N.C.

Monitoring transition metal ions (TMI) in oxide catalysts during (re)action: the power of *operando* EPR[†]

A. Brückner*

Institut für Angewandte Chemie Berlin-Adlershof e.V., R.-Willstätter-Str. 12, D-12489, Berlin, Germany. E-mail: brueckner@aca-berlin.de

Received 23rd May 2003, Accepted 20th August 2003 First published as an Advance Article on the web 5th September 2003

Tailoring the properties of transition metal oxide catalysts so as to provide optimum performance for the desired reaction is a major goal in catalysis research that can only be reached by deep understanding of structure-reactivity relationships of active sites. *Operando* EPR is a versatile tool for that purpose since it provides simultaneous information on valence state, coordination geometry and electronic interactions of paramagnetic TMI in relation to activity and selectivity of the catalysts. This is demonstrated by illustrative examples comprising the action of different TMI: (i) structure and function of V ions in vanadia-based catalysts used for the oxidative dehydrogenation of propane to propene (ODP) and the selective oxidation of toluene to benzaldehyde; (ii) activity and stability of Cr sites in supported chromium oxides during dehydrogenation of propane; (iii) structure and function of Mn ions in MnO_x storage catalysts for selective catalytic reduction of NO_x. Benefits arising from combined operando EPR/UV-vis/on-line GC studies are also shown. This combination provides an excellent opportunity to monitor the reaction-dependent interconversion of diamagnetic and paramagnetic TMI.

1. Introduction

Transition metal oxides are of outstanding importance as constituents of catalysts used in heterogeneous catalytic redox processes such as partial oxidation and hydrogenation/dehydrogenation of hydrocarbons. They are applied in high diversity, *e.g.*, as unsupported crystalline pure and mixed oxide phases or in amorphous form supported on different carriers. Activity, selectivity and stability of such catalysts depend sensitively on the properties of the catalytically active transition metal ions (TMI), *e.g.*, on their valence state, coordination geometry and dispersion. Tailoring those properties so as to provide optimum performance for the desired reaction is a major goal in catalysis research that can only be reached by a deep understanding of structure–reactivity relationships of active sites.

Electron paramagnetic resonance (EPR) is a unique tool for analyzing structural and electronic peculiarities of paramagnetic TMI¹⁻⁹ since it provides simultaneous information on valence state, coordination geometry and electronic interactions of TMI between each other and with reactant molecules and with the support. While the valence state of TMI determines the total spin which must be different from zero for EPR detection, differences in the coordination geometry are sensitively reflected by intrinsic interactions of the electron spin with the orbital momentum (g-tensor), as well as with the spin of the nucleus (A-tensor) and, if present, with other electrons in the same atom (D-tensor). Thus, it is possible to distinguish between V^{4+} species supported on different positions of diamagnetic oxides such as Al_2O_3 ,¹⁰ WO₃/TiO₂ and TiO₂¹¹ or zeolites,¹² since anchoring of VO_x species on support surfaces leads to distortions of their local geometry. The above described splittings are not resolved in EPR spectra of closely neighbouring TMI due to spin-spin dipolar and/or exchange

† Presented at the International Congress on Operando Spectroscopy, Lunteren, The Netherlands, March 2–6, 2003. interactions and details of the local geometry are not accessible. However, it will be shown below that in those cases information about the interaction of TMI with each other and with reactant molecules can be obtained by evaluating the line shape and intensity of the EPR signals.

Fortunately, EPR can be applied under true operating conditions, *i.e.*, at elevated temperatures, under reactant gas flow and by using flow cells the geometry of which does not differ much from conventional catalytic fixed-bed microreactors used in lab scale.^{9,13} The outlet of such EPR reactors can be connected to a product analysis device (gas chromatograph or mass spectrometer). Thus, it is possible to follow the behaviour of active sites in catalysts simultaneously together with the catalytic performance in the same experiment. For those types of investigations the term "*operando* spectroscopy" has been recently introduced,^{14–16} to distinguish from "*in situ* spectroscopy" which is commonly used in a broader sense not necessarily implying product analysis and sometimes performed under conditions quite far away from those of the catalytic reaction.

Despite the above described benefits, *in situ* and *operando* EPR investigations of TMI are still being performed by a few research groups only. Most important examples comprise the behaviour of

• unsupported VPO catalysts during selective oxidation 17,18 and ammoxidation $^{18-20}$ of *n*-butane and toluene,

 \bullet supported vanadia catalysts during oxidation of ${\rm SO_2}^{21,22}$ and oxidative dehydrogenation of propane, 23,24

 \bullet supported molybdena-based catalysts during propylene oxidation 25 and oxidative dehydrogenation of methanol, 26

• supported chromium oxides during aromatization of octane²⁷ and dehydrogenation of propane,²⁸

• TMI such as Fe,²⁹ Mn,³⁰ Cu^{31–33} in molecular sieve matrices during interaction with gas phase molecules such as O_2 , H_2 , H_2O , NH_3 , NO and hydrocarbons.

Besides, there are numerous examples in which TMIcontaining catalysts were pretreated with certain gaseous

Phys. Chem. Chem. Phys., 2003, 5, 4461–4472 4461

reactants at elevated temperatures but the EPR spectra were recorded after cooling to room or lower temperatures (*e.g.* refs. 6 and 34). Although those experiments provide valuable information about persisting changes of the respective TMI, they do not fulfill the condition of *in situ* EPR and, less than ever, of *operando* EPR. Therefore, they are not subject of this paper.

Another group of important *in situ* EPR studies comprises the detection of hydrocarbon and oxygen radical intermediates formed upon contact of hydrocarbon reactants with oxide surfaces.^{35–38} However, these systems do not contain TMI and are, therefore, not considered in this paper.

The reason for the limited activities in operando EPR may be due to two aspects: On the one hand, the opportunities of this technique seem to be still not adequately recognized. Thus, it is frequently stated that useful information can only be obtained from non-interacting isolated paramagnetic species (a situation which is hardly realized in real transition metal oxide catalysts) while paramagnetic bulk phases frequently present in those materials are poorly suitable for EPR detection due to strong magnetic interactions between paramagnetic centres giving rise to line broadening.³⁹ It will be demonstrated below that it is just this property which can be exploited to learn more about catalyst-reactant interactions in paramagnetic bulk phases and clusters of TMI. On the other hand it is true, that operando EPR at elevated temperatures is restricted to the detection of paramagnetic TMI with sufficiently long relaxation times and does not see diamagnetic TMI in high oxidation states (e.g. V^{5+} , Cr^{6+} , Mo^{6+}) which, however, may play an important role in the catalytic cycle. It will be shown below that this drawback can be beneficially circumvented by simultaneously coupling EPR and UV-vis diffuse reflectance spectroscopy (DRS).

It is the aim of this paper to demonstrate the benefits that can be drawn from operando and in situ EPR studies for elucidating structure-reactivity relationships in heterogeneous catalytic gas-phase reactions performed over transition metal oxide catalysts. A short section presenting suitable experimental setup is followed by selected examples in which the information potential as well as limits of the application of operando EPR are illustrated. These comprise the action of different TMI: (i) structure and function of V ions in vanadiabased catalysts used for the oxidative dehydrogenation of propane to propene (ODP) and the selective oxidation of toluene to benzaldehyde; (ii) activity and stability of Cr sites in supported chromium oxides during dehydrogenation of propane; (iii) structure and function of Mn ions in MnO_x storage catalysts for selective catalytic reduction of NO_x . Benefits arising from coupled operando EPR/UV-vis/on-line GC studies are also shown. This novel combination provides an excellent opportunity to monitor the reaction-dependent interconversion of paramagnetic and diamagnetic TMI and, thus, widens the variety of spectroscopically accessible species.

