbauer spectroscopy; the construction of valuable spectroscopic-reaction cells and the possibilities and limitations to monitor real time catalytic events are reviewed. Several case studies describing the use of *in situ* spectroscopy in catalysis research are discussed.

Introduction

Catalysis plays a key role in nature and society since almost every reaction requires a catalytic material.[1] Fig. 1 gives an overview of the different catalytic materials presently available.[2] Three groups of materials can be recognized: homogeneous catalysts, biocatalysts (*e.g.* enzymes) and heterogeneous catalysts. Heterogeneous catalysts are solids, which are heavily used in (petro-)chemical, pharmaceutical and environmental industries.[3] It is estimated that they are responsible for the production of more than 85% of all bulk chemicals as well as

Bert M. Weckhuysen was born in Aarschot (Belgium) in 1968. He obtained his Master's degree in chemical and agricultural engineering in 1991 from the University of Leuven (K.U. Leuven) and remained at Leuven for his PhD under the supervision of Robert A. Schoonheydt. After obtaining his PhD degree in 1995 he was a postdoctoral fellow of the Fund of Scientific Research (FWO-Flanders) with Israel E. Wachs (Lehigh University, USA), Jack H. Lunsford (Texas A&M University, USA) and Robert A. Schoonheydt (K.U. Leuven, Belgium). In 2000 he was promoted to Full Professor of Inorganic Chemistry and Catalysis at the University of Utrecht (The Netherlands). He is also a visiting professor at K.U. Leuven. His research interests are in the field of in situ spectroscopic characterization of catalytic materials, the synthesis and characterization of microporous and mesoporous molecular sieves and the molecular design of metal complexes in inorganic hosts for catalytic and sensor applications. He is author of more than 80 papers in international journals; editor of the book Spectroscopy of Transition Metal Ions on Surfaces; *and serves on the editorial board of* Vibrational Spectroscopy.
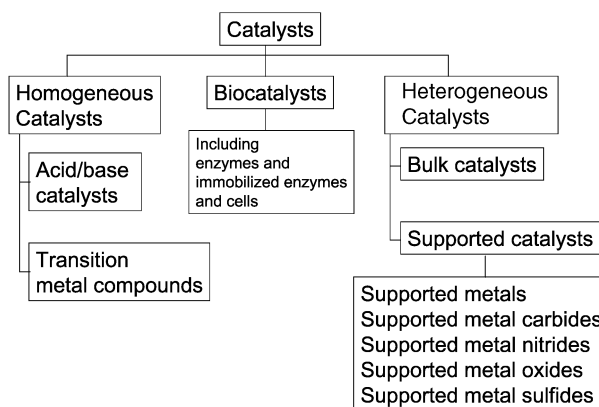
Fig. 1 Overview of the field of catalysis, including homogeneous catalysis, heterogeneous catalysis and biocatalysis.

intermediates and fine chemicals, and for the destruction of pollutants, such as NO_x and chlorinated hydrocarbons. Some important industrial heterogeneous catalysts are summarized in Table 1.[4]

Table 1 A selection of important industrial heterogeneous catalysts and their applications

Heterogeneous catalyst	Applications
V_2O_5/TiO_2	Selective oxidation of o-xylene to phthalic anhydride; selective reduction of NO_x with NH_3
CrO_3/Al_2O_3	Dehydrogenation of light alkanes
CrO_3/SiO_2	Polymerization of olefins
Re_2O_7/Al_2O_3	Metathesis of olefins
Ni/Al_2O_3	Steam reforming of methane
$CuO/ZnO/Cr_2O_3$	Synthesis of methanol
Pt/Al_2O_3	Isomerization of light gasoline
Zeolite Y; ZSM-5	Alkylation of benzene with ethylene
Zeolite Y	Fluid catalytic cracking
$K_2O/Cr_2O_3/Fe_3O_4$	Dehydrogenation of ethylbenzene to toluene

Catalysts facilitate a chemical reaction by lowering the energy barrier of the reaction pathway and thus increasing the reaction rate.[5] Monitoring the events taking place in such materials is crucial for understanding the reaction mechanisms of many important chemical processes and would allow the rational design of new or better catalytic solids. This monitoring includes the observation of reaction intermediates, the discrimination between spectator species and active sites, the quantification of unusual oxidation states and coordination environments of metal ions in catalyst materials as well as the migration and mobility of species at the catalyst surface.[6] This is the field of *in situ* spectroscopy where *in situ* refers to the study of catalytic materials at their working place under real reaction conditions;[7] *e.g.*, in a gas stream of reactants and at high

temperatures.[8] Researchers are nowadays working to develop analytical tools that allow them to follow the physicochemical processes taking place in an active catalyst in real time and under operating conditions; *i.e.*, they are using *in situ* characterization techniques to understand the working of catalyst materials.[9] Alternative but also attractive names for this discipline could be *in vivo* spectroscopy[10] or *operando* spectroscopy.[11] Because of the already wide use of *in situ* spectroscopy in the field of catalysis these alternative names will, however, not be further used in the text.

The goal of this feature article is to give an overview of the possibilities of different spectroscopic techniques nowadays available to probe the catalytic events under reaction conditions. The scope of the paper is limited to spectroscopic techniques based on the interaction of photons with catalytic solids, excluding many very valuable surface science techniques (*e.g.* XPS and Auger spectroscopy),[12] electron microscopy techniques (*e.g.* TEM and SEM) as well as diffraction techniques (*e.g.* XRD).[13] In addition, spectroscopic measurements after quenching to room temperature or to liquid-nitrogen or -helium temperature will not be included nor the use of an *in situ* transfer line to *e.g.* a high-vacuum chamber and the use of low-vacuum spectroscopic techniques (*e.g.* soft X-ray absorption spectroscopy). The main reason is that restructuring of the catalyst material during quenching, transferring to a high vacuum chamber or low vacuum experimentation often results in a solid with physicochemical properties away or far away from those of the real operating catalyst. This catalyst restructuring points towards the importance of the development of *in situ* characterization methods.

Therefore, this paper will be concentrating on: (1) the possibilities and limitations of different real *in situ* spectro-

scopic techniques; (2) the design and construction of spectroscopic-reaction cells; and (3) the quantification and detection of active sites; the discrimination between spectator species and active sites; the observation of reaction intermediates as well as the elucidation of reaction mechanisms.

The paper closes with a selected number of case studies covering different fields of heterogeneous catalysis and a short discussion on the future challenges in this exciting field of catalysis. It is important to stress that because of the breadth of this research topic this feature article cannot be seen as a review paper with a complete list of relevant references. Rather it was the intention of the author to touch on several important aspects, which should be considered when setting up in situ characterization experiments in the field of catalysis.

From conventional spectroscopy to *in situ* spectroscopy

Fig. 2 gives an overview of the lifespan of a catalytic solid starting from its genesis up to the deactivation of the catalyst material.[14] In a first step, the catalytic solid is prepared from its precursor material. An example of such preparation step is the impregnation of a porous solid (S) with an aqueous solution of a transition metal oxide (MO_x^{n+}). A whole variety of porous solids are available to the catalyst scientist and Table 2 gives an overview of frequently used catalyst supports. The next step is a heat or calcination treatment of the freshly prepared catalyst precursor material. The impregnated metal oxide will now anchor onto the porous solid through interaction with its hydroxyl groups and an MO_x^{n+}–S catalyst precursor material is formed. In a third step, the catalytic material is activated and this activation treatment often consists of a reduction treatment in
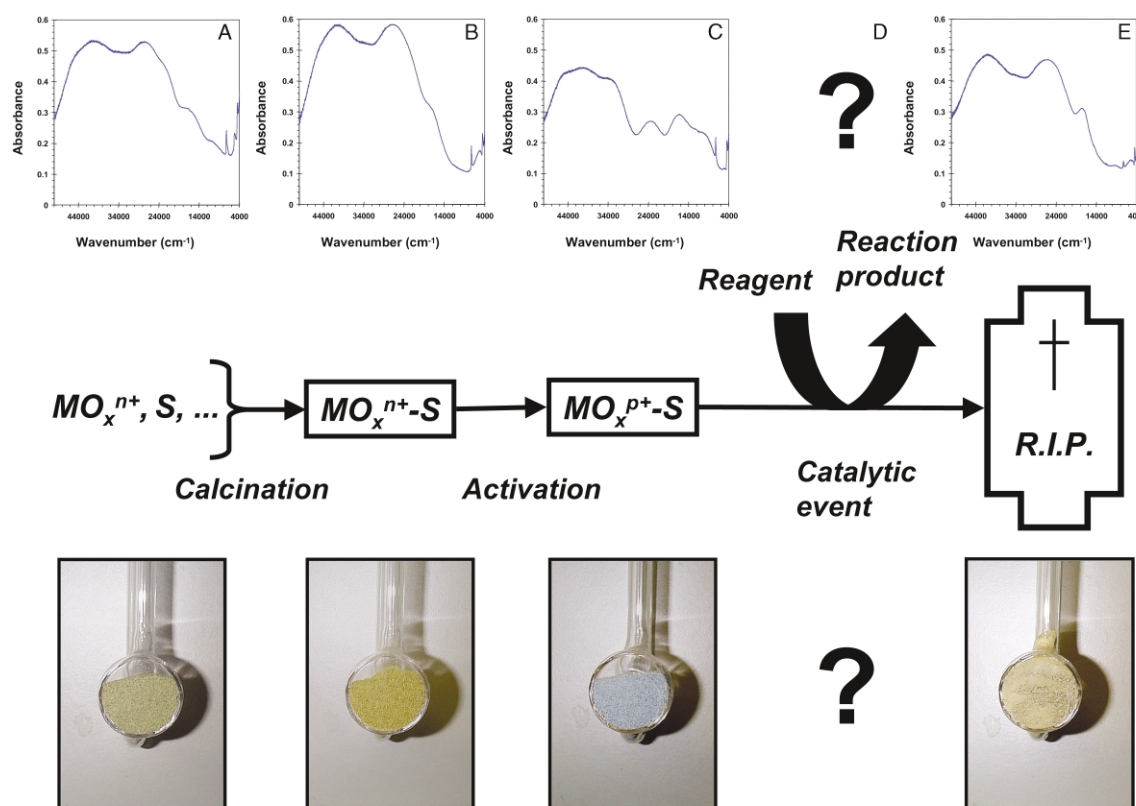
Fig. 2 The life span of a catalyst, indicating the preparation, activation, catalytic event, and deactivation process of the catalyst material. M and S are the metal ion and support, respectively. The figure also shows the UV–VIS spectra of a freshly prepared (A), calcined (B), reduced (C) and partially deactivated (E) 8 wt% CrO_3/Al_2O_3 dehydrogenation catalyst. Calcination of the catalyst was performed at 550 °C overnight, while reduction was done at 550 °C in H_2 for 1 h. Partial deactivation was induced by cycling the catalyst 20 times in a propane feed at 550 °C for 30 min followed by an oxygen treatment at the same temperature for 30 min. The unknown situation of the catalyst material in the reactor system is represented by the question marks (situation D). The bottom part of the figure shows pictures of the catalyst material placed in the spectroscopic UV–VIS cell and taken after the different treatments.

Table 2 Overview of frequently used catalyst supports for making heterogeneous catalysts

Type	Structure	Pore dimensions	Support
Amorphous			SiO_2, Al_2O_3, $SiO_2.Al_2O_3$, TiO_2, ZrO_2, MgO, La_2O_3, SnO_2, HfO_2, ZnO, CeO_2, …
Crystalline	Two-dimensional		Clay minerals, layered double hydroxides, …
	Three-dimensional	Microporous	Aluminosilicates, silicates, aluminophosphates, metallophosphates, …
		Mesoporous	Mesoporous crystalline materials, hexagonal mesoporous silica, aluminophosphates, …

which the oxidation state of the active metal oxide phase is changed (MO_x^{p+}–S with $p < n$). The obtained solid is now ready for catalytic operation and will be able to convert a specific reactant molecule to the desired reaction product (often after an initial induction period). Gradually, the catalytic solid will deactivate because of *e.g.* coke formation (short term deactivation) or a change in dispersion of the active metal oxide phase (long term deactivation). In some particular cases, this deactivated catalyst material can be regenerated.