2. Experimental

The vast majority of heterogeneous catalytic reactions that use transition metal oxide catalysts, proceed at elevated temperatures. To follow these processes by *in situ* EPR spectroscopy, suitable reaction cells have to be implemented into the EPR cavity that can be heated and connected to some equipment for dosing reactant mixtures and analyzing product compositions. Different experimental solutions being restricted to X-band continuous wave EPR have been recently reviewed.^{9,40,41} In some cases, commercially available variable-temperature control units (*e.g.* Wilmad Glass Co.) or high-temperature cavities (*e.g.*, Bruker) equipped with some specially designed home-made flow tubes have been used to which heat is transferred by a pre-heated stream of inert gas.⁹ Temperature

control with these devices is done by automatic tuning of the heater current and the gas flow velocity implying that a certain time is required to adjust the desired temperature value. This should be kept in mind when measuring catalyst samples that undergo fast temperature-dependent changes.

The experiments described in this paper were performed by an ELEXSYS 500-10/12 c.w. spectrometer (Bruker) in X-band using a home-made fixed-bed quartz reactor heated by a bifilar winding of 0.2 mm Pt wire (Fig. 1). This principle was first described in the late 1950s for the investigation of carbon radical species during pyrolysis of carbonaceous materials^{42,43} and has later been adapted also for the study of heterogeneous cat-alytic reactions.^{38,44} The heatable reaction tube (i.d. 3 mm) was placed by ground joints into an evacuated quartz Dewar for protecting the EPR cavity from high temperatures. The temperature was controlled using an Eurotherm 902-904 temperature programmer and a Pt/Rh thermocouple. The reactant gas flow was mixed by a gas/liquid dosing system containing mass flow controllers (Bronckhorst) and thermostated saturators. For on-line product analysis in the case of propane dehydrogenation, the reactor outlet was connected to a GC 17AAF capillary gas chromatograph (Shimadzu) equipped with a FID and a 30 m \times 0.32 mm Silicaplot column (Chrompack). In the case of toluene oxidation, product analysis was performed off line after collecting the products in a cold trap filled with ethanol using a 25 m \times 0.25 mm SE-54-CB column.

For simultaneous recording of UV-vis reflectance spectra during oxidative and non-oxidative dehydrogenation of propane, a fibre optics AVS-PC-2000 plug-in spectrometer (Avantes) equipped with a CCD array detector responsive from 200 to 1100 nm was used. The two channels of the spectrometer (master: 200-500 nm; slave: 500-1100 nm) as well as a DH-2000 deuterium-halogen light source were connected to a cylindrical quartz sensor (Optran WF, length 200 mm, diameter 1.5 mm) by fibre optic cables (length 2 m) consisting of a core of pure silica (diameter 0.4 mm) coated with polyimide. The sensor fits into the reactor through a Teflon sealing disk which is fixed by a screwing at the top end of the reaction tube. The tip of the sensor is a plane polished surface. It is placed within the catalyst bed. The feed-through of the thermocouple at the bottom end of the reaction tube is realized in the same way (Fig. 1).



Fig. 1 Experimental set-up for simultaneous *operando* EPR/UV-vis/ on-line GC measurements consisting of a fixed-bed flow reactor heated with a bifilar winding of Pt wire and an implemented UV-vis fibre optic sensor.

3. Application examples

3.1. Structure and function of V ions in vanadia-based selective oxidation catalysts

Selective oxidation of toluene to benzaldehvde. From an industrial point of view, benzaldehyde is a very important aromatic aldehyde. A possible way of production is selective gas-phase oxidation of toluene using catalysts based on vanadia. However, low conversion rates have to be maintained to avoid deeper oxidation and even in this case the benzaldehyde selectivities are low.⁴⁵ Thus, improvement of the catalytic performance by rational catalyst design is of considerable industrial interest. Comprehensive studies of the ammoxidation of toluene to benzonitrile proceeding with high yields over unsupported vanadium phosphorus oxide catalysts, e.g. over (VO)2- P_2O_7 , revealed that benzaldehyde is an intermediate in this reaction.^{46,47} Thus, it was expected that $(VO)_2P_2O_7$ in the absence of NH₃ should be a suitable material, too, to catalyze the selective formation of benzaldehyde. However, in contrast to the ammoxidation of toluene, in which selectivities as high as 90% were obtained at conversions of up to 70%, maximum benzaldehyde selectivities in the selective oxidation of toluene did not exceed 15-47%, and these values were only achieved at toluene conversions as low as 5%.48 By operando EPR studies, supplemented by FTIR investigations, it was possible to elucidate reasons for this disappointing result and to suggest opportunities for improving benzaldehyde yields.

Vanadyl pyrophosphate is a paramagnetic bulk phase in which the EPR-active $V^{4+}O_6$ octahedra form ladder-like double chains along which they are coupled by magnetic spin-spin exchange interactions. Due to these interactions, splittings arising from the spin-orbit and electron-nuclear spin interaction (reflected by the principle components of g and A tensors, respectively) are not resolved and a rather narrow isotropic singlet is observed in the operando EPR spectrum at 658 K (Fig. 2). As soon as the inert nitrogen atmosphere is replaced by the feed mixture (1 mol% toluene or 4-methoxytoluene, respectively, in air) the apparent height of the EPR signal decreases (Fig. 2(a) and (b)). This is also true for the relative double integrals (Fig. 2(c)) since marked line broadening leads to the disappearance of intensity in the outer wings of the spectrum. Thus, only a part of the EPR intensity is comprised by double integration. This effect has also been observed in previous operando EPR studies of vanadyl pyrophosphate



Fig. 2 EPR spectra of $(VO)_2P_2O_7$ (70 mg) measured at 385 °C in N₂ flow and reactant feed: (a) 1 mol% toluene/air, (b) 1 mol% 4-methoxytoluene/air, total flow: 34 ml min⁻¹) and relative intensity of the EPR signals (double integrals) as a function of time on stream and feed composition (open symbols: 1 mol% toluene/air, filled symbols: 1 mol% 4-methoxytoluene/air).

during the ammoxidation of toluene.¹⁹ It was attributed to a perturbation of the spin–spin exchange between neighbouring VO^{2+} ions in the vanadyl double chains of the $(VO)_2P_2O_7$ structure. This perturbation is caused by transfer of electron density from the adsorbed aromatic ring to surface vanadyl sites and further delocalization over a certain range of the vanadyl chains. From Fig. 2(b) and (c) it is seen that the effect is even more pronounced when the basicity of the aromatic ring is enhanced by additional electron donating substituents such as a 4-methoxy group.

While the spectral changes occur immediately upon replacing the nitrogen flow by the reactant mixture, the shape of the EPR signal is only slowly reversible when changing from the reactant mixture (toluene/air) back to nitrogen flow (Fig. 2(c)). This indicates that the aromatic reactant and/or product is very strongly adsorbed and difficult to remove from the catalyst surface. The temporal decrease of the EPR signal intensity is the more pronounced, the higher the toluene conversion and, as a consequence, the lower the benzaldehyde selectivity (Fig. 3) indicating that more and more surface VO²⁺ sites are involved in the reaction cycle and, thus, contribute to the spin-spin exchange perturbation. FTIR studies performed on the same system revealed that, besides adsorbed benzaldehyde, cyclic anhydrides are formed by deeper oxidation of the aromatic ring which finally might be converted to CO_x .⁴⁸ As a reason for this undesired strong adsorption it was found that P-O-P and/or P-O-V bonds of the catalyst surface are hydrolyzed by water which is a product of the oxidation reaction. This hydrolysis creates Brønsted acidic sites that form hydrogen bonds with the carbonyl group of benzaldehyde and, thus, hinder its desorption and facilitate total oxidation.4

For 4-methoxytoluene and its corresponding aldehyde the interaction with the Brønsted acidic sites is even stronger as for pure toluene due to the inductive effect of the substituent. The VO²⁺ operando EPR signal is superimposed by a very narrow line which arises from carbon radical species generated by oxidative degradation of the aromatic ring system (Fig. 2(b)). It is interesting to note that, on the catalysts discharged from the reactor after reaction, no coke deposits are detected. Thus, the carbon radical species have to be regarded as intermediates in the total oxidation of the aromatic hydrocarbons for which operando EPR is a unique detection method. They are only hardly visible in toluene/air flow (Fig. 2(a)), for which total oxidation is less pronounced. Analysis of the product mixture leaving the EPR flow reactor revealed that benzaldehyde was formed with 20% selectivity at a toluene conversion of 26% (Fig. 3) while 4-methoxybenzaldehyde was obtained with only 8% selectivity at the same degree of conversion. In contrast to



Fig. 3 Relative decrease of the EPR signal intensity (double integral) of $(VO)_2P_2O_7$ (70 mg) in a flow of 1 mol% toluene/air (total flow: 34 ml min⁻¹) (white bars, $I_{rel}(N_2) = 100\%$) and corresponding benzalde-hyde selectivity (black bars) *versus* toluene conversion obtained after 1 h time on stream (values determined by GC analysis of the product mixture).

It is very probable that the higher benzonitrile selectivities observed in the ammoxidation of toluene over $(VO)_2P_2O_7$ are due to facilitated product desorption which might arise from blocking of the generated Brønsted sites by ammonia. Following this idea, pyridine was added to the feed in the selective oxidation of toluene to act as a competitive adsorbate which displaces benzaldehyde from the acidic surface sites and, thus, prevents its total oxidation. This approach led to an increase of the benzaldehyde selectivity by a factor of 2.2 at the same degree of toluene conversion. From Fig. 4 it is seen that the operando EPR signal intensity decreases as expected when switching from N2 to toluene/air flow. No further changes are observed when water vapour is added to the feed by passing a part of the air flow through a water-filled saturator. However, when a 4 wt% pyridine/water solution is used instead of pure water, the EPR signal intensity starts returning to its initial value. This indicates that benzaldehyde may be displaced from the VO²⁺ surface adsorption sites removing the temporal perturbation of the spin-spin exchange is reversible. This conclusion was also confirmed by in situ FTIR measurements, in which adsorbed benzaldehyde could be no longer detected in the presence of pyridine.48

In summary, it has been shown that operando EPR investigations supplemented by FTIR measurements were able to identify strong product adsorption as the major selectivity limiting factor in the selective oxidation of toluene to benzaldehyde. Blocking of Brønsted surface sites formed under reaction conditions by competitive adsorbates such as pyridine, which is not oxidized under the applied reaction conditions, has been shown to be a possible way of improving the catalytic performance in this reaction. Alternatively, other catalysts which do not tend to the easy formation of Brønsted acidic sites have been suggested following the conclusions of the above described studies. First promising results were obtained with V_2O_5 modified by alkali ions.¹⁹ Moreover, it has been clearly shown that operando EPR is a valuable tool not only for monitoring more or less isolated vanadyl ions, as will be demonstrated in the following section, but also for following reaction-dependent changes of pure paramagnetic bulk phases by analyzing their intrinsic magnetic interactions.

Oxidative dehydrogenation of propane to propene (ODP). Vanadia-based catalysts are used, too, for the oxidative

Fig. 4 Relative intensity (double integral) of the EPR signal of 70 mg $(VO)_2P_2O_7$ at 385 °C as a function of reaction time in two different experiments (1: white symbols, 2: black symbols) upon switching the feed composition (total flow: 34 ml min⁻¹) subsequently from N₂ to air/toluene = 100/1 to air/toluene/water vapour = 100/1/1 (experiment 1, white symbols) or air/toluene/water vapour (containing 4 wt% pyridine) = 100/1/1 (experiment 2, black symbols) and again to N₂.

dehydrogenation of propane to propene. This could be an interesting alternative to the currently applied cracking processes since it uses cheap and environmentally friendly starting materials. However, there is a major drawback that keeps the ODP reaction still far from being attractive for industrial application: Maximum propene yields obtained so far hardly exceed 20% since total combustion of both propane and propene leads to low selectivities, in particular at higher degrees of conversion. Based on a comprehensive study of structurereactivity relationships in bulk MeVO phases (Me = Mg, Zn, Pb) and first promising results with a supported $VO_{x/x}$ MCM catalyst²³ it was assumed that highly dispersed, preferably tetrahedrally coordinated V sites supported on high surface area carriers of low surface acidity could improve the propene selectivity. In this section, simultaneous operando EPR/UV-vis/on-line GC measurements performed with the novel setup shown in Fig. 1 are presented, by which key properties of good ODP catalysts could be identified.

Catalysts containing VO_x species on mesoporous SiO₂ (SBA-15 and MCM-48) and mesoporous Al₂O₃ supports were prepared by wet impregnation with NH4VO3 as described elsewhere.²⁴ In the case of SBA-15, support materials with two different pore diamters (190.5 and 52.6 nm) were used to check the influence of the latter on the catalytic performance. In the following, the SBA-15-supported catalysts are denoted as $VO_x/SBA-15/200$ and $VO_x/SBA-15/50$. Structural and catalytic properties of these materials are listed in Table 1. In the fresh catalysts, the vanadium species are mainly pentavalent giving rise to intense charge-transfer (CT) transitions in the UV-vis diffuse reflectance spectra (Fig. 5). From the position of the low-energy CT band conclusions on the coordination number and the degree of V site agglomeration can be derived. In the spectra of fresh $VO_x/MCM-48$ and $VO_x/SBA-15/200$ samples which are very similar these bands occur above 450 nm suggesting octahedral coordination⁴⁹ (Fig. 5(A)). After heating in air to 500 °C these signals disappear since the octahedral V sites lose coordinated water ligands and become tetrahedral. Accordingly, the most intense low-energy CT band occurs at 320 nm being characteristic of mainly isolated tetrahedral VO₄ sites. This process is reversible upon rehydration at room temperature. A similar reversible change between tetrahedral and octahedral symmetry of the V centres due to desorption/readsorption of water molecules was also observed by other authors using in situ-UV-vis-DRS.50,51 In $VO_x/SBA-15/200$, the small band around 380 nm indicates the presence of some VO₄ sites connected via V–O–V bridges, too (Fig. 2(a)⁵²). The latter band is not visible in VO_x/MCM -48, probably due to its very high surface area (Table 1) which facilitates high V dispersion. These spectral changes are completely reversible by rehydrating the samples in ambient atmosphere suggesting that all V sites are exposed on the surface and accessible to water ligands and, thus, also to potential reactant molecules. Thus, it is justified to calculate VO_x surface densities and turnover frequencies (TOF) assuming that all V sites are exposed (Table 1).

Virtually no spectral changes are observed when heating VO_x/Al_2O_3 in air (Fig. 5). In this catalyst, most of the V sites are tetrahedrally coordinated as evidenced by CT bands located below 400 nm.^{49,52} However, a weak band at 455 nm points to the presence of a small amount of octahedrally coordinated, rather oligomeric vanadium sites which do not become tetrahedral upon heating (Fig. 5(B)).

From the UV-vis-DRS measurements it can be concluded that the degree of V sites connected *via* V–O–V bridges increases in the order VO_x/MCM-48 \approx 0 < VO_x/SBA-15/ 200 < VO_x/Al₂O₃. This might be due to the surface area of the supports which decreases in the same order (Table 1).

Operando EPR/on-line-GC/UV-vis results under ODP conditions are plotted in Fig. 6 for VO_x/Al_2O_3 . UV-vis spectra of the fresh catalyst at 20 °C are dominated by CT bands of V⁵⁺.