Conventional spectroscopy focuses on the study of the fresh, calcined, reduced and deactivated catalysts measured under conventional conditions; *i.e.*, at room temperature and under hydrated and dehydrated conditions. This is illustrated in Fig. 2 by showing photographs of a fresh, calcined, reduced and partially deactivated CrO_3/Al_2O_3 alkane dehydrogenation catalyst together with the corresponding diffuse reflectance spectra in the UV–VIS–NIR region. Although interesting information can already be obtained from these spectra about the molecular structure of Cr^{6+}-species (*via* its charge transfer transitions) and Cr^{3+}-species (*via* its d–d transitions) on the surface of a porous alumina they do not provide any insight about what is going on in the catalyst material during the alkane dehydrogenation reaction. In other words, only knowing the 'before-reaction part' (hydrated, calcined and reduced catalyst) or 'after-reaction part' (partially or totally deactivated catalyst) does not provide sufficient insight in how the CrO_3/Al_2O_3 catalyst behaves in the dehydrogenation reactor itself. As was pointed out recently by Gabor Somorjai '*it is like studying a life with access only to the prenatal and postmortem states*'.[15] In order to surpass this problem researchers often measure an active catalyst after quenching the material to room temperature and transferring it

in *e.g.* a glove box in a spectroscopic cell for characterization. This methodology is often coined as 'fossilization of the catalyst material'. Although already much more relevant this approach is still not ideal because the catalyst material will restructure during cooling down and because of the absence of the reactant molecules. The only solution is then to adapt spectroscopic techniques in such a way that they are able to measure solids during catalytic action. This requires the selection of suitable spectroscopic techniques, as well as the intelligent construction of *in situ* spectroscopic-reaction cells.

This approach is illustrated in Fig. 3(A), which shows a scheme of an experimental set-up for the *in situ* UV–VIS catalyst characterization of a catalytic solid under reaction conditions in combination with *on line* activity/selectivity measurements. About 50–100 mg of the catalyst material is placed as a powder in the stainless steel reaction chamber. This chamber is equipped with a dome with spectroscopic windows and consists of three gas ports for evacuation of the chamber and/or for introducing a gas stream. The temperature near the catalyst bed can be controlled by an electronically steered heating system and circulating tap water is used for cooling the outer section of the reaction chamber. This chamber allows the study of catalysts under dynamic conditions and the gases introduced can be *on line* analyzed with gas chromatography. The reaction chamber has to be used in connection with a praying mantis diffuse reflectance attachment for a particular UV–VIS spectrometer. The catalyst activity/selectivity and molecular structure of a 0.4 wt% CrO_3/Al_2O_3 catalyst have been studied with this system for the dehydrogenation of butane at 500 °C during 1 h.[16] The scan time for measuring one UV–VIS spectrum was 1 min so 60 different UV–Vis spectra of the
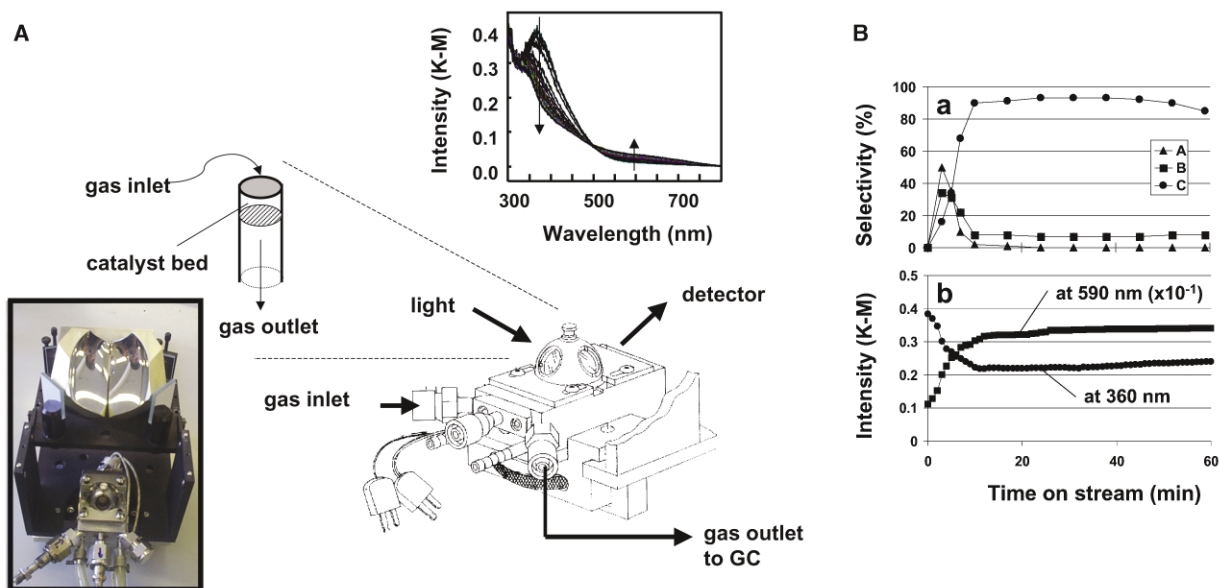

Fig. 3 (A) Illustration of the *in situ* approach for measuring UV–VIS spectra of a 0.4 wt% CrO_3/Al_2O_3 dehydrogenation catalyst in a spectroscopic–catalytic reactor with *on line* gas chromatography detection. The *in situ* UV–VIS spectra of the catalytic solid were obtained at 500 °C in a stream of 18% *n*-butane in nitrogen as a function of time on stream. (B): (a) Selectivity (%) as a function of time on stream (min) for the dehydrogenation of *n*-butane at 500 °C over a 0.4 wt% CrO_3/Al_2O_3 catalyst in the *in situ* UV–VIS cell with (A) CO/CO_2, (B) cracking products (C_1, C_2 and C_3) and (C) but-1-ene and but-2-ene; and (b) intensity profiles of the absorption maxima at 360 and 590 nm for the a 0.4 wt% CrO_3/Al_2O_3 catalyst in the *in situ* UV–VIS cell.

catalytic solid could be measured. An example of a set of UV–VIS spectra is given in Fig. 3(A) which shows a gradual decrease of the absorption maximum at around 360 nm with increasing reaction time at the expense of a new weak band with an absorption maximum at around 590 nm. An isobestic point at around 490 nm is clearly visible, suggesting the presence of two different Cr-species. The first species is typical for Cr^{6+}, whereas the broad absorption band at 590 nm is indicative for the presence of Cr^{3+}. By measuring the intensity of the absorption band at 590 and 360 nm as a function of time on stream, one can measure the amount of Cr^{6+} and Cr^{3+} in the catalytic solid during reaction. This is shown in Fig. 3(B). It is clear that the amount of Cr^{6+} gradually decreases at the expense of the formation of Cr^{3+} and that after 10 min on stream all the Cr^{6+} is reduced. These results are confirmed by the GC data, since CO and CO_2 are mainly formed during the first 10 min on stream and the production of but-1-ene and but-2-ene from *n*-butane must be associated with the formation of surface Cr^{3+}-species in the catalytic solid.

Possibilities and limitations of *in situ* spectroscopic techniques

The *in situ* spectroscopic characterization of catalytic solids is rather involved because incident photons will probe, at the same time, the gas or liquid phase in contact with the catalyst, the catalyst surface as well as the bulk catalyst material. Fig. 4 gives
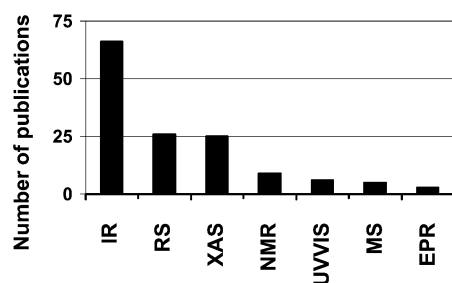
Fig. 4 Number of *in situ* publications for a specific spectroscopic technique for the year 2000 (IR, infrared spectroscopy; RS, Raman spectroscopy; XAS, X-ray absorption spectroscopy, including EXAFS–XANES; NMR, nuclear magnetic resonance; UV–VIS, electronic spectroscopy in the UV–VIS region; MS, Mössbauer spectroscopy and EPR, electron paramagnetic resonance).

an overview of the most important spectroscopic techniques used in the year 2000 for conducting *in situ* studies of catalytic solids under reaction conditions.[17] By far the most important is

infrared spectroscopy (IR),[18] while both Raman (RS)[19] and X-ray absorption spectroscopy (XAS)[20] are almost equally used in this research field. Other frequently applied spectroscopic techniques are nuclear magnetic resonance (NMR),[21] electronic spectroscopy in the UV–VIS region (UV–VIS),[22] Mössbauer spectroscopy (MS)[23] and electron paramagnetic resonance (EPR).[24] Each of these techniques has its own advantages and disadvantages and Table 3 summarizes the potentials and limitations of IR, RS, XAS, NMR, UV–VIS, MS and EPR for conducting *in situ* studies. Each technique has a specific potential for quantitatively or qualitatively probing the oxidation state, coordination environment and dispersion of supported metal oxides and metals. It is needless to say that none of the characterization techniques listed in Table 3 will be capable of providing all the information needed for complete characterization of the catalytic solid under the reaction conditions. In this respect, it is remarkable that most of the present *in situ* studies are based on one spectroscopic technique only. Thus more research efforts have to be directed to an intelligent combination of two or more spectroscopic techniques which provide complementary information about the structure of the catalyst. The combinations of EXAFS, UV–VIS and RS for gas phase catalysis with solids are under design,[25] while the combination of EPR and UV–VIS has already been used for studying the synthesis process of CoAPO-5, CrAPO-5 and VAPO-5 molecular sieves[26] and for monitoring the changes taking place in a propane dehydrogenation catalyst.[27] On the other hand, several research groups have reported the combination of a particular spectroscopic technique with a diffraction technique, *e.g.* XRD.[28]

Three other aspects concerning the selection of a specific spectroscopic technique for a catalytic problem are also of importance: (1) the mode of measuring the electromagnetic radiation absorption by the catalytic solid. Two main options are the transition mode (*e.g.* regular XAFS measurements) and fluorescence, phosphorescence, reflectance or scattering mode (*e.g.* fluorescence XAFS measurements and DRIFT spectroscopy). The mode of measurement is mainly determined by the absorption properties of the solid catalysts (*e.g.* amount of the active phase at the surface of the support).

(2) The relative sensitivity of the spectroscopic technique towards (a) the gas or liquid phase above the catalyst sample (to detect the reaction intermediates formed during catalytic operation); (b) the catalyst surface (to detect the active sites and surface intermediates during catalytic operation); and (c) the bulk catalytic solid (to detect solid-state reactions and migration processes in the catalyst material during catalytic operation.

Table 3 Selected spectroscopic techniques for *in situ* studies of catalytic solids and the obtained information about the catalyst material

Technique	Potentials				Limitations/comments
	Oxidation state	Coordination	Dispersion	Quantitative	
IR	+	+	−	+/−	Transition metal oxide vibrations are often overshadowed by the support vibrations; small molecules (*e.g.* CO) indirectly probe the coordination environment of the metal ion.
RS	+	+	+/−	−	The Raman effect is not a sensitive process and as a consequence low metal oxide loadings are difficult to study.
XAS	+	+	+/−	−	Average coordination numbers are obtained; complicated data analysis
NMR	−	+	−	+	Spectrum resolution is improved by lowering the measurement temperature; Not applicable to all nuclei and quenching problems may occur in the presence of paramagnetic metal ions.
UV–VIS	+	+	−	+	Broad and overlapping absorption bands complicate spectrum interpretation; quantitative measurements only possible at a low metal oxide loading.
MS	+	+	−	+	Spectral resolution is improved by lowering the measurement temperature; only applicable to a limited number of nuclei (most studied nucleus in catalysis is ^{57}Fe).
EPR	+	+	+/−	+	Only applicable to paramagnetic nuclei (*e.g.* V^{4+} (d^1)).

(3) Speed of measuring spectra with a good signal-to-noise ratio (S/N ratio) by a particular spectroscopic technique. This enables the detection of short-lived intermediates formed during catalytic operation. An example is the use of step-scan IR for detecting acetyl radicals in the cages of zeolites after photolysis.[29] This spectroscopic technique enables the detection of reaction intermediates at the microsecond and nanosecond timescale.[30] It is also important to stress that the detector type and the use of a specific monochromator determine how fast a spectrum can be measured. The use of a wavelength selector has the implication that each wavelength is measured after each other in such a way that recording one spectrum takes *e.g.* 1 min as is the case for the set-up shown in Fig. 3(A). If the physicochemical changes in a catalyst are taking place at a faster timescale the spectroscopic data will not be useful to study the particular catalytic process.

Finally, there is a trend towards quicker, smaller and more robust spectrometer systems.[31] This is of interest if one wants to combine different *in situ* spectroscopic techniques for elucidating the behavior of a particular catalyst in an *on line* characterization mode.