Table 1 Structural properties of catalysts with 2.8 wt% of V and catalytic results obtained at 500 °C: Turn-over frequencies (TOF) and propene selectivities (S) measured at propane conversions of 2.5–3.9%, maximum propene yields (Y) and space-time yields (STY) measured at propane conversions between 20 and 30%

Sample	Surface density ^a / V nm ⁻²	$S_{\rm BET}/{ m m}^2~{ m g}^{-1}$	Pore volume/cm ³ g ⁻¹	Mean pore diameter/Å	$\mathrm{TOF}^a \ /\mathrm{s}^{-1}$	S (%)	Y _{max} (%)	$\begin{array}{l} STY_{max}/kg_{C_{3}H6} \\ (kg_{cat} \ h)^{-1} \end{array}$
VO_x/Al_2O_3	1.0	273	0.38	48.2	0.44	73.3	12.3	5.8
$VO_x/SBA-15/50$	0.43	645	0.70	52.6	0.18	83.3	14.5	6.8
$VO_x/SBA-15/200$	0.7	421	1.74	190.5	0.26	82.3	12.4	5.8
$VO_x/MCM48$	0.37	889	0.39	26.2	0.21	80.1	18.0	12.6
^a Apparent values,	calculated assuming e	exposure of all V	sites					

By raising the temperature stepwise to 400 °C, light absorption increases gradually above 500 nm due to partial reduction of V^{5+} to V^{4+} , the d–d transitions of which fall in the higher wavelength range of the spectrum⁵³ (Fig. 6, left). In the corresponding EPR spectra, this reduction which starts already well below the onset of propene formation, is reflected by a growing EPR signal of octahedrally coordinated interacting and isolated VO²⁺ species (Fig. 6, middle).

Further heating above 400 °C gives rise to a strong increase of absorbance in the whole visible range of the UV-vis spectrum (Fig. 6, left). This is caused by the formation of carbon deposits which have been detected, also, by FTIR spectroscopy. Following the product composition by on-line-GC shows that propene selectivity is strongly increasing in the initial period of the reaction. Moreover, the catalyst is not deactivated by the carbon deposits (Fig. 6, right). Obviously, those carbonaceous residues are mainly deposited on the support material while the active VO_x species remain free. This might reduce the surface acidity of the support under reaction conditions and, thus, favour rapid desorption of the basic propene molecules which reflects itself in increasing selectivity.

A rather similar behaviour in the *operando*-EPR/on-line-GC/UV-vis experiments was also observed for the silicasupported samples with the exception that for these catalysts only a very small (VO_x/SBA-15/200, Fig. 7) or even no EPR signal (VO_x/MCM-48) could be observed upon reduction of V⁵⁺ (evidenced in the corresponding UV-vis spectra). This is due to the fact that in these samples the active V sites are essentially tetrahedrally coordinated at reaction temperatures (Fig. 5) and V⁴⁺ in tetrahedral symmetry has short relaxation times and is only visible at low temperatures. To illustrate the strong influence of carbon deposits on the UVvis spectra, the gas flow over sample VO_x/SBA-15/200 was switched to pure H₂ after 1 h time on stream under ODP conditions. From Fig. 7 it can be seen, that carbon deposits can be at least partly removed by hydrogenation.

Catalytic tests revealed that the intrinsic activity of the VO_x sites reflected by TOF values as well as the propene selectivities do not differ much for the three silica-supported VO_x catalysts (Table 1). This agrees well with the fact that their local structure and valence state under reaction conditions is also very similar. Due to the much higher surface area of sample VO_x/MCM-48, the maximum propene yield achieved with this catalyst is higher in comparison to the two VO_x/SBA-15 samples.

The intrinsic activity of VO_x/Al₂O₃ (TOF values, Table 1) is higher in comparison to that of VO_x/SBA-15/50, VO_x/SBA-15/200 and VO_x/MCM-48. As shown by the *operando* studies described above, a certain amount of octahedral vanadium sites is present under reaction conditions in VO_x/Al₂O₃. These species and the higher number of V–O–V bonds might be the reason for the higher intrinsic activity of the VO_x sites in comparison to VO_x/SBA-15 and VO_x/MCM-48. However, propene selectivities over VO_x/Al₂O₃ are lower than over the silica-supported samples. This might be due to the higher concentration and strength of Lewis acidic sites that have been detected on VO_x/Al₂O₃ by FTIR spectroscopy of pyridine adsorption.

From the above described *operando* experiments in connection with results of catalytic tests, the following conclusions can be derived: under reaction conditions, the V sites being mainly pentavalent in the fresh catalysts are considerably reduced which might improve the propene selectivity due to the lower redox potential. Another beneficial effect on selectivity is obviously caused by carbon deposits formed under propane-rich reaction conditions which do not deactivate the catalysts since they might rather cover acidic sites of the support materials while active V sites remain free. These are unique observation that are only possible by *operando*



Fig. 5 Room-temperature UV/VIS-DRS spectra of samples 2.8% V/Al₂O₃ (left), 2.8% V/SBA-15/200 (middle) and 2.8% V/MCM-48 (right) before (A) and after heating in air at 500 °C (B).



Fig. 6 Operando EPR/UV-vis/on-line GC measurement of sample VO_x/Al_2O_3 (5.8 wt% V) during ODH of propane (feed: 60% $C_3H_8/30\% O_2/N_2$, W/F = 1.25 g h mol⁻¹).

EPR/UV-vis/on-line-GC experiments. Furthermore it is obvious that V sites with more than four oxygen ligands are more active but less selective than tetrahedral VO₄ species. Isolated VO_x sites are selective but less active than V sites connected via V-O-V bonds. The beneficial effect of supported VO_x catalysts with high surface area is first of all reflected by maximum achievable space-time yields. In particular, for VO_x/MCM -48 the STY value (Table 1) is much higher than for bulk VMgO catalysts which, so far, belong to the best catalytic systems for the ODP.²³ However, it is also roughly twice as high compared to the two SBA-15-supported catalysts although the structure of the V sites (Fig. 5) as well as the selectivities at low conversion (Table 1) are rather similar. The main difference between MCM-48 and SBA-15 is related to the pore structure. While MCM-48 contains a three-dimensional cubic system of unimodal mesopores, SBA-15/50 is characterized by well-ordered hexagonal arrays of cylindrical parallel-oriented pores which are interconnected by smaller sized windows. The expanded SBA-15/200 structure is less well-defined and contains foam-like large-sized cavities which are three-dimensionally interconnected. Moreover, the mean pore diameter in the two SBA-15 catalysts is markedly higher than in MCM-48 which leads to higher pore volumes (Table 1). It is possible that, at the same flow rate, more propane passes the larger pores of the SBA-15-supported catalysts without conversion in comparison to VO_x/MCM-48. This is illustrated by the values in Table 2. Thus, lower yields and STY values result for SBA-15 samples.

In summary, catalysts containing highly dispersed VO_4 sites with a mean valence state close to +4 on non-acidic supports of very high surface area seem to be promising materials on which future catalyst development should be focused.

3.2. Activity and stability of Cr sites in supported chromium oxides during dehydrogenation of propane

Supported chromium oxides are industrially important catalysts being used, *e.g.*, in several industrial processes for the



Fig. 7 Operando EPR/UV-vis/on-line GC measurement of sample $VO_x/SBA-15/200$ (2.8 wt% V) during ODH of propane (feed: 60% $C_3H_8/30\%$ O_2/N_2 , W/F = 1.25 g h mol⁻¹).

Table 2 Propane conversion and propene selectivity for the three mesoporous silica supported catalysts at 500 °C under identical reaction conditions (W/F = 1.4 g h (mol_{C3H8})⁻¹, propane/oxygen/helium = 2/1/2)

	$VO_x/MCM-48$	$VO_x/SBA-15/50$	VO _x /SBA-15/200		
X _{C₂H8} (%)	32.8	29.2	25.9		
$S_{C_{3}H6}$ (%)	53.0	48.9	47.8		

dehydrogenation of propane.⁵⁴ Moreover, they revealed to be promising materials for the aromatization of alkanes leading to considerably higher selectivities than obtained with common reforming catalysts based on noble metals.^{55,56} Unfortunately, they deactivate rather quickly by coke formation. Previous *operando* EPR investigations of CrO_x/ZrO_2 catalysts in the aromatization of octane revealed that isolated CrO_x sites are less active but more stable against coke deposition than Cr_2O_3 clusters.²⁷ Moreover, it was found that doping the catalysts with lanthanum stabilizes the CrO_x sites on the surface.⁵⁷ The *operando* EPR/UV-vis/on-line-GC technique was used to study the influence of the support material on activity and stability of the CrO_x sites.