Design of spectroscopic-reaction cells

In order to obtain relevant information about the catalyst material, spectroscopic and catalytic measurements have to be done on the *same* catalyst at the *same* time under *optimal* spectroscopic and catalytic conditions. A scheme of an experimental set-up has already been shown in Fig. 3(A). The catalyst material has to be placed in a catalytic reactor, which allows measuring spectroscopic data at high temperatures in the presence of a reactant. The catalytic activity and selectivity of the catalyst material can then be obtained *via on line* gas chromatography or mass spectrometry. A crucial step in order to obtain spectroscopic and catalytic data, which can be connected with each other, is the appropriate design and construction of spectroscopic-reaction cells, also defined as *in situ* spectroscopic cells. Most laboratories have spent a lot of effort in doing so and Fig. 5 shows the design of *in situ* EXAFS cells developed in our research group at Utrecht university for transmission mode *in situ* experiments of catalytic solids.[32] More recently several companies involved in spectroscopy have also *in situ* cells on sale. In addition, some companies even use the term *in*

situ in their brand name making the word *in situ* a real buzzword in the field of catalysis.[33]

One important challenge is that the optimal conditions for performing spectroscopic and catalytic measurements are not identical and thus a compromise has to be found between both types of measurements. Generally speaking high measurement temperatures and pressures always give rise to less resolved spectra, which make their analysis more difficult.

Furthermore, finding a good compromise between spectroscopy and catalysis often implies that suboptimal catalytic performances are measured in a spectroscopic-reaction cell. For example, the *in situ* UV–VIS cell of Fig. 3(A) can reach conversions of about 10% for a given dehydrogenation CrO_3/Al_2O_3 catalyst at 550 °C, which in a catalytic reactor would give a dehydrogenation activity of more than 40% under otherwise identical conditions. The reason is that both the flow pattern and the catalyst bed temperature are not identical to values found in a catalyst bed in a real dehydrogenation reactor. Nevertheless, the *in situ* cells nowadays available enable the study of catalytic processes up to 700–1000 °C and 50–100 bar with properties often close to those of real catalytic reactors.

Based on our experience the following aspects have to be considered if one wants to construct a high quality spectroscopic-reaction cell: (1) *Catalyst temperature*: it is not uncommon that the actual temperature at the catalyst bed is lower (or higher) than indicated by a temperature read-out. This phenomenon is responsible for a lower (or higher) catalytic performance as would be expected for a real catalytic reactor. These changes in temperatures will also affect the spectroscopic data and this problem can be partially solved by a careful choice of the placement of the thermocouple near the catalyst bed. The inferior catalytic activity is also partially due to some heat loss *via* the spectroscopic window. This may result in temperature gradients over the catalyst material, which in turn will affect the spectroscopic and catalytic data. A temperature increase of the catalyst bed can also be related with the light source used for measuring spectroscopic data.

(2) *Catalyst form*: the catalyst can be placed in the *in situ* cell either as a powder, granules or as a pressed wafer. Powdered samples or catalyst granules allow measurement under flowing conditions. Such continuous operation is very similar to a fixed bed catalytic reactor and gases flow in and out through the catalyst bed. In the case of catalyst wafers, the reactant gases
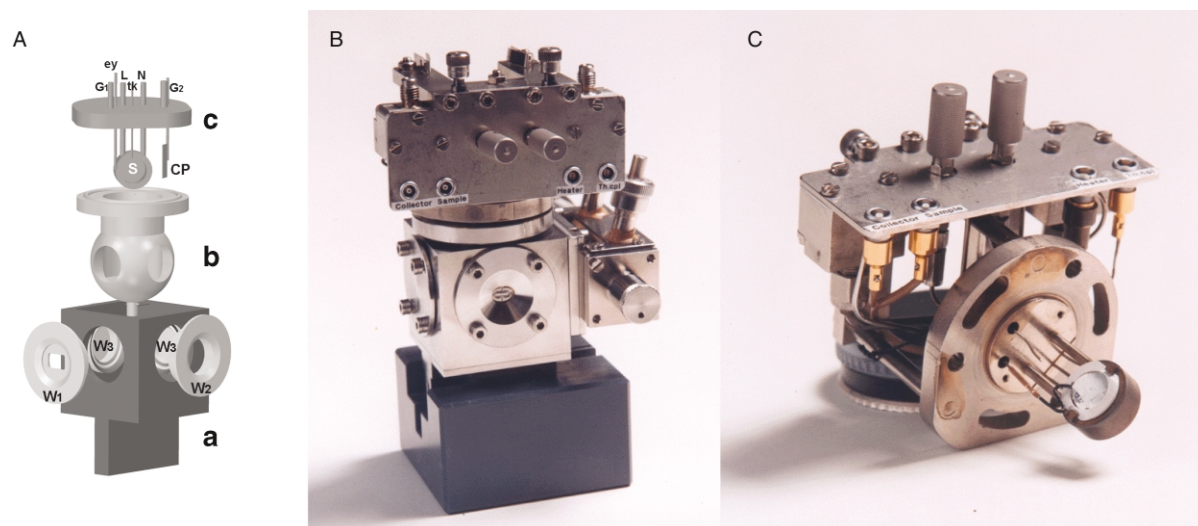
Fig. 5 (A) Schematic drawing of the *in situ* EXAFS cell: (a) stainless steel cube with window holders; (b) the reaction chamber; (c) the flange containing the sample holder and all the feedthroughs (S, sample; CP, collector plate; ey, electron yield; tk, thermocouple; L and N, coolant; G_1 and G_2, gas supply; W_1, entrance; W_2, exit and W_3, blank). (B) Illustration of the *in situ* EXAFS cell. At the front in the middle a window holder is visible with a window glued in. On the front panel the electrical connections are visible, and the gas connections are situated on the top; On the right, the integrated gas proportional counter is partly visible. (C) Illustration of part of the *in situ* EXAFS cell. The reaction chamber with the sample holder.

can only flow along the sides of the pressed wafer, and irreproducible gas stream profiles and concentration gradients may occur. This results in inferior catalytic properties.

(3) *Catalyst damage*: this is often an underestimated problem. The used light source for *in situ* spectroscopy can affect the physicochemical properties of the catalyst material. An example is the laser-induced dehydration of catalysts when applying *in situ* Raman spectroscopy. The intense laser source results in an increase of the temperature of the catalyst near the laser focus spot. UV laser radiation may even lead to coke formation during catalyst investigations. This problem can be solved by lowering the laser power, by changing the laser frequency, by using a rotating laser beam or by using an *in situ* cell with a rotating sample. Catalyst damage can also take place with synchrotron-based radiation (*e.g.* EXAFS–XANES) and a careful selection of the beamline station can (partially) solve this problem.

(4) *Catalyst activity and selectivity*: besides the intrinsic lower activity and selectivity one might also expect another activity/selectivity pattern in the *in situ* cell. This can be due to some background activity of the *in situ* cell itself (due to the presence of *e.g.* a thermocouple, metal parts, *etc.*). Another problem is that gas molecules, such as oxygen and water, may leak into the *in situ* cell, giving rise to different reaction pathways. An example of the latter could be that a total combustion process instead of a selective oxidation reaction is studied by *in situ* spectroscopy. Alternatively, reagents and reaction products may also leak out the *in situ* cell. *On line* monitoring of the reaction products formed in the *in situ* cell is therefore crucial.

(5) *Reaction cell volume*: the dead space volume of an *in situ* cell should be as small as possible in order to reduce the absorption of the gas phase which could interfere with the absorption of the active catalyst material and to avoid gaseous bypass in the cell. A small reaction cell volume is also beneficial if one wants to perform transient reaction studies. Another advantage is that isotopic labeling experiments for elucidating reaction mechanisms will become less expensive.

(6) *Spectroscopic window*: high-quality spectroscopic windows (*e.g.* high-purity quartz for UV–VIS measurements) have to be used because of the already inherent lower $S:N$ ratio of the *in situ* spectra. This is also important in the case of *in situ* EPR measurements because small impurities of Fe^{3+} within the *in situ* cell material may show up in the spectroscopic data.

(7) *Safety*: this is especially relevant for experiments at high pressures and temperatures. A safety valve could be installed in order to avoid explosion of the *in situ* cell or blow out of the spectroscopic window, while appropriate temperature isolation is a must when an *in situ* cell is under design. This is important for the safety of the scientist involved as well as to protect the spectrometer system.

Fig. 6 gives a selection of the spectroscopic-reaction cells nowadays available for performing *in situ* spectroscopic measurements during gas- and liquid-phase catalysis with inorganic solids. Most of the spectroscopic-reaction cells reported in the literature are used for studying gas phase catalytic reactions (for example the *in situ* Raman cell of Fig. 6(A)) and only a small number of *in situ* characterization studies are devoted to the study of liquid phase catalysis. The main reason is that the catalyst is dispersed in the solvent/reagent mixture making the spectroscopic analysis in such an *in situ* cell most probably more involved. An example of an *in situ* UV–VIS cell for studying liquid phase catalysis is given in Fig. 6(B). The spectroscopic-reaction cells shown in Figs. 6(A) and (B) should be used as spectroscopic attachments and placed in the optical path of a spectrometer system. A totally different design is based on the use of a reflection probe in connection with optical fiber technology or an attenuated total reflection (ATR) sensor. The former set-up is illustrated in Fig. 6(C) and allows measuring *in situ* time-resolved UV–VIS spectra of a solid catalyst in a gas-phase catalytic reaction. The latter set-up is schematically shown in Fig. 6(D) and can be used for measuring *in situ* time-resolved IR spectra in liquid phase catalysis.[34] The most important difference is that a conventional or close to conventional catalytic reactor can be used and that the spectrometer is optically connected with the reactor system. The main advantage of this methodology is that the operation of the catalyst material is much less disturbed than in the case of the more classic spectroscopic-reaction cells. Another advantage is that this set-up can be used for *on line* monitoring of a catalytic process and thus suitable for the development of an expert
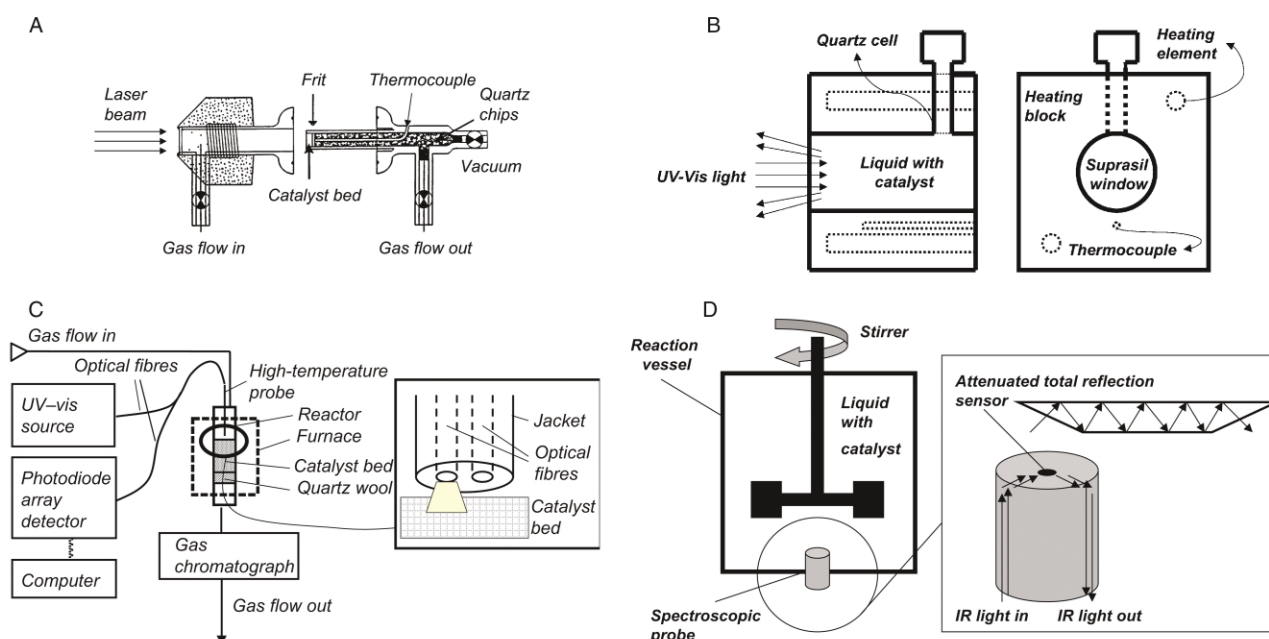
Fig. 6 (A) Schematic drawing of an *in situ* Raman cell for *on line* measurements of a catalytic solid active in a particular gas phase reaction. (B) Scheme of an *in situ* UV–VIS cell for measuring a catalytic material in a liquid phase reaction. (C) Schematic drawing of an *in situ* spectroscopic reaction set-up for measuring on line UV–VIS spectra of a solid catalyst using a high temperature probe and optical fiber technology. (D) Schematic drawing of an *in situ* spectroscopic-reaction set-up for measuring on line IR spectra of a catalyst using an attenuated total reflection sensor.

system for catalytic systems and the measuring of kinetic profiles of reagents and reaction products.