Three different catalysts have been studied. 1 wt% Cr/Al₂O₃ $(S_{BET} = 200 \text{ m}^2 \text{ g}^{-1})$ and 0.5 wt% Cr/La,ZrO₂ $(S_{BET} = 104 \text{ m}^2 \text{ g}^{-1})$ were prepared by impregnating γ -Al₂O₃ and a commercial 7 wt% La₂O₃/Zr(OH)₄ support (MEL Chemicals), respectively, with an aqueous (NH₄)₂CrO₄ solution followed by calcination in air at 600 °C. Cr/La,Al₂O₃ $(S_{BET} = 345 \text{ m}^2 \text{ g}^{-1})$ was obtained by thermal decomposition of ammonium dawsonite, NH₄Al(OH)₂CO₃, doped with 10 wt% Cr and 3.9 wt% La.

Prior to the *operando* EPR/UV-vis/on-line-GC experiments, the redox behaviour of the catalysts was studied separately by EPR and UV-vis spectroscopy (Fig. 8). UV-vis spectra of as-synthesized catalysts are characterized by intense CT bands of hexavalent chromate species at 370 nm.⁵⁸ In the corresponding EPR spectra a narrow line is detected arising from traces of isolated Cr^{5+} ions. After heating in hydrogen flow to 500 °C, the chromate CT bands in the UV-vis spectra disappear and very broad bands of d–d transitions of Cr^{3+} appear around 630 nm⁵⁸ indicating that Cr^{6+} is completely reduced. (The remaining band around 290 nm in the spectrum

of sample Cr/La,ZrO₂ is due to the support.) This reduction is well reflected in the related EPR spectra in which two different signals can be distinguished at effective g-values of $g' \approx 4.3$ and $g' \approx 2$. They are assigned to coordinatively unsaturated, isolated Cr³⁺ ions in distorted geometry on the catalyst surface and to magnetically interacting Cr³⁺ ions in Cr₂O₃ clusters, respectively.^{59,60} The former are most pronounced in Cr/ La,ZrO₂ and almost not visible in Cr/Al₂O₃. This points to the stabilizing effect of La dopants being able to retain Cr species in high dispersion on the surface.^{27,57} Treatment of the reduced catalysts in oxygen flow at 500 °C shows that Cr species in Cr/La,ZrO₂ are almost completely reoxidizable while this ability is partially lost for Cr/La,Al₂O₃ and even more for Cr/Al₂O₃. This is most probably due to the fact that Cr³⁺ ions formed upon reduction tend to be incorporated in Al lattice positions of the catalyst volume and, thus, are no longer accessible by reactants. It seems that La-doping can suppress this effect only partly.

When the catalysts are heated in a mixture of 23% propane/ N₂ (W/F = 16.2 g h mol⁻¹), the CT bands of chromate around 370 nm vanish and d-d bands of Cr³⁺ appear in the UV-vis spectra (Figs. 9 and 10, left) as observed, too, upon treatment in H₂ (Fig. 8). Simultaneously, the narrow EPR singlets of Cr^{5+} disappear and a broad singlet at $g' \approx 2$ arises from weakly interacting Cr^{3+} species (Figs. 9 and 10, middle). By comparing these results with the catalytic data (Figs. 9 and 10, right) it is clearly evident that the reduction of Cr^{6+} and Cr^{5+} to Cr^{3+} occurs already at temperatures well below the onset of the dehydrogenation reaction. This information cannot be derived post mortem from measurements of quenched catalysts and shows that Cr sites in oxidation states higher than +3 do not exist under reaction conditions. With increasing time on stream at 810 K the propane conversion over the Cr/La,ZrO₂ catalysts drops markedly (Fig. 9). This is due to the partial coverage of active Cr^{3+} sites by coke deposits.²⁷ As a consequence, the EPR singlet of Cr^{3+} loses intensity since magnetic interaction with paramagnetic coke species may cause line broadening. In the UV-vis spectra, deactivation leads to a gradual increase of absorbance in the visible range of the spectrum with a maximum around 470 nm arising from higher condensed carbon species such as polyaromatics and condensed rings.61



Fig. 8 Room-temperature UV-vis (left) and EPR spectra (right, 3 mT $< B_0 < 690$ mT) of Cr/La,ZrO₂ (A), Cr/Al₂O₃ (B) and Cr/La,Al₂O₃ (C) in as-synthesized form (solid lines), after 1 h reduction at 500 °C and cooling in H₂ flow (dashed lines) and after 1 h reoxidation at 500 °C and cooling in O₂ flow (dotted lines).



Fig. 9 Operando EPR/UV-vis/on-line GC measurement of sample $Cr/La, ZrO_2$ during dehydrogenation of propane (feed composition: 23% C_3H_8/N_2 , W/F = 16.2 g h mol⁻¹).

In comparison to sample Cr/La,ZrO₂, the Cr/La,Al₂O₃ catalyst is, despite higher BET surface area and Cr content, less active but more stable against deactivation (Fig. 10). Here, the maximum of absorbance arising from carbon deposits is shifted to lower wavelength around 360 nm being characteristic of less condensed rather linear polyenylic species⁶¹ which might be less deactivating. Besides the different nature of the carbon species, the lower activity of the Cr/La,Al₂O₃ catalyst is most probably due to the fact that a considerable part of the Cr ions migrates into the bulk of the support and, thus, is not accessible by reactants. As suggested by the non-reversibel redox behaviour, this effect should be most pronounced for lanthanum-free Cr/Al₂O₃ (Fig. 8). For this sample, repeated reaction/regeneration cycles have been followed by operando EPR at 550 °C (Fig. 11). It can be seen that during regeneration in air, only the signals of isolated Cr3+ and Cr5+ species reappear the concentration of which is small. In contrast, the signal at $g' \approx 2$ due to interacting Cr^{3+} is not influenced. This suggests that only a minor amount of rather isolated Cr species remains accessible on the surface accounting for the catalytic activity.

The recoverage of Cr^{3+} in oxidative atmosphere is surprising. Under these conditions, Cr^{3+} ions can only be formed by oxidation of deeper reduced Cr species which are EPRsilent. This means that during propane dehydrogenation Cr species on Al₂O₃ supports may be reduced to lower oxidation states than +3. This is supported by the results of quasi-in situ-XPS measurements, in which the catalyst has been treated in a flow of 23% propane/ N_2 in a reaction cell installed in the lock to the analysis chamber. After subsequent cooling to room temperature the sample was transferred to the analysis chamber without contact to ambient atmosphere. In the fresh catalyst, the Cr $2p_{3/2}$ peak was found to be a superposition of contributions from Cr^{6+} and Cr^{3+} at binding energies of 579.4 and 576.8 eV (corrected with respect to the C 1s signal at 284.5 eV). After treatment in the reactant gas mixture, the peak is shifted to a binding energy of 574.5 eV which is markedly lower than expected for pure Cr³⁺ suggesting that deeper reduced Cr species must have been formed. However, the latter are not stable in air at ambient atmosphere. After storing for 20 h in air at room temperature the Cr $2p_{3/2}$ peak is again



Fig. 10 *Operando* EPR/UV-vis/on-line GC measurement of sample Cr/La,Al₂O₃ during dehydrogenation of propane (feed composition: 23% C_3H_8/N_2 , W/F = 16.2 g h mol⁻¹).



Fig. 11 Left: *Operando* EPR spectra of sample 1 wt% Cr/γ -Al₂O₃ at 500 °C after 30 min under reactant feed (thick lines, feed composition: 23% C_3H_8/N_2 , W/F = 16.2 g h mol⁻¹) and subsequently after 30 min in air flow (thin-lines). Cycles were repeated three times. Right: propene yields determined after 2, 15 and 30 min within each period under reactant feed.

shifted back to 576.8 eV, indicating that Cr^{3+} species of lower valence states have been reoxidized to Cr^{3+} .

Based on the above described results, it can be concluded that the lower activity of Cr/Al_2O_3 and $Cr/La,Al_2O_3$ in comparison to $Cr/La,ZrO_2$ is due to the dilution of active Cr surface sites which is very likely caused by migration of Cr^{3+} into the volume of the Al_2O_3 support. This, in turn, leads to the formation of weaker condensed, less deactivating carbon deposits. In addition, reduction of the Cr sites to valence states lower than +3 may also contribute to the activity decrease. Since isolated Cr surface sites revealed to be rather stable against deactivation, a possible way of catalyst improvement could be their stable dispersion on supports of high surface area. These should expose a higher amount of such isolated sites and guarantee sufficient overall activity.

3.3. Structure and function of Mn ions in MnO_x storage catalysts for selective catalytic reduction of NO_x

The removal of NO_x from exhaust gases by selective catalytic reduction (SCR) is one of the most important issues in environmental catalysis. In the case of diesel and lean burn gasoline engines, special problems arise from the oxygen excess in the exhaust gas. For effective NO_x abatement, periodic operation under oxidative and reductive reaction conditions is applied requiring catalysts which are able to store NO_x at lower temperatures in oxygen excess and desorb it at higher temperatures under the conditions of selective catalytic reduction. Supported MnO₂ revealed to be a suitable catalyst.⁶²⁻⁶⁴ However, the nature of adsorbed NO_x species, the mechanism leading to their formation and, in particular, the role of the catalysts components in this process are not fully understood so far. A further important issue is the stability of the storage catalysts against deactivation by impurities present in the exhaust gases such as sulfur-containing compounds or water vapour. In situ EPR studies in connection with in situ FTIR measurements have been performed to investigate the interaction of NO, O₂, H₂O and SO₂ (used as reducing agent).⁶⁵ The 5 wt% MnO₂/NaY catalyst used in this study was prepared by precipitating MnO2 on commercial zeolite NaY or SiO₂ (Aerosil).⁶

The as-synthesized catalyst contains tetravalent manganese ions which do not give rise to an EPR signal at ambient temperature. Upon heating in a flow of 0.5% NO/N₂ (100 mg catalyst, total flow 7.5 ml min⁻¹) an EPR signal at $g' \approx 2$ appears (Fig. 12(a)). By spectra simulation it was found,⁶⁵ that this signal is a superposition of two sub-lines with hyperfine structure characteristic of isolated octahedrally coordinated Mn²⁺ ions and a broad singlet arising from magnetically interacting Mn²⁺ ions.⁶⁶ The starting temperature of Mn²⁺ formation ($\approx 225 \,^{\circ}$ C) agrees very well with the onset of NO_x conversion observed during catalytic tests of these materials.⁶⁴ By related *in situ* FTIR measurements it has been shown that intermediate NO₂⁻ species are formed and further converted to NO₃⁻ ions which are stored at the Na ions of the zeolite support (eqn. (1)).⁶⁵ From EPR results it is clear that this process goes along with a reduction of Mn⁴⁺ to Mn²⁺. This means that lattice oxygen participates in this redox process.

$$NO \xrightarrow{O_{surface}^{2-}} NO_2^{-} \xrightarrow{O_{surface}^{2-}} NO_3^{-}$$
(1)

After passing a maximum at \approx 355 °C the intensity of the EPR signal decreases again suggesting that Mn²⁺ is re-oxidized. This is accompanied by thermal decomposition of the adsorbed nitrate species.



Fig. 12 EPR spectra of MnO_2/NaY (100 mg) recorded during heating in a flow (7.5 ml min⁻¹) of (a) 0.5% NO/N₂, (b) 0.5% NO, 50% O_2/N_2 and (c) 0.5% NO, 50% O_2 , 2.3% H_2O/N_2 .

When oxygen is added to the feed in a molar ratio of NO/ $O_2 = 1/100$, Mn^{2+} ions start to form at lower temperature and in a higher amount than in the absence of O_2 (Fig. 12(b)). This was quite surprising since the opposite was expected in oxidizing atmosphere. Corresponding FTIR experiments have shown that nitrate formation is also strongly enhanced in the presence of O₂.⁶⁵ The results of both methods support the conclusion that NO oxidation and, as a consequence, Mn⁴⁺ reduction to Mn²⁺ proceeds via lattice oxygen of the MnO₂ component not only in NO/N2 flow but also in an excess of gas-phase oxygen. In the latter case, Mn^{2+} ions formed upon NO oxidation can be readily re-oxidized by O₂ and, thus, participate in the redox cycle again. In the absence of O_2 , gradual reduction of MnO₂ obviously leads to a saturation of the surface with Mn²⁺ being the reason why nitrate formation does not exceed a certain limit.

When 2.3% water vapour is additionally added to the feed, Mn^{2+} formation is markedly suppressed (Fig. 12(c)). This suggests that water is a competitive adsorbate for NO and blocks a certain part of the active sites. A similar conclusion has also been drawn from the FTIR results which indicated that less nitrate is formed when pre-adsorbed water is present on the surface. However, the inhibiting effect of water was found to be less pronounced in the presence of O₂ which favours the formation of HNO₂ and finally HNO₃ as sources for nitrite and nitrate (eqns. (2)–(4)).⁶⁵

$$NO + 0.5 O_2 \rightarrow NO_2$$
 (2)

$$2 \text{ NO}_2 + \text{H}_2\text{O} \rightarrow \text{HNO}_2 + \text{HNO}_3 \tag{3}$$

$$3 \text{ NO}_2 + \text{H}_2\text{O} \rightarrow 2 \text{ HNO}_3 + \text{NO} \tag{4}$$

The spin-Hamiltonian parameters of the Mn^{2+} centres have been derived by spectra simulation.⁶⁵ To achieve a satisfactory fit of experimental and calculated spectrum, two slightly different hfs signals for octahedrally coordinated isolated Mn^{2+} ions⁶⁷ and one isotropic singlet for interacting Mn^{2+} sites had to be superimposed. The spin-Hamiltonian parameters as well as the relative intensities of the three sub-signals are very similar during treatment with the various feed compositions indicating that the local structure of the respective Mn^{2+} centres remains almost unchanged. The only difference comes from the total EPR signal intensity (Fig. 12) which reflects the extent of Mn^{4+} reduction.