Active sites, reaction intermediates, spectator species and reaction mechanisms

Solid catalyst materials are very complex materials. Several species are simultaneously present at the catalyst surface mostly with small surface coverages. The following species can be distinguished:

Active sites; i.e., surface species, which can catalyze a chemical reaction. Each of these species may bind a molecule, giving rise to an *active site–reaction intermediate surface complex. Reaction intermediates* are mostly short-lived and therefore difficult to detect. The different active sites show a different activity and selectivity towards a molecule and a particular active site may be responsible for an unwanted side reaction resulting in byproduct formation. Because of this the concept of turnover frequency (TOF) is actually loosely defined.[35] It is also important to stress that the active sites are mostly present in low concentrations and its identification is far from easy.

Spectator species; i.e., surface species which do not actively participate in the catalytic reaction but are formed during the reaction and thus in appreciable amounts at the surface, complicating the spectroscopic analysis.

It is clear that it will be necessary to discriminate between true active sites and spectator species, which is only possible by a careful selection of a battery of complementary characterization techniques and the development of site-selective spectroscopic techniques with sufficient discriminative power.

Another important challenge in the field of catalysis is the quantification of active sites in a working catalyst. The ideal situation would be that we have a quantitative determination of each fraction of surface species on the basis of spectroscopic data only, but to the best of our knowledge this has not been possible up to now. This is mainly due to the lack of knowledge about the extinction coefficients of the unusual surface species. The extinction coefficients of such species cannot be simply found in spectroscopic textbooks nor can they be easily measured in a specific experiment. An alternative approach is based on the chemisorption of the reactant molecule that will be tested in a particular catalytic reaction followed by measuring the formed surface intermediate with a particular spectroscopy or by performing a temperature programmed desorption (TPD) step in which the amount of chemisorbed molecules is quantified. There are a few examples available in the literature on this matter. Methanol oxidation has been used for studying several supported metal oxide catalysts[36] and ethylamine was used as a probe molecule for studying the hydrodenitrogenation on sulfides and carbides.[37] It is very important in this method to choose the correct experimental conditions. For the selective oxidation of methanol to formaldehyde, the adsorption of methanol was performed in a helium flow at 100 °C. The temperature of 100 °C was chosen because this temperature is above the desorption temperature of physically adsorbed molecular methanol, at the temperature where methanol dissociatively adsorbes as surface methoxy intermediates and below the decomposition temperature of the surface methoxy intermediates.

Another important aspect associated with the presence of unusual surface species in a working catalyst is that the interpretation of the spectroscopic data in terms of active sites and spectator species is far from trivial. A solution can be given by using advanced theoretical tools for calculating experimental spectroscopic data. This requires the construction of relevant computer cluster models of a series of potential active sites. An example of such approach—although not yet done for catalyst

materials under real reaction conditions—can be found for the characterization of dehydrated Cu- and Co-exchanged zeolites in the presence and absence of probe molecules, such as H_2O and NH_3.[38] Another example can be found in the work of Haw *et al.* on the interpretation of reaction intermediates identified with *in situ* NMR techniques.[39]

There is also an obvious trend in obtaining time-resolved *in situ* spectroscopic data of an operating catalytic solid with an increasing time resolution (s, ms and even in a limited number of cases μs). However, measuring such data under steady-state conditions has the following disadvantages/limitations:

(1) Often the time-resolved spectra do not really change with time under steady-state conditions and one can even ask what the relevance is of a better time resolution (*e.g.* below ms) since only similar spectroscopic data will be accumulated. Only if you go to the time scale of bond breaking and bond formation will the time resolution become really important. This is the field of femtosecond laser spectroscopy and has been pioneered by the Nobel Prize winner A. H. Zewail. It is expected that the further application of femtosecond spectroscopy and the expected extension to attosecond spectroscopy will lead to a better understanding of catalytic phenomena in the future.[40] Presently, the most common solution is to disturb the catalyst material by instantly changing the gas composition or temperature and measuring the effect of this action on the spectroscopic data. An example of such an approach is the study of the decomposition of nitric oxide over barium oxide supported on magnesium oxide and *in situ* Raman spectroscopy revealed the presence of a barium–nitro surface intermediate under reaction conditions.[41]

(2) Very large spectroscopic datasets are obtained (typically more than 500 spectra for an experiment of 1 min with a time resolution of 100 ms) and each individual spectrum cannot be investigated one after another. The solution is here to use chemometrical techniques (*e.g.* principal component analysis (PCA)), which has the advantage that pure component spectra and their corresponding intensity profiles can be obtained for the different surface species in the catalyst material.[42]

Finally, it is important to recall that important band shifts and intensity changes occur when you are measuring solid catalysts at elevated temperatures. This is illustrated in Fig. 7 for UV–
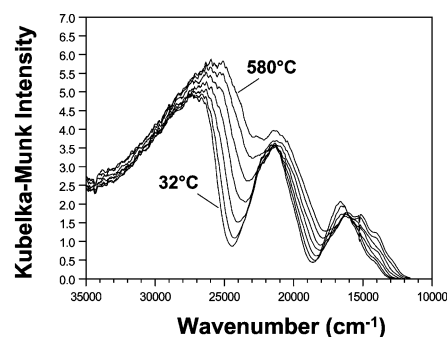

Fig. 7 Effect of the measurement temperature on the positions and intensities of absorption bands of a Cr_2O_3 catalyst in the range 32–580 °C. The spectra were measured with an *in situ* UV–VIS–NIR spectrometer.

VIS spectra of a Cr_2O_3 catalyst measured in the range 32–580 °C.[43] It is clearly seen that the main d–d transitions shift to lower energy with increasing temperature and that the band intensities also change but not in a very systematic way. Similar observations were recently made by Bell and coworkers by measuring the Raman and UV–VIS spectra of a series of catalytic solids, such as V_2O_5, WO_3, MoO_3 and Nb_2O_5, as a function of temperature.[44] For example, these authors observed that the Raman frequency of the Nb=O vibration in a Nb_2O_5 solid undergoes a red shift of about 10 cm^{-1} when heating the

solid from room temperature to 500 °C. The interpretations of these effects are less straightforward and must be associated with the changes in bond lengths of atoms in the catalytic solid, the changes in the population difference between ground and excited level and the changes in optical absorbance of the oxidic material upon heating. Other commonly observed effects are the small shifts in band positions due to the chemical interaction between reagents or reaction product and the catalyst material. An example is the influence of the presence of water on the Raman frequencies of supported metal oxide catalysts. Wachs and coworkers have investigated the effect of water vapor on the Raman frequencies of supported vanadium oxide catalysts.[45] It was shown that the Raman band of the terminal V=O bond shifts to lower wavenumbers by about 5–30 cm^{-1} and broadens upon exposure to moisture. Above 230 °C, the small Raman shift of the surface vanadium oxide species in the presence of water suggests that the surface VO_x species form a hydrogen bond with some of the adsorbed moisture. This results in a lengthening of the V=O bond and thus a red shift of the V=O vibration.

With all this knowledge on the active site and the presence of one or more reaction intermediates it should be possible in principle to propose a valid reaction mechanism, consisting of a series of elementary chemical reaction steps. This mechanism has to be validated by theoretical calculations and kinetic experiments. This requires the collaboration between physical chemists, theoreticians and reaction engineers.

Case studies

In what follows, the use of different spectroscopic techniques important for *in situ* catalyst characterization techniques, namely IR, RS, UV–VIS, EPR, NMR, XAS and MS, will be illustrated by some case studies. Each case study will focus on the application of one particular spectroscopic technique and catalytic reactions with supported metal oxide catalysts, bulk metal oxides and zeolitic materials will be discussed. Special attention is directed towards the identification of active sites and reaction intermediates as well as the development of a possible reaction mechanism or deactivation mechanism.

1. Infrared spectroscopy

V_2O_5/TiO_2 catalysts are industrially used for the selective catalytic reduction (SCR) of NO with NH_3 in power plants (Table 1). Topsoe *et al.* have investigated in a series of papers the reaction mechanism of this important reaction using *in situ* IR spectroscopy.[46] They used *in situ on line* IR to measure the changes in the concentration of surface vanadium species and some surface intermediates simultaneously with changes in SRC activity. The latter was done with *on line* mass spectrometry. Fig. 8 shows the *in situ* IR spectra obtained for 6 wt% V_2O_5/TiO_2 catalysts during SCR with 500 ppm NH_3 and 500 ppm NO in O_2, together with the NO_x conversion observed under the various conditions applied. It can be seen that the intensity of the V–OH band is the highest in the SCR mixture with 8% O_2 and the position of this band does not change appreciable when the O_2 concentration is reduced to 1%. After O_2 has been switched off, however, the V–OH band shifts progressively upward compared to the frequency observed in the presence of oxygen and a higher V–OH band frequency suggests a more reduced state of V. Besides the band shift, the width of the bands also increases, reflecting a possible distribution of V–OH sites. Under SCR conditions in the presence of O_2, three V=O bands at 2040, 2025 and 1995 cm^{-1} can be seen in Fig. 8, and these bands are due to the terminal V=O groups in different coordination environments. The intensity of the 2025 cm^{-1}
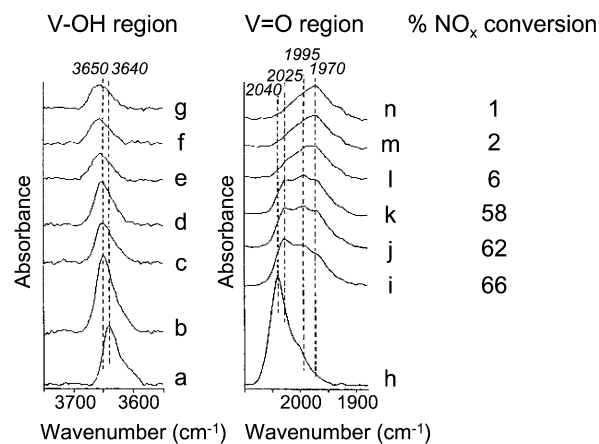
Fig. 8 *In situ* IR spectra of a 6 wt% V_2O_5/TiO_2 catalyst showing the V–OH region during the selective catalytic reduction (SCR) of NO with NH_3 in 8% O_2 (b); during the SCR reaction in 1% O_2; after switching off O_2 for 3 min (d); 30 min (e); 65 min (f); and 90 min (g). The corresponding V=O overtone regions are shown in (i)–(n). Spectra (a) and (h) show the V–OH and V=O overtone band region in the oxidized sample prior to the SCR reaction.

band decreases as the concentration of O_2 decreases from 8 to 1%. Upon removal of O_2, this band is notably missing and only the band at 1970 cm^{-1} associated with reduced vanadium species dominates. It appears from the results that the presence of the more oxidized terminal V=O groups located at 2025 cm^{-1} are important for the SCR reaction. In the absence of oxygen, these species cannot be regenerated and are not present in appreciable amounts. Under these conditions, one observes the simultaneous presence of V–OH species associated with reduced V cations. The absence of the band at 2040 cm^{-1} under SCR reaction conditions suggests that the vanadyl species associated with this band are not regenerated at a sufficiently rapid rate in O_2 to be available for the SCR reaction.

All the experimental observations reported in these studies were then used to propose a reaction mechanism for the catalytic removal of NO_x over V_2O_5/TiO_2 catalysts (Fig. 9).
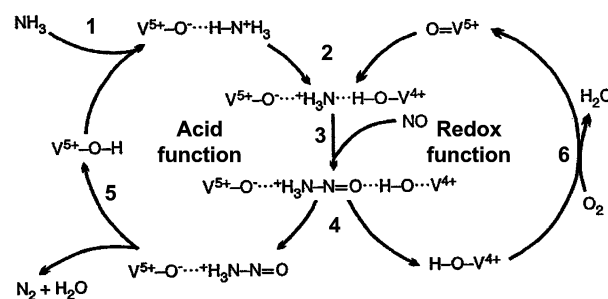
Fig. 9 Possible reaction mechanism for the selective catalytic reduction of NO with NH_3 over V_2O_5/TiO_2 catalysts.

There are two distinct catalytic functions on the V_2O_5/TiO_2 catalyst, namely an acid and redox function. The SCR reaction is initiated by the adsorption of NH_3 on a V^{5+}–OH or Brönsted acid site (step 1 in Fig. 9). The adsorbed NH_3 is then activated by the transfer of a hydrogen atom to the V^{5+}=O site, which becomes partly reduced (step 2). Gaseous, or more likely weakly adsorbed, NO subsequently reacts with this activated NH_3 (step 3). Then, V^{4+}–OH is released together with another intermediate. However, this intermediate is never been experimentally observed and undergoes rapid decomposition (step 5) to yield the reaction products, N_2 and H_2O. This results in a release of the V^{5+}–OH species. In order to complete the catalytic cycle, V^{4+}–OH must be reoxidized to V^{5+}=O. This is done in step 6 of Fig. 9.

2. Raman spectroscopy

Chlorinated hydrocarbons have widespread industrial applications, but their use is seriously restricted because of the suspected toxicity and carcinogenic properties of these molecules. Therefore, researchers are worldwide searching for clean and effective methods to destroy chlorinated hydrocarbons. One way to do this is to use basic metal oxides, which are very reactive towards *e.g.* CCl_4 at moderate reaction temperatures.[47] It has been recently shown that alkaline earth metal oxides and lanthanide oxides are very active in the destructive adsorption of chlorinated hydrocarbons and the destruction activity increases in the order: $MgO < CaO < SrO < BaO$ and $CeO_2 < La_2O_3$.[48]

In situ Raman spectroscopy has been used to monitor the physicochemical changes taking place in these solids during the destructive adsorption of CCl_4. Fig. 10 shows the *in situ* Raman
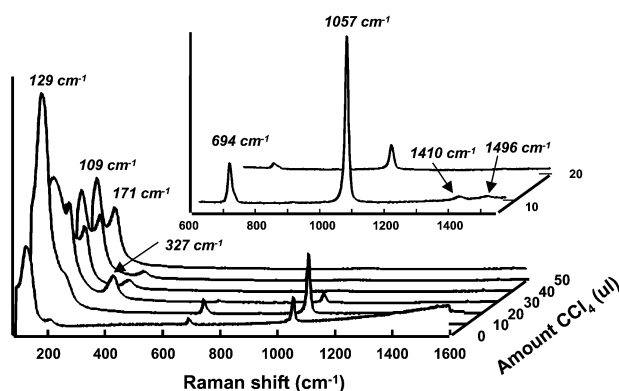
**Fig. 10** *In situ* Raman spectra of BaO during the conversion of CCl_4 to CO_2 as a function of the amount of CCl_4 dosed to the reaction system. The reaction temperature is 400 °C. The insert in the figure illustrates the formation of CO_2, which is readsorbed on the surface of the basic oxide.

spectra for the BaO solid measured at 600 °C in the presence of CCl_4. Because the sampling depth is about 0.3 μm, the state of the bulk BaO material is primarily probed. The Raman spectrum of the calcined BaO is characterized by Raman shifts at 129 and 208 cm^{-1}, which are typical of defect lattice modes. In addition, vibrations at 694 and 1057 cm^{-1} were detected, indicating the presence of surface carbonates. After injecting 10 μl of CCl_4 the amount of surface carbonates increased and two additional bands at 1410 and 1496 cm^{-1} due to monodentate surface carbonates became clearly visible. This suggests that CO_2 formed during CCl_4 destruction is readsorbed onto the metal oxide surface. Additional doses of CCl_4 resulted in an overall decrease in the amount of surface carbonates. Furthermore, new Raman bands at 109 and 171 cm^{-1} became apparent, which are due to Ba–Cl lattice modes and the formation of $BaCl_2$ was confirmed by XRD. An additional band centered at around 327 cm^{-1} was also observed, and its intensity reached a maximum after injecting 20 μl of CCl_4. This band is due to the formation of a metal oxide chloride, namely Ba_4OCl_6, which can be envisaged as a structure in which three out of four oxygen atoms are replaced by chlorine atoms. The formation of such unusual metal oxide chloride intermediate was also observed for SrO (Sr_4OCl_6 with Raman frequency at 372 cm^{-1}), CaO (Ca_4OCl_6 with Raman frequency at 398 cm^{-1}), La_2O_3 (LaOCl with Raman frequencies at 125, 188, 215, 335 and 440 cm^{-1}) and CeO_2 (CeOCl with Raman frequencies at 125, 188, 217, 321 and 469 cm^{-1}) but not for MgO. It is also important to stress that the solid reaction intermediates were not always detected and their formation depends on the reaction temperature as well as on the amount of CCl_4 added to the nitrogen stream.

The *in situ* Raman results, together with *in situ* IR and NMR results obtained on the same systems, suggest a possible reaction scheme for the destructive adsorption of CCl_4 on basic

oxides. This is shown in Fig. 11. The first step involves the physisorption of CCl_4 on the metal oxide surface. The covalent
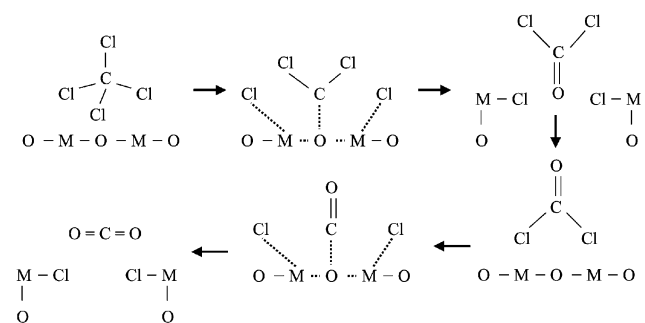

Fig. 11 Possible reaction mechanism for the destruction of CCl_4 on basic oxides, such as BaO. The formation of phosgene molecules can only be observed with *in situ* IR spectroscopy at high reaction temperatures.

C–Cl bond is then polarized/broken by the ionic M–O lattice. This step must be fast since no surface reaction intermediates could be detected by *in situ* spectroscopies. The polarization of the C–Cl bond is more pronounced on ionic surfaces. Thus, the destruction activity parallels the ionicity of the basic earth alkaline metal oxides; *i.e.*, the activity decreases in the order: $BaO > SrO > CaO > MgO$. The overall result of this process is the formation of $COCl_2$ (which could be observed with *in situ* IR of the gas phase above the solid) and a partially chlorinated MO surface, which becomes less reactive. In the second step, $COCl_2$ is readsorbed, and further reacts with the surface to form CO_2, which readsorbs onto the metal oxide surface to form a monodentate surface carbonate. Further chlorination results in the formation of a fully chlorinated material, and CO_2 is finally released into the atmosphere. This CO_2 is detected by *in situ* RS, IR and NMR. Except with MgO, metal oxide chloride phases occur as solid intermediates, whereas $COCl_2$ is a reaction intermediate.

## 3. Electronic spectroscopy

CrO_3/Al_2O_3 catalysts are known as industrial dehydrogenation catalysts for the production of propene (Table 1). Although already studied for many years their operation and long-term deactivation is not well understood. Recently, the use of *in situ* optical fiber UV–VIS diffuse reflectance spectroscopy has been used to monitor *on line* a series of CrO_3/Al_2O_3 catalysts during successive propane dehydrogenation cycles.[49] This study has been done with the reactor set-up shown in Fig. 6(C). This set-up allows to measure UV–VIS spectra in less than a second. A representative set of *in situ* UV–VIS spectra of a fresh 2 wt% CrO_3/Al_2O_3 catalyst during three catalytic cycles at 580 °C is given in Fig. 12. A catalytic cycle consists of four steps; *i.e.*, an oxygen treatment of 40 min; a helium flush of 30 min; a propane dehydrogenation treatment of 20 min and a helium flush of 30 min. The fresh CrO_3/Al_2O_3 catalyst led to a propane yield of 13%. During the oxidation treatment almost exclusively Cr^{6+} is formed in the catalytic solid as can be seen from the intense $O \rightarrow Cr^{6+}$ charge transfer transition located at around 26 000 cm^{-1}. The surface Cr^{6+} present in the fresh catalyst was readily reduced during the first 30 s of propane on stream. The surface Cr^{3+}-species formed during the initial reduction are characterized by absorption bands at 15 600 and 23 100 cm^{-1}. During the propane feed, coke was also formed on the catalyst surface as evidenced by the increasing intensity in the whole wavenumber range of the spectrum. The presence of coke can be seen in the UV–VIS spectra because polycyclic aromatic structures have wide absorption bands in this spectral region, while darkening of the sample may also increase the overall intensity of the spectra. During the following oxidative regeneration, the overall spectral intensity decreased due to
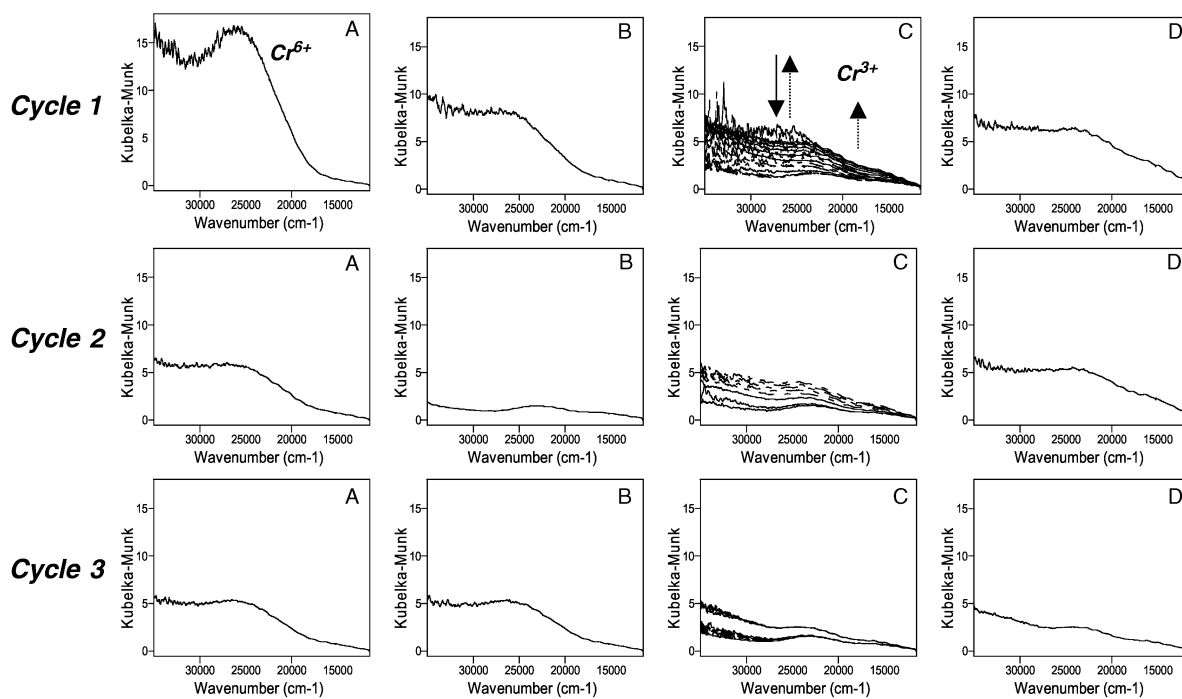
Fig. 12 *In situ* UV–VIS spectra of a working 2 wt% CrO_3/Al_2O_3 catalyst at 550 °C during three catalytic cycles. A catalytic cycle consists of four steps, namely an oxidation treatment (A), a helium flush to remove the gaseous oxygen in the reactor (B), a propane dehydrogenation treatment (C) and a helium flush to remove the gaseous propane in the reactor (D).

coke burning and the Cr^{6+}-signal reappeared. However, the Cr^{6+}-signal intensity never reached its original intensity during the 40 min oxidation suggesting that the oxidation of Cr^{3+} to Cr^{6+} seems to be a considerably slower process than reduction of Cr^{6+} to Cr^{3+}. A possible explanation could be that the Cr^{3+}-sites are stabilized at the alumina surface in octahedral vacancies, which prevents their oxidation to Cr^{6+}. Fig. 13
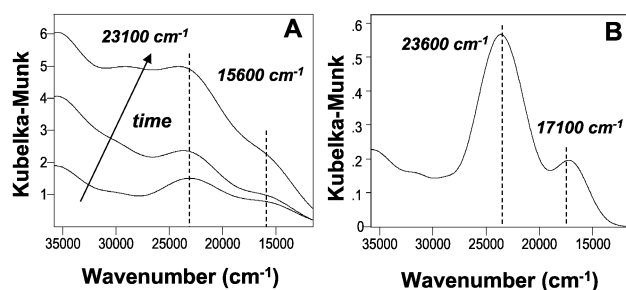
**Fig. 13** Comparison between the *in situ* UV–VIS spectra of a fresh (A) and deactivated (B) 2 wt% CrO_3/Al_2O_3 catalyst measured during the propane dehydrogenation step at 580 °C.