In the presence of SO₂, the extent of Mn^{2+} formation by reduction of Mn^{4+} decreases markedly with increasing amount of SO₂ present in the feed (Fig. 13(a)–(c)). This is surprising since by FTIR measurements it vas found that, upon adsorption, SO₂ is converted to SO₄²⁻ (stored on both the Mn and Na ions of the catalyst) the formation of which must involve a redox step.⁶⁶ A possible explanation for the partially suppressed Mn²⁺ formation can be given by eqns. (5)–(9). From these equations it is seen that, in the presence of NO, O₂ and traces of water, oxidation of SO₂ to sulfate ions needs not necessarily to involve Mn ions.

$$SO_2 + 2 NO_3^- + 2 H^+ \rightarrow SO_3 + 2 NO_2 + H_2O$$
 (5)

$$SO_3 + H_2O \rightarrow H_2SO_4$$
 (6)

$$SO_2 + H_2O \rightarrow H_2SO_3$$
 (7)

$$NO + 0.5 O_2 \rightarrow NO_2$$
 (8)

$$H_2SO_3 + NO_2 \rightarrow H_2SO_4 + NO$$
 (9)

From Fig. 13(b) and (c) it is also seen that, the more SO₂ is in the feed, the lower is the degree of Mn^{4+} reduction. Furthermore, Mn^{2+} formation in NO/O₂ flow starts at higher temperatures when the catalyst had been pretreated in a flow of 600 ppm SO₂/33% O₂/He (Fig. 13(d)). This suggests that the sulfate species formed during this pre-treatment block active Mn sites which are required for the conversion of NO to



Fig. 13 EPR spectra of MnO_2/NaY (100 mg) recorded during heating in a flow (7.5 ml min⁻¹) of 0.3% NO, 30% O_2/N_2 (a) without SO₂, (b) with 40 ppm SO₂, (c) with 550 ppm SO₂, and (d) after pretreatment in a flow of 600 ppm SO₂, 33% O_2/He at 250 °C.

nitrate. Since this conversion proceeds *via* lattice oxygen species, it must involve reduction of Mn^{4+} to Mn^{2+} . These results reflect one of the main problems of these NO_x storage catalysts, namely, their sensitivity against sulfur-containing impurities in fuels which poison the active Mn sites by sulfate deposition.

By critically evaluating the results described above it is evident that the major benefit does not arise from *in situ* EPR alone but from the combination with *in situ* FTIR. Using this approach, it was possible to follow both the behaviour of the active Mn sites by EPR and the formation of adsorbed intermediates by FTIR spectroscopy. Based on this complex information, mechanistic insights could be obtained.

4. Summary: Opportunities and limitations of *operando* EPR

Operando EPR, although still rather seldom used in catalysis research so far, is a unique tool to follow the action of paramagnetic transition metal ions (TMI) in oxide catalysts during the catalytic process. This has been demonstrated by the application examples presented in this paper. Experimental conditions can be chosen almost identical to those in fixed-bed microreactors, thus, making sure that the obtained results are properly reflecting the true reaction behaviour. The method provides a great deal of information on the role of paramagnetic TMI in oxide catalysts which cannot be adequately obtained by other methods. Thus, reaction-dependent changes of coordination and valence state of TMI as well as their electronic interactions between each other and with electrons of reactant molecules can be elucidated simultaneously. Using vanadia-based selective oxidation catalysts as an example, it has been shown that such investigations are not only restricted to well isolated TMI, as frequently supposed. Rather it has been demonstrated that closely neighbouring TMI which are coupled by effective spin-spin exchange interactions in oxidic clusters or even in bulk phases can be studied, too, by analyzing temporal changes of the EPR line shape and intensity. In fact, it is just these interactions which have been exploited to derive conclusions on catalyst-reactant interactions in the selective oxidation of toluene. The application examples presented above comprise only a limited selection out of the wide variety of catalytically relevant TMI accessible by operando EPR. A more comprehensive treatise of this issue is given in ref. 40

Despite the undisputable benefits of *operando* EPR, the major drawbacks of this technique have to be mentioned,

too. The EPR signal intensity of paramagnetic species is inversely proportional to the temperature. Although EPR is a highly sensitive method, this may lead to poor signal-to-noise ratios when catalytic reactions have to be studied at high temperatures and the concentration of paramagnetic species is low, i.e., in the case of isolated TMI. Moreover, certain TMI can have very short relaxation times depending on their particular coordination symmetry and electronic configuration so that at ambient or elevated temperatures no EPR signal can be observed. This holds, e.g., for V^{4+} in weakly distorted octahedral or tetrahedral symmetry, for V^{3+} , Mn^{3+} and for various other TMI with an even number of unpaired electrons as well as for most of the rare earth ions for which strong spin-orbit coupling shortens the relaxation times. Weak dipolar or weak spin-spin exchange interactions between TMI of medium mutual distance which do not give rise to exchange-narrowing can broaden the EPR signal beyond the limit of detection completely excluding the respective catalysts from in-situ EPR measurements.

Besides certain paramagnetic TMI that escape EPR detection for reasons discussed above, all TMI in highest oxidation states which do not possess unpaired electrons are not EPRactive. However, those species (e.g. V5+, Cr6+) may well be involved in catalytic reaction steps. Visualizing their changes requires the combination with other suitable spectroscopic techniques. It has been demonstrated above that the coupling of operando EPR/UV-vis-DRS/on-line GC is very beneficial in this respect since it extends the variety of simultaneously detectable valence states of TMI and their interconversion during reaction. Other information that cannot be gained from operando EPR concerns, e.g., the particular structure of diamagnetic intermediates and products adsorbed on the catalyst surface which, however, is provided by operando FTIR spectroscopy. For elucidating comprehensive structure-reactivityrelationships it is, thus, very helpful to study the respective catalytic system by different in-situ methods. The advantages of this approach have been reviewed very recently.¹³

All operando EPR investigations published so far have been performed in X-band (microwave frequency: ≈9.5 GHz) using the continuous wave (cw) technique. Although modern pulse-EPR methods have rapidly developed in recent years, their application with respect to TMI in solid catalysts is limited since both, low concentration of paramagnetic species and low recording temperatures being intrinsic requirements of pulse-EPR echo techniques are far beyond the conditions which have to be met for investigations of real catalysts during reaction. Operando EPR measurements at higher microwave frequencies (e.g. at \approx 35 GHz in Q-band), which would be helpful in certain cases for assigning complex spectra, have not been performed so far since the dimensions of the EPR cavity set an upper limit for the diameter of a catalytic flow reactor. With a similar equipment as shown in Fig. 1, operando measurements in Q-band would require reaction tube diameters of less than 1 mm which are not suitable for catalytic flow reactors.

Despite the above mentioned limitations, operando EPR has been shown to be a very useful tool for investigating, in particular, heterogeneous catalytic gas-phase reactions over transition metal oxide catalysts. Therefore, it is desirable that this technique will receive more future attention.

Acknowledgements

The author thanks U. Bentrup, A. Martin, J. Radnik, D. L. Hoang, I. Pitsch, R. Fricke and M. Baerns for fruitful cooperation. Financial support by the German Federal Ministry of Education and Research (project no. 03C0280) is gratefully acknowledged.