compares the *in situ* UV–VIS spectra of a fresh and deactivated CrO_3/Al_2O_3 catalyst measured during the dehydrogenation of propane at 580 °C. Two important differences can be noticed. First, the absorption bands of the Cr^{3+}-species present in the deactivated CrO_3/Al_2O_3 catalyst are located at 17 100 and 23 600 cm^{-1}, whereas they are at lower energy for the fresh CrO_3/Al_2O_3 catalyst. Secondly, almost no coke formation could be observed since there was no increase in the overall spectrum intensity during the propane dehydrogenation step. Fig. 13 can be used to investigate the changes that had taken place during catalyst deactivation since the positions of the absorption bands are characteristic for the coordination environment of Cr^{3+}. For UV–VIS spectra measured at room temperature, Cr^{3+} located inside an α-alumina is characterized by absorption bands at 18 150 and 24 700 cm^{-1}, whereas Cr^{3+} in Cr_2O_3 has character- istic absorption bands at 16 600 and 21 700 cm^{-1}. Taking into account the temperature effect discussed in Fig. 7, the shift in

the absorption band maxima indicates that most of the Cr^{3+}-ions present in the deactivated CrO_3/Al_2O_3 catalyst have been incorporated in the alumina phase and are thus unavailable for catalytic action. This explains the low activity (propane yield of 4%). Thus, the Cr^{3+}-species characterized by absorption bands at 15 600 and 23 000 cm^{-1} can be considered as the active dehydrogenation sites.
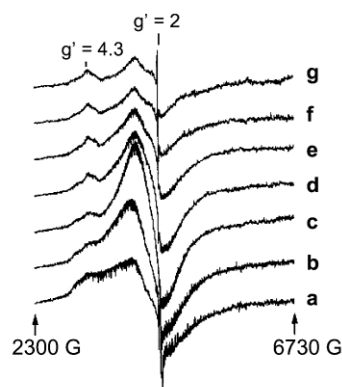
4. Electron paramagnetic resonance

An interesting catalytic reaction is the dehydroaromatization of *n*-octane over supported chromium oxide catalysts. It has been claimed that Cr^{3+}- as well as Cr^{4+}-ions are the active sites in this reaction,[50] but no further information on their particular coordination state has been given. Brückner *et al.* have used *in situ* EPR spectroscopy to study these catalytic systems and to investigate the different coordination geometries of Cr^{3+}-species present during the aromatization of *n*-octane in the active catalyst system.[51] This was made possible by using a special *in situ* EPR flow reactor with *on line* GC analysis. A schematic drawing of this *in situ* spectroscopic-reaction cell is given in Fig. 14, while a representative set of *in situ* EPR spectra obtained with this set-up is shown in Fig. 15 for a 1 wt% CrO_3/ZrO_2 catalyst. The as-synthesized catalyst after calcination contains mainly Cr^{6+} (d^0), which is EPR-inactive, besides some small amounts of Cr^{5+}- (d^1) and Cr^{3+}- (d^3) species, which are EPR-active. The characteristic γ–signal with $g_{\parallel} = 1.959$ and $g_{\perp} = 1.978$ are typical for magnetically isolated axially symmetric Cr^{5+} surface species. The two additional broad lines that are visible at $g' = 2$ and $g' = 4.3$ are assigned to magnetically interacting Cr^{3+}-ions in Cr_2O_3-like clusters (β-signal) and magnetically isolated coordinatively unsaturated Cr^{3+}-ions (δ-signal) on the zirconia surface, respectively. It was previously shown that the appearance of the δ-signal is associated with Cr^{3+}-species with very high values for the zero field parameters ($D = 0.490$ and $E = 0.163$ cm^{-1}) indicating a strong distortion of the octahedral Cr^{3+} coordination geometry.[52] Upon heating the catalyst material in a gas mixture of 0.6 mol% *n*-octane in N_2 the γ–signal immediately disappears above 260 °C, while the intensity of both the β- and δ-signals increase. This is indicative
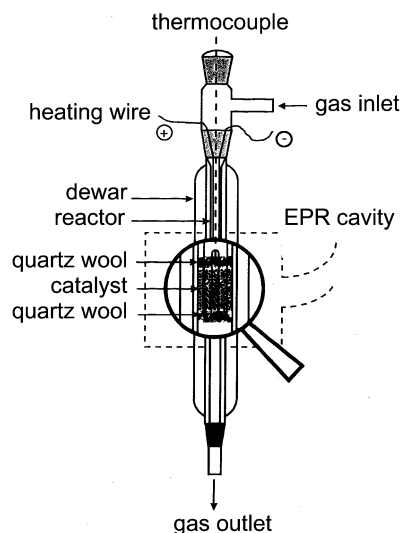
Fig. 14 Scheme of an *in situ* EPR cell for high temperature measurements of a catalytic solid and *on line* activity measurements. Granulated catalyst powder is placed in the spectroscopic-reaction cell, which is mounted in the X-band EPR cavity, and heating of the cell is possible by the electric current through a platinum wire pasted onto the reactor tube.

for the formation of Cr^{3+}-species by reduction of surface Cr^{6+}- and Cr^{5+}-species. Thus, Cr^{5+}- and Cr^{6+}-species can already be ruled out to be the active site for the dehydroaromatization of *n*-octane. The intensity of the β-signal passes through a maximum at the very beginning of the dehydroaromatization reaction as evident from the EPR spectra, while *on line* GC results indicates a gradual decrease of the catalyst activity. Thus, the intensity of the β-signal diminishes with time on stream and this phenomenon is accompanied by a deactivation of the catalyst material. The partially deactivated catalyst is black and shows a narrow EPR signal at $g' = 2.003$, which is characteristic for coke radicals. The changes in the intensity of the various EPR signals indicate that the initial reduction stage is governed by the formation of magnetically isolated Cr^{3+}-signals (δ-signal) and further reduction raises the intensity of the β-signal indicating a clustering of the Cr^{3+}-species at the surface. With increasing time on stream the intensity of the β-signal drops significantly and this must be due to some dipolar interactions between Cr^{3+} and the paramagnetic coke species. From Fig. 15 it is clear that the β-signal more rapidly decreases in intensity compared to the δ-signal. This may suggest that the coke deposition occurred preferentially at the surface of the Cr_2O_3 clusters. Thus, the remaining activity of the CrO_3/ZrO_2 catalyst after 75 min on stream at 400 °C must be due to the presence of the still accessible and active isolated Cr^{3+}-species. Summarizing, the *in*

situ EPR results indicate that the active dehydroaromatization catalyst contains exclusively Cr^{3+}-species in two distinct coordination environments, Cr_2O_3-like clusters and highly distorted, magnetically isolated Cr^{3+}-ions. Catalyst deactivation is due to covering of the active Cr^{3+}-species by coke deposition. This deactivation process is more pronounced for the Cr_2O_3-like clusters than for the magnetically isolated and highly distorted Cr^{3+}-species.
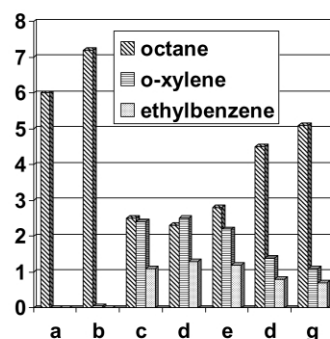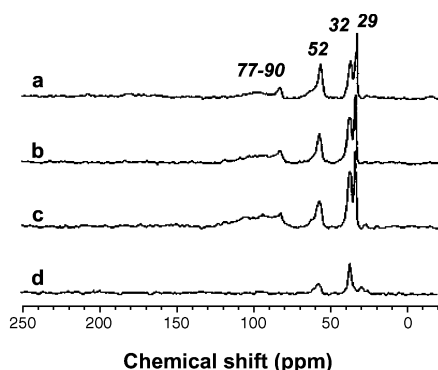
5. Nuclear magnetic resonance

Hunger and coworkers using *in situ* [13]C magic angle spinning (MAS) NMR spectroscopy have studied under flowing conditions the formation of methyl *tert*-butyl ether (MTBE) from methanol and isobutene on acidic zeolites, such as H-Y, H-Beta and H-ZSM-5.[53] Fig. 16 shows a scheme of the used
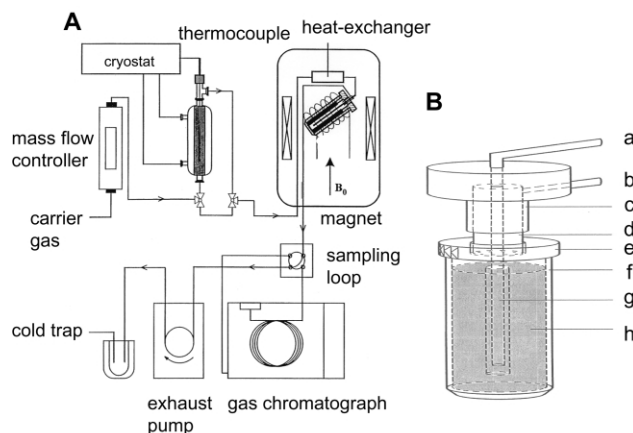
Fig. 16 (A) Set-up for *in situ* NMR spectroscopy with *on line* GC analysis and (B) *in situ* MAS NMR rotor reactor for *on line* measuring spectra of a working catalyst.

experimental set-up.[54] *On line* gas chromatography was used for analysis of the reaction products leaving the *in situ* MAS NMR rotor reactor and nitrogen gas loaded with a ^{13}C-labeled methanol/isobutene feed continuously injected in the rotor reactor. *On line* gas chromatographic investigations indicated that the steady state situation of the catalyst was reached after 1 h on stream. No deactivation was observed up to 8 h on stream. This time period of at least 6 h enabled the researchers to measure, on a continuous basis, *in situ* MAS NMR spectroscopic data of the working catalyst. Fig. 17 shows a representative set of *in situ* ^{13}C MAS NMR spectra obtained under steady state conditions for the synthesis of MTBE on calcined zeolite H-Beta. The spectra were measured at 60 °C. The NMR line at 52 ppm is due to strongly adsorbed methanol molecules, while

Fig. 15 *In situ* EPR spectra of a 1 wt% CrO_3/ZrO_2 catalyst during the catalytic reaction in a 0.6 mol% octane/N_2 mixture and *on line* GC signal areas of the product mixture (unreacted octane and formed *o*-xylene and ethylbenzene): a, $T = 300$ °C; b, $T = 350$ °C; c, $T = 400$ °C, $t = 0$ min; d, $T = 400$ °C, $t = 10$ min; e, $T = 400$ °C, $t = 20$ min; f, $T = 400$ °C, $t = 50$ min and g, $T = 400$ °C, $t = 75$ min.

Fig. 17 ^{13}C MAS NMR spectra recorded in the steady state of the synthesis of MTBE at 60 °C on a calcined H-Beta zeolite with modified residence times (W_{CAT}/F_{IB}) and molar methanol/isobutene feed ratios (n_{ME}/n_{IB}): (a) W_{CAT}/F_{IB} = 150 and n_{ME}/n_{IB} = 2; (b) W_{CAT}/F_{IB} = 150 and n_{ME}/n_{IB} = 2; (c) W_{CAT}/F_{IB} = 150 and n_{ME}/n_{IB} = 2; and (d) after purging the zeolite material with dry nitrogen.

the NMR line at 32 ppm is caused by the presence of methyl groups of isobutene oligomers and dimers. The NMR lines appearing at 29 and 77–90 ppm can be attributed to an isobutoxy species. The disappearance of these signals after purging the zeolites with dry nitrogen gas indicates the low stability of this surface alkoxy species. Comparing the GC results of the gas stream leaving the MAS NMR rotor with the formation of alkoxy species as observed by *in situ* spectroscopy indicate that its presence is a prequisite for high yields of MTBE and *vice versa*. Thus, the synthesis of MTBE with acidic zeolites requires the reaction of isobutene with a bridging OH group of the zeolite leading to the formation of an isobutoxy species with carbenium-like properties. These carbenium ions react then further with a nucleophilic methanol molecule and after deprotonation of the intermediate, MTBE is formed.

6. X-Ray absorption spectroscopy

Supported vanadium oxide catalysts are widely used for the partial oxidation of hydrocarbons (Table 1). These systems have also been studied for the oxidation of CO and *in situ* XAS has been used to investigate the state of the supported vanadium oxide catalysts after calcination, during CO oxidation and during CO reduction.[55] For this reason, a self-supporting wafer of a 17.5 wt% V_2O_5/Al_2O_3 catalyst material was mounted in a transmission mode *in situ* EXAFS cell equipped with beryllium wafers. An EXAFS cell design similar to that shown in Figs. 5(A)–(C) was used. The gas mixture consisted of 1% CO and 5% O_2 in He for the oxidation experiments, while the reduction experiments were performed in a 1% CO in He atmosphere. *On line* mass spectrometry was used to monitor the conversion levels of the V_2O_5/Al_2O_3 catalyst during CO oxidation conditions. At a temperature of 350 °C a CO conversion level of 4% was reached, while at 450 °C the CO conversion level increased to about 23%. Fig. 18(A) shows the *in situ* vanadium K-edge XAS spectra obtained after calcination, during CO oxidation at 350 °C, and during CO reduction at 350 °C. The spectrum of the calcined supported vanadium oxide catalyst is typical for vanadium in a distorted tetrahedral coordination with one short V–O bond of 1.62 Å and three longer V–O bonds of 1.82 Å (O=V–(O–S)$_3$, S = support). The spectra obtained after calcination and those obtained for the catalyst during CO oxidation at 350 °C are very similar and only minor changes in the first peaks around the absorption edge could be observed. There is also almost no difference between the *in situ* XAS spectra taken during the steady state oxidation experiment and the *in situ* XAS spectra obtained during CO reduction. Thus, under these conditions both the oxidation state and coordination environment of the supported vanadium oxide are unaltered. A
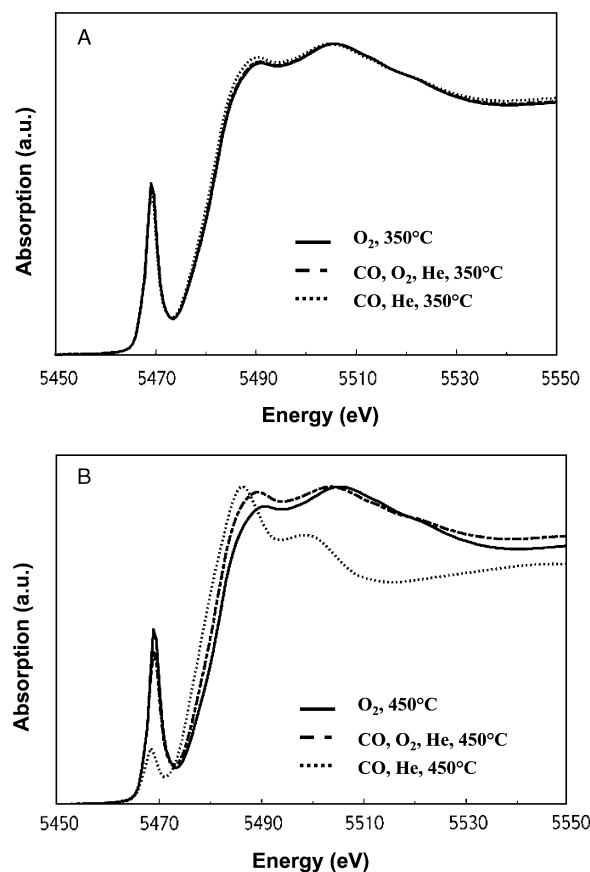
Fig. 18 (A) Vanadium K-edge spectra of a 17.5 wt% V_2O_5/Al_2O_3 catalyst after calcination, during CO oxidation and after CO reduction at 350 °C. (B) Vanadium K-edge spectra of a 17.5 wt% V_2O_5/Al_2O_3 catalyst after calcination, during CO oxidation and after CO reduction at 450 °C.

totally different situation is observed when the 17.5 wt% V_2O_5/Al_2O_3 catalyst is studied at higher temperatures, namely 450 °C. The corresponding *in situ* XAS spectra are shown in Fig. 18(B). It was noticed that the first scans of the catalyst material under these reaction conditions are clearly different from those obtained after calcination. Furthermore, switching off the oxygen turned out to have an even more substantial effect on both the pre-edge as well as on the absorption edge of the XAS spectra and both edges shifted to lower energies. This implies that the molecular structure of the supported vanadium oxides must have changed drastically under the CO oxidation and CO reduction conditions. Indeed, as was confirmed by temperature programmed reduction (TPR) studies a reduction has taken place from V^{5+} to V^{3+}. The V^{3+}-species formed during these CO treatments at 450 °C can be envisaged as a supported vanadium oxide characterized by three V–O bonds with a distance of 1.97 Å and three V–O bonds with a distance of 2.10 Å. Thus, V^{3+}-species in distorted octahedral coordination are observed under steady-state CO oxidation conditions at 450 °C in a V_2O_5/Al_2O_3 catalyst.

7. Mössbauer spectroscopy

In situ Mössbauer spectroscopy has been mainly used in the catalysis literature for studying the state of iron in Fisher–Tropsch catalysts and selective oxidation catalysts, such as $Fe_xCo_{1-x}MoO_4$–$Bi_2(MoO_4)_3$ bulk mixtures. The example which we will discuss focuses on the latter systems and *in situ* MS has been used to study the evolution of iron in iron and cobalt molybdate catalysts ($Fe_xCo_{1-x}MoO_4$) and their mixtures with $Bi_2(MoO_4)_3$.[56] These catalysts are used for the selective oxidation of propene to acrolein. Vedrine and coworkers[56] have

studied the $Fe_xCo_{1-x}MoO_4$–$Bi_2(MoO_4)_3$ system under flowing conditions in a mixture of propene, oxygen and nitrogen in the temperature range between 360 and 415 °C. It was shown that ferrous molybdate ($FeMoO_4$) was progressively oxidized to ferric molybdate and ferric oxide. *In situ* MS was also able to explain the catalytic properties of the $Fe_xCo_{1-x}MoO_4$ system. The catalytic results show that: (1) ferric, ferrous and cobaltous molybdates are poor catalysts for the partial oxidation of propene to acrolein; (2) solid solutions of $Fe_xCo_{1-x}MoO_4$ are neither very active nor selective for this selective oxidation reaction; (3) the addition of $Bi_2(MoO_4)_3$ to the $Fe_xCo_{1-x}MoO_4$ matrices increases the catalyst selectivity and activity to acrolein to a great extent.

In situ MS showed that the Fe^{2+}-sites in the $Fe_xCo_{1-x}MoO_4$ system could not be oxidized to a great extent and the $CoMoO_4$ system seems even to protect Fe^{2+}-species against oxidation. In other words, cobalt ions act as inhibitors for the oxidation of Fe^{2+} in the molybdate lattice. On the other hand, $Bi_2(MoO_4)_3$ stabilized the Fe^{3+}-sites and a good correlation was observed between the catalytic properties and the presence of Fe^{3+}-species stabilized by $Bi_2(MoO_4)_3$. Thus, the simultaneous presence of $CoMoO_4$ and $Bi_2(MoO_4)_3$ leads to the conservation of a Fe^{2+}–Fe^{3+} pair in the $Fe_xCo_{1-x}MoO_4$ system. This Fe^{2+}–Fe^{3+} pair appears to be essential in the catalytic oxidation mechanism. Bi^{n+}–Co^{m+} are proposed as the adsorption sites for propene molecules, while Fe^{2+}–Fe^{3+} pairs ensure the high electrical conductivity favouring the electron exchange in the Mars-Van Krevelen oxidation mechanism.

Conclusions and future directions

The development and rigorous use of *in situ* spectroscopic techniques to study the catalytic solid under real working conditions inside the reactor results in fundamental knowledge about the catalytic process in terms of active site, reaction intermediates and reaction mechanism. This knowledge can then be used to develop relevant structure–activity relationships and to gather insight in the deactivation processes of heterogeneous catalysts. This approach is heavily needed if researchers want to move away from the classical trial-and-error approach for the design of new or improved catalytic systems. In other words, *in situ* spectroscopic studies deliver the tools necessary to gather information for the *a priori* design of heterogeneous catalysts. On the other hand, *in situ* spectroscopy of heterogeneous catalytic systems have also changed the way researchers envisage catalytic materials. Heterogeneous catalysts are indeed very dynamic solids and small changes in the reaction environment may result in tremendous changes in the molecular structure of the catalyst material. Thus, *in situ on line* characterization techniques are a must for all future investigations on catalytic systems.

The main challenges in this exciting field of heterogeneous catalysis are:

(a) The further development of time-resolved spectroscopy.

(b) The need for more advanced theoretical tools for spectrum interpretation.

(c) The combination of several complementary spectroscopic techniques in one experiment in order to compare the characterization results obtained under reaction conditions.

(d) The combination of spectroscopy and microscopy in order to conduct *in situ* three-dimensional characterization studies. One way to realize this could be the development of 3D TEM-EELS spectroscopy.

(e) The further development of site-selective spectroscopic techniques. An example of such approach is the recent development of site selective XAS spectroscopy.[57,58]

(f) The development of expert systems for *on line* control of catalytic systems in a chemical reactor.

Finally, it should also be clear that the described methodologies in this paper can also be applied to study *e.g.* chemical reactions in solutions, to understand how inorganic compounds can dissolve and react in liquids and to elucidate how solid compounds react with each other. Thus, *in situ* spectrosopy will be very important in the future to understand chemical processes in other areas as well.

Notes and references

1 *Handbook of Heterogeneous Catalysis*, ed. G. Ertl, H. Knözinger and J. Weitkamp, Wiley-VCH, Weinheim, 1997; J. M. Thomas and W. J. Thomas, *Principles and Practice of Heterogeneous Catalysis*, VCH, Weinheim, 1997.

2 B. M. Weckhuysen and I. E. Wachs, in *Handbook of Surfaces and Interfaces of Materials*, ed. H. S. Nalwa, Academic Press, San Diego, CA, 2001,vol. 1, p. 613.

3 J. M. Thomas and R. Raja, *Chem. Commun.*, 2001, 675.

4 J. Hagen, *Industrial Catalysis, A practical Approach*, Wiley-VCH, Weinheim, 1999; H. F. Rase, *Handbook of Commercial Catalysts*, CRC Press, New York, 2000.

5 *Catalysis from A to Z, A concise encyclopedia*, ed. B. Cornils, W. A. Herrmann, R. Schlögl and C. H. Wong, Wiley-VCH, Weinheim, 2000.

6 J. W. Niemantsverdriet, *Spectroscopy in Catalysis, An Introduction*, VCH, Weinheim, 1993; *Spectroscopy of Transition Metal Ions on Surfaces*, ed. B. M.Weckhuysen, P. Van Der Voort and G. Catana, Leuven University Press, Leuven, 2000.

7 Latin word for at its place; the opposite word is *ex situ* and most of the past work on catalyst characterization was done in this way.

8 B. M. Weckhuysen, P. Van Der Voort and G. Catana, in *Spectroscopy of Transition Metal Ions on Surfaces*, ed. B. M. Weckhuysen, P. Van Der Voort and G. Catana, Leuven University Press, Leuven, 2000; B. M. Weckhuysen and R. A. Schoonheydt, *Rev. Roum. Chim.*, 1999, **44**, 1047.

9 G. J. Hutchings, A. Desmartinchomel, R. Olier and J. C. Volta, *Nature*, 1994, **368**, 41; J. M. Thomas, *Angew. Chem., Int. Ed.*, 1999, **38**, 3589; J. M. Thomas, *Chem. Eur. J.*, 1997, **3**, 1557; H. Topsoe, *Stud. Surf. Sci. Catal.*, 2000, **130**, 1; B. S. Clausen, H. Topsoe and R. Frahm, *Adv. Catal.*, 1998, **42**, 315; M. Hunger and J. Weitkamp, *Angew. Chem., Int. Ed.*, 2001, **40**, 2954.

10 In analogy with medical sciences one could envisage catalysts as living materials because of their dynamic nature in a reaction environment. This name has been proposed as an alternative for *in situ* spectroscopy by Israel E. Wachs during an informal discussion.

11 From the Latin *gerund*, which means operating or working. This name has been proposed as an alternative for *in situ* spectroscopy by Miguel Banares during a lively discussion between Eric Gaigneaux, Gerhard Mestl, Bert Weckhuysen and Miguel Banares at the 220th ACS National Meeting in Washington, DC (August 2000). *Operando* spectroscopy is the shortened version of spectra of an *operando* or a working catalyst.

12 G. A. Somorjai, *Catal. Tech.*, 1999, **3**, 84.

13 For a more general overview of the field we refer to two special issues of *Topics in Catalysis* (*Top. Catal.*, 1999, **8**, 1–140 and *Top. Catal.*, 2001, **15**, 1–82) devoted to catalyst characterization under reaction conditions and *in situ* characterization of catalytically active surfaces, respectively. The first issue is a collection of papers originating from a special symposium at the ACS National Meeting in Dallas (USA) in 1998, while the latter issue is a collection of characterization papers presented at the Eurocat IV Congress in Rimini (Italy) in 1999.