References

- 1 Z. Sojka, Catal. Rev.-Sci. Eng., 1995, 37, 462.
- K. Dyrek and M. Che, Chem. Rev., 1997, 97, 305.
- 3 K. Dyrek and M. Che, in Spectroscopy of Transition Metal Ions on Surfaces, ed. B. M. Weckhuysen, P. Van Der Voort and G. Catana, Leuven University Press, Leuven, 2000, p. 45. M. Che and E. Giamello, *Stud. Surf. Sci. Catal. B*, 1989, **57**, 265.
- 5 J. C. Vedrine, in Characterization of Heterogeneous Catalysts, ed. F. Delannay, Marcel Dekker, Inc., New York, 1984, p. 161.
- M. Labanowska, Chem. Phys. Chem., 2001, 2, 712.
- Z. Sojka and M. Che, C. R. Acad. Sci. Paris, Ser. IIc, Chim., 2000, 3, 163.
- 8 D. M. Murphy and C. C. Rowlands, Curr. Opin. Solid State Mater. Sci., 2001, 5, 97.
- 9 A. Brückner, in *Spectroscopy of Transition Metal Ions on Surfaces*, ed. B. M. Weckhuysen, P. Van Der Voort and G. Catana, Leuven University Press, Leuven, 2000, p. 69.
- K. Nowinska and A. B. Wieckowski, Z. Phys. Chem. NF, 1989, 10 162. 231.
- 11 M. C. Paganini, L. Dall'Acqua, E. Giamello, L. Lietti, P. Forzatti and G. Busca, J. Catal., 1997, 166, 195.
- A. M. Prakash and L. Kevan, J. Phys. Chem., 1999, 103, 2214. 12
- A. Brückner, Catal. Rev.-Sci. Eng., 2003, 45, 97. 13
- 14 B. M. Weckhuysen, Chem. Commun., 2002, 97.
- 15 M. A. Banares, M. O. Guerriero-Pérez, J. L. G. Fierro and G. Garcia Cortez, J. Mater. Chem., 2002, 12, 3337.
- H. Topsøe, J. Catal., 2003, 216, 155. 16
- A. Brückner, B. Kubias, B. Lücke and R. Stößer, Colloids Surf. A: 17 *Physikochem. Eng. Aspects*, 1996, **115**, 179. A. Brückner, *Appl. Catal. A: General*, 2000, **200**, 287.
- 18
- A. Brückner, A. Martin, N. Steinfeldt, G.-U. Wolf and B. Lücke, 19 J. Chem. Soc., Faraday Trans., 1996, 92, 4257.
- A. Brückner, A. Martin, B. Lücke and F. K. Hannour, Stud. Surf. 20Sci. Catal., 1997, 110, 919.
- 21 K. M. Eriksen, R. Fehrmann and N. J. Bjerrum, J. Catal., 1991, 132. 263.
- 22 C. Oehlers, R. Fehrmann, S. G. Masters, K. M. Eriksen, D. E. Sheinin, B. S. Bal'zhinimaev and V. I. Elokhin, Appl. Catal. A: General, 1996, 147, 127.
- 23 P. Rybarczyk, H. Berndt, J. Radnik, M.-M. Pohl, O. Buyevskaya, M. Baerns and A. Brückner, J. Catal., 2001, 202, 45
- A. Brückner, P. Rybarczyk, H. Kosslick, G.-U. Wolf and M. 24 Baerns, Stud. Surf. Sci. Catal. B, 2002, 142, 1141.
- K. M. Sancier, T. Dozono and H. Wise, J. Catal., 1971, 25 23, 270.
- Z. Sojka and M. Che, J. Phys. Chem., 1995, 99, 5418. 26
- 27 A. Brückner, J. Radnik, D.-L. Hoang and H. Lieske, Catal. Lett., 1999, 60, 183
- A. Brückner, Chem. Commun., 2001, 2122.
- 29 A. Brückner, U. Lohse and H. Mehner, Microporous Mesoporous Mater., 1998, 20, 207.
- 30 U. Lohse, A. Brückner, E. Schreier, R. Bertram, J. Jähnchen and R. Fricke, Microporous Mater., 1996, 7, 139.
- A. V. Kucherov, J. L. Gerlock, H.-W. Jen and M. Shelef, Zeolites, 31 1995, 15, 9.
- A. V. Kucherov, J. L. Gerlock, H.-W. Jen and M. Shelef, Zeolites, 32 1995, 15, 15.
- 33 A. V. Kucherov, J. L. Gerlock, H.-W. Jen and M. Shelef, J. Catal., 1995, 152, 63.
- K. Dyrek, D. Kiessling, M. Labanowska, G. Wendt and J. 34 Widziszewska, Colloids Surf. A: Physikochem. Eng. Aspects, 1993, 72, 183.
- 35 M. Hunger and J. Weitkamp, Angew. Chem., Int. Ed., 2001, 40, 2954.
- 36 W. Matir and J. H. Lunsford, J. Am. Chem. Soc., 1981, 103, 3728.
- J. H. Lunsford, Catal. Today, 1990, 6, 235. 37
- 38 H. G. Karge, J.-P. Lange, A. Gutsze and M. Laniecki, J. Catal., 1988, **114**, 144.
- 39 J. C. Vedrine, in Characterization of Heterogeneous Catalysts, ed. F. Delannay, Marcel Dekker, Inc., New York, 1984
- 40 A. Brückner, in In situ Spectroscopy of Catalytic Solids, ed. B. M. Weckhuysen, Academic Science Publishers, in press.
- Z. Sojka and M. Che, Appl. Magn. Reson., 2001, 20, 433. 41
- D. J. E. Ingram, in Proceedings of the 3rd Conference on Carbon, 42 Pergamon Press, New York, 1959, p. 94.
- 43 L. S. Singer, W. H. Smith and G. Wagoner, Rev. Sci. Instrum., 1961, 32, 213.
- A. Brückner, B. Kubias and B. Lücke, Catal. Today, 1996, 44 32, 215.

- Y. Zhang, A. Martin, H. Berndt, B. Lücke and M. Meisel, J. Mol. 46 Catal.: A, 1997, 118, 205.
- A. Martin, A. Brückner, Y. Zhang and B. Lücke, in Heteroge-47 neous Catalysis and Fine Chemicals IV, ed. H. U. Blaser, A. Baiker and R. Prins, Elsevier Science B. V., Amsterdam, 1997, p. 377.
- A. Martin, U. Bentrup, A. Brückner and B. Lücke, Catal. Lett., 48 1999, 59, 61.
- G. Centi, S. Perathoner, F. Trifiró, A. Aboukais, C. F. Aissi and 49 M. Guelton, J. Phys. Chem., 1992, 96, 2617.
- M. Mathieu, P. Van Der Voort, B. M. Weckhuysen, R. R. Rao, 50 G. Catana, R. A. Schoonheydt and E. F. Vansant, J. Phys. Chem. B, 2001, 105, 3393.
- M. Morey, A. Davidson, H. Eckert and G. Stucky, Chem. Mater., 51 1996, 8, 486.
- 52 X. Gao and I. E. Wachs, J. Phys. Chem., 2000, 104, 1261.
- 53
- C. J. Ballhausen and H. B. Gray, *Inorg. Chem.*, 1962, **1**, 111. F. Buonomo, D. Sanfilippo and F. Trifiró, in *Handbook of Hetero*-54 geneous Catalysis, ed. G. Ertl, H. Knözinger and J.Weitkamp, Wiley, 1996, p. 2140.
- 55 K. Arata, M. Hino and M. Matsuhashi, Appl. Catal. A: General, 1993, 100, 19.
- H. Lieske and D. L. Hoang, Ger. Pat., DE 196 12 000 A1 56 (18 March 1996).

- A. Trunschke, D. L. Hoang, J. Radnik and H. Lieske, J. Catal., 57 2000 191 456
- B. M. Weckhuysen, L. M. De Ridder and R. A. Schoonheydt, 58 J. Phys. Chem., 1993, 97, 4756.
- S. De Rossi, G. Ferraris, S. Fremiotti, V. Indovina and A 59 Cimino, Appl. Catal. A: General, 1993, 106, 125.
- B. M. Weckhuysen, R. A. Schoonheydt, F. E. Mabbs and D. 60 Collison, J. Chem. Soc., Faraday Trans., 1996, 92, 2431.
- H. G. Karge, M. Laniecki, M. Ziolek, G. Onvestvak, A. Kiss, 61 P. Kleinschmit and M. Siray, in Zeolites: Facts, Figures, Future, ed. P. A. Jacobs and R. A. van Santen, Elsevier, Amsterdam, 1989, p. 1327.
- 62 F. Kapteijn, L. Singoredjo, M. van Driel, A. Andreini, J. A. Moulijn, G. Ramis and G. Busca, J. Catal., 1994, 150, 105.
- K. Eguchi, M. Watabe, S. Ogata and H. Arai, Bull. Chem. Soc. 63 Jpn., 1995, 68, 1739.
- M. Richter, H. Berndt, R. Eckelt, M. Schneider and R. Fricke, 64 Catal. Today, 1999, 54, 531.
- 65 U. Bentrup, A. Brückner, M. Richter and R. Fricke, Appl. Catal. B: Environmental, 2001, 32, 229.
- A. Brückner, U. Bentrup, J. Radnik, M. Richter and R. Fricke, 66 4th Tokyo Conference on Advanced Catalytic Science and Technology (TOCAT), July 14th-19th, 2002.
- Z. Levi, M. Raitsimring and D. Goldfarb, J. Phys. Chem., 1991, 67 95, 7830.