14 D. M. Hercules, A. Proctor and M. Houalla, *Acc. Chem. Res.*, 1994, **27**, 387.

15 M. Jacoby, *Chem. Eng. News*, 1998, **May 4**, 41.

16 B. M. Weckhuysen, A. Bensalem and R. A. Schoonheydt, *J. Chem. Soc., Faraday Trans.*, 1998, **94**, 2011.

17 This literature analysis is based on a Chemical Abstract search in the period 1967–2000 with the keywords catalyst/catalysis/catalytic and *in situ* characterization/investigation. It is anticipated that not all papers on *in situ* characterization of catalytic systems were found with this search and thus the given numbers have to be seen as estimations. Figure 4 shows the trend for the year 2000, but similar plots can be made for earlier years. This literature search also shows the evolution of the number of *in situ* spectroscopy papers in the catalysis literature. Starting from the year 1990 the use of *in situ* spectroscopy became really important in the field of catalysis as it is still today. The number of research papers is expected to increase above 200 for the year 2001.

18 For example: J. A. Lercher, V. Veefkind and K. Vajerwerg, *Vib. Spectrosc.*, 1999, **19**, 107; I. A. Fisher and A. T. Bell, *J. Catal.*, 1998, **178**, 153; G. Spoto, F. Geobaldo, S. Bordiga, C. Lamberti C, D. Scarano and A. Zecchina, *Top. Catal.*, 1999, **8**, 279; V. A. Matyshak and O. V. Krylov, *Catal. Today*, 1995, **25**, 1.

19 For example: G. Mestl, *J. Mol. Catal. A: Chem.*, 2000, **158**, 45; H. Knözinger and G. Mestl, *Top. Catal.*, 1999, **8**, 45; I. E. Wachs, *Top. Catal.*, 1999, **8**, 57; H. Knözinger, *Catal. Today*, 1996, **32**, 71; W. M. Zhang and S. T. Oyama, *J. Phys. Chem.*, 1996, **100**, 10759; M. A. Banares, M. Martinez-Huerta, X. Gao, I. E. Wachs and J. L. G. Fierro, *Stud. Surf. Sci. Catal.*, 2000, **130**, 3125; M. A. Banares, J. H. Cardoso, F. Agullo-Rueda, J. M. Correa-Bueno and J. L. G. Fierro, *Catal. Lett.*, 2000, **64**, 191.

20 A special issue of *Topics in Catalysis* (*Top. Catal.*, 2000, **10**, 141) was devoted to the role of XAFS spectroscopy in the field of catalysis and edited by D. C. Koningsberger and B. L. Mojet.

21 For example: M. Hunger, M. Seiler and T. Horvath, *Catal. Lett.*, 1999, **103**, 2385; J. F. Haw, *Top. Catal.*, 1999, **8**, 81; J. F. Haw, P. W. Goguen, T. Xu, T. W. Skloss, W. G. Song and Z. K. Wang, *Angew. Chem. Int. Ed.*, 1998, **37**, 948; T. Horvath, M. Seiler and M. Hunger, *Appl. Catal. A: Gen*, 2000, **193**, 227; M. Hunger, U. Schenk, M. Seiler and J. Weitkamp, *J. Mol. Catal. A: Chem.*, 2000, **156**, 153; M. Seiler, U. Schenk and M. Hunger, *Catal. Lett.*, 1999, **62**, 139.

22 For example: B. M. Weckhuysen, A. A. Verberckmoes, J. Debaere, K. Ooms, I. Langhans and R. A. Schoonheydt, *J. Mol. Catal. A: Chem.*, 2000, **151**, 115; B. M. Weckhuysen and R. A. Schoonheydt, *Catal. Today*, 1999, **49**, 441; B. M. Weckhuysen, A. Bensalem and R. A. Schoonheydt, *J. Chem. Soc., Faraday Trans.*, 1998, **94**, 2011; M. A. Banares, M. C. Martinez-Huera, X. Gao, J. L. G. Fierro and I. E. Wachs, *Catal. Today*, 2000, **61**, 295.

23 For example: J. W. Niemantsverdriet and W. N. Delgass, *Top. Catal.*, 1999, **8**, 133.

24 For example: U. Bentrup, A. Brückner, A. Martin and B. Lucke, *J. Mol. Catal. A. Chem.*, 2000, **162**, 383; A. Brückner, J. Radnik, D. L. Hoang and H. Lieske, *Catal. Lett.*, 1999, **60**, 183; A. Brückner, B. Kubias and B. Lucke, *Catal. Today*, 1996, **32**, 215; A. Brückner, A. Martin, N. Steinfeldt, G. U. Wolf and B. Lucke, *J. Chem. Soc., Faraday Trans.*, 1996, **92**, 4257.

25 An experimental set-up is currently under design at Utrecht University.

26 B. M. Weckhuysen, D. Baetens and R. A. Schoonheydt, *Angew. Chem., Int. Ed.*, 2000, **39**, 3419.

27 A. Brückner, *Chem. Commun.*, 2001, 2122.

28 M. Epple, G. Sankar and J. M. Thomas, *Chem. Mater.*, 1997, **9**, 3127; G. Sankar and J. M. Thomas, *Top. Catal.*, 1999, **8**, 1; T. Ressler, R. E. Jentoft, J. Wienold and O. Timpe, *J. Synchrotron Radiat.*, 2001, **8**, 683.

29 S. Vasenkov and H. Frei, *J. Am. Chem. Soc.*, 1998, **120**, 4031.

30 H. Sun and H. Frei, *J. Phys. Chem. B*, 1997, **101**, 205; S. Vasenkov and H. Frei, *J. Phys. Chem. A*, 2000, **104**, 4327.

31 B. J. Kip, T. Berghmans, P. Palmen, A. van der Pol, M. Huys, H. Hartwig, M. Scheepers and Dietrich Wienke, *Vibr. Spectrosc.*, 2000, **24**, 75.

32 A. M. J. van der Eerden, J. A. van Bokhoven, A. D. Smith and D. C. Koningsberger, *Rev. Sci. Instrum.*, 2000, **71**, 3260.

33 The word *in situ* is also sometimes misused and a number of *in situ* papers in the literature contain results, which can hardly be seen as real *in situ* studies. In addition, the word *in situ* is used in connection with a specific handling and examples are *in situ* regeneration and *in situ* activation. All this could be reason to launch a new name for this field

as suggested above. The advantage would be a clear distinction between *in situ* spectroscopic studies of a working catalyst and other *in situ* studies.

34 J. E. Rekoske and M. A. Barteau, *Ind. Eng. Chem. Res.*, 1995, **34**, 2931; R. LeBlond, J. Wang, R. Larsen, C. Orella and Y. K. Sun, *Top. Catal.*, 1998, **5**, 149.

35 TOF is defined as the number of reagent molecules reacted over the number of active sites per second.

36 L. E. Briand and I. E. Wachs, *Stud. Surf. Sci. Catal.*, 2000, **130**, 305.

37 V. Schwartz, V. Teixeira da Silva and S. T. Oyama, *J. Mol. Catal. A: Chem.*, 2000, **163**, 251.

38 K. Pierloot, A. Delabie, M. H. Groothaert and R. A. Schoonheydt, *Phys. Chem. Chem. Phys.*, 2001, **3**, 2174; A. Delabie, K. Pierloot, M. H. Groothaert, B. M. Weckhuysen and R. A. Schoonheydt, *Microporous Mesoporous Mater.*, 2000, **37**, 209; K. Pierloot, A. Delabie, C. Ribbing, A. A. Verberckmoes and R. A. Schoonheydt, *J. Phys. Chem. B*, 1998, **102**, 10789.

39 J. F. Haw, J. H. Zhang, K. Shimizu, T. N. Venkatraman, D. P. Luigi, W. G. Song, D. H. Barich and J. B Nicholas, *J. Am. Chem. Soc.*, 2000, **122**, 12561; D. H. Barich, J. B. Nicholas, T. Xu and J. F. Haw, *J. Am. Chem. Soc.*, 1998, **120**, 12342; J. F. Haw and T. Xu, *Adv. Catal.*, 1998, **42**, 115.

40 For example: J. S. Baskin and A. H. Zewail, *J. Chem. Educ.*, 2001, **78**, 737.

41 S. B. Xie, G. Mestl, M. P. Rosynek and J. H. Lunsford, *J. Am. Chem. Soc.*, 1997, **119**, 10 186.

42 B. M. Weckhuysen, A. A. Verberckmoes, A. R. DeBaets and R. A. Schoonheydt, *J. Catal.*, 1997, **166**, 160; B. M. Weckhuysen, A. Bensalem and R. A. Schoonheydt, *J. Chem. Soc. Faraday Trans.*, 1998, **94**, 2011; F. Thibault-Starzyk, A. Vimont, C. Fernandez and J. P. Gilson, *Chem. Commun.*, 2000, 1003.

43 R. L. Puurunen and B. M. Weckhuysen, unpublished results.

44 S. B. Xie, E. Iglesia and A. T. Bell, *J. Phys. Chem. B*, 2001, **105**, 5144.

45 J. M. Jehng, G. Deo, B. M. Weckhuysen and I. E. Wachs, *J. Mol. Catal. A: Chem.*, 1996, **110**, 41.

46 N. Y. Topsoe, *Science*, 1994, **265**, 1217; N. Y. Topsoe, H. Topsoe and J. A. Dumesic, *J. Catal.*, 1995, **151**, 226; N. Y. Topsoe, J. A. Dumesic and H. Topsoe, *J. Catal.*, 1995, **151**, 241.

47 It is important to note that this cannot be regarded as a heterogeneous catalytic process and this destruction method denoted 'destructive adsorption' should be envisaged as a surface-initiated dechlorination reaction, which results in a partial or complete conversion of the metal oxide to the corresponding metal chloride.

48 B. M. Weckhuysen, G. Mestl, M. P. Rosynek, T. R. Krawietz, J. F. Haw and J. H. Lunsford, *J. Phys. Chem. B*, 1998, **102**, 3773; B. M. Weckhuysen, M. P. Rosynek and J. H. Lunsford, *Chem. Phys. Phys. Chem.*, 1999, **1**, 3157.

49 R. L. Puurunen, B. G. Beheydt and B. M. Weckhuysen, *J. Catal.*, 2001, **204**, 253; R. L. Puurunen and B. M. Weckhuysen, *J. Catal.*, submitted for publication.

50 A. Cimino, D. Cordischi, S. De Rossi, G. Ferraris, D. Gazzoli, V. Indovina, M. Occhiuzzi and M. Valigi, *J. Catal.*, 1991, **127**, 761; K. Arata, M. Hino and H. Matsuhashi, *Appl. Catal. A: Gen.*, 1993, **100**, 19.

51 A. Bruckner, J. Radnik, D. L. Hoang and H. Lieske, *Catal. Lett.*, 1999, **60**, 183; A. Brückner, in *Spectroscopy of Transition Metal Ions on Surfaces*, ed. B. M. Weckhuysen, P. Van Der Voort and G. Catana, Leuven University Press, 2000, p. 69.

52 B. M. Weckhuysen, R. A. Schoonheydt, F. E. Mabbs and D. Collison, *J. Chem. Soc., Faraday Trans.*, 1996, **92**, 2431.

53 T. Horvath, M. Seiler and M. Hunger, *Appl. Catal. A: Gen.*, 2000, **193**, 227; M. Hunger, T. Horvath and J. Weitkamp, *Microporous Mesoporous Mater.*, 1998, **22**, 357.

54 M. Hunger, M. Seiler and T. Horvath, *Catal. Lett.*, 1999, **57**, 199.

55 Matthijs Ruitenbeek, *Characterisation of vanadium-based oxidation catalysts*, PhD Thesis, Utrecht University, The Netherlands, 1999.

56 B. Benaichouba, P. Bussiere and J. C. Vedrine, *Appl. Catal. A: Gen.*, 1995, **130**, 31.

57 F. M. F. de Groot, A. Battiston, J. H. Bitter, J. A. van Bokhoven, A. van der Eerden, M. Garriga-Oostenbrink, J. de Graaf, E. Kassapidou, S. Lemaux, M. Oudenhuijzen, T. Ros and D. C. Koningsberger, *Debye Institute Annual Report*, Utrecht University, 1999, p. 1.

58 F. M. F. de Groot, *Top. Catal.*, 2000, **10**, 179.