In situ investigation of active sites in zirconia-supported chromium oxide catalysts during the aromatization of n-octane

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Dedicated to Professor Dr. Manfred Baerns on the occasion of his 65th birthday

Supported chromium oxide catalysts containing 0.5 and 4.0 wt% Cr, respectively, on a 7 wt% La_2O_3/ZrO_2 carrier were studied by *in situ* EPR equipped with on-line GC during the catalyst pretreatment in flowing H_2 and the aromatization of n-octane in the range $293 < T < 823$ K. Active catalysts contain almost exclusively Cr^{3+} in the form of Cr_2O_3 clusters and isolated, coordinatively unsaturated Cr^{3+} species on the surface. The latter appear to be less sensitive to poisoning by coke deposition and govern residual catalytic activity.

Keywords: *in situ* EPR, chromium oxide catalysts, n-octane aromatization, catalyst deactivation, coke deposition

1. Introduction

Supported chromium oxides are well known as catalysts in a number of reactions [1]. Besides TiO_2, Al_2O_3 and SiO_2, also ZrO_2 has been used as a support material due to its beneficial thermal stability and the particular redox and acid–base properties of the surface [2–5]. While polymerization, hydrogenation, and dehydrogenation of hydrocarbons have been extensively studied over these catalysts (see, e.g., [5–7]), only few investigations of hydrocarbon aromatization have been published so far [8,9]. Thus, aromatization of hexane over Cr_2O_3/ZrO_2 catalysts led to markedly higher benzene selectivities than obtained with common reforming catalysts based on supported noble metals [8]. It has been shown that also other aliphatics such as octane can be dehydrocyclisized with high selectivities using chromia–zirconia catalysts [10].

There is general agreement, that chromium ions are constituents of the active sites in these catalysts. However, their coordination and valence state and, in particular, their behaviour in the catalytic reaction are still ambiguous. Thus, isolated, coordinatively unsaturated Cr^{3+} surface species have been regarded as active sites for isobutane and propane dehydrogenation [3,6]. Any participation of Cr^{2+} was excluded for these reactions. In another investigation, the interconversion of different chromium oxidation states has been studied probing the catalyst surface by selective reduction and oxidation experiments. Thus, two distinct redox couples, Cr^{3+}/Cr^{5+} and Cr^{2+}/Cr^{6+}, were identified [11]. In the aromatization of hexane, both Cr^{3+} as well as Cr^{4+} ions were assumed to be active, although no further information on their particular coordination was given [8,9].

The above conclusions were mostly obtained from investigations of catalysts before and after usage in the catalytic reactions. The resulting lack of information on their behaviour under reaction conditions is presumably a reason for the discrepancies in the described results. Thus, it is necessary to investigate the nature of active species by *in situ* methods, which provide more insight into the details of the catalytic reaction. In this work changes of the state of the chromium sites on a zirconia-based support during the aromatization of octane have been studied for the first time by *in situ* EPR. In addition, XPS measurements of the quenched active surface after appropriate treatment in a reaction chamber were performed.

2. Experimental

2.1. Catalyst preparation

Catalysts were prepared by impregnating a commercial 7 wt% La_2O_3/ZrO_2 support (MEL-CAT XZ0681/01, MEL Chemicals) with aqueous solutions containing the appropriate amount of $(NH_4)_2CrO_4$ so as to yield samples with 0.5 (sample Cr-0.5) and 4.0 wt% Cr (sample Cr-4.0). Before immersing in the $(NH_4)_2CrO_4$ solution, the support was dried at 120 °C for 12 h in air. By ammonia addition, the solution pH was kept at 10. Under stirring, the excess water was slowly evaporated at 50–60 °C. The obtained products were then dried at 120 °C for 12 h and, finally, calcined in air at 600 °C for 4 h. By XRD measurements no crystalline Cr-containing phases were detected. All products were kept dry till further use.

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2.2. EPR measurements

EPR spectra were recorded by the c.w. spectrometer ELEXSYS 500-10/12 (Bruker) in X-band. *In situ* investigations under catalytic reaction conditions were performed using a home-made flow reactor which was placed into the cavity of the spectrometer [12]. The reactor was equipped with a temperature programmer. The respective feed composition and the gas flow through the sample tube were adjusted by a system of mass flow controllers and a thermostated saturator. In each run, 250 mg catalyst particles (0.5–1 mm) were treated with a total gas flow of 1.75 $\mathrm{l\,h^{-1}}$ consisting of 0.6 mol% octane (unless stated otherwise) and varying amounts of H_2 and N_2 in the range $293 < T < 823$ K. In certain cases, the catalysts have been pre-treated for 1 h at 823 K in flowing hydrogen since hydrogen treatment is known to suppress rapid deactivation due to coke formation [3]. For on-line product analysis the reactor outlet was connected to a GC 17AAF capillary gas chromatograph (Shimadzu) equipped with a 25 m × 0.25 mm SE-54-CB column and a FID. Simulation of the EPR spectra was done using the computer program of Lozos et al. [13].

2.3. XPS measurements

X-ray photoelectron spectra were obtained by a VG ESCALAB 220 iXL spectrometer (VG Instruments) at room temperature with a Mg Kα source operating at 20 mA and 13 kV. The residual pressure inside the analysis chamber was below 2×10^{-9} mbar. The spectra were corrected with respect to the O 1s signal at 530.5 eV since the binding energy of the O 1s signal of the support was found to be not influenced by treatment with hydrogen. The normalized intensities of the different signals were calculated by multiplying the relative area of the corresponding peaks by the sensitivity factors. With the exception of a Cr-4.0 sample which was removed from the EPR flow reactor after heating in 0.6 mol% octane/N_2 at 773 K, all spectra were recorded after appropriate treatment in the reactant gas mixture at ambient pressure and elevated temperatures using a reaction cell installed in the lock to the analysis chamber (pressure in the lock was below 3×10^{-6} mbar). After subsequent cooling to room temperature the samples were transferred into the analysis chamber of the spectrometer without contact to ambient atmosphere. In due course XPS measurements performed in this way are labelled *in situ*, although the data acquisition itself was performed at room temperature in high vacuum.

3. Results

The EPR spectra of the two as-synthesized catalysts Cr-4.0 and Cr-0.5 show the characteristic γ-signal of isolated axially symmetric Cr^{5+} ions (figures 1 (a), (b) and 2(a)). For Cr-0.5, spectra simulation shown in figure 1(a) resulted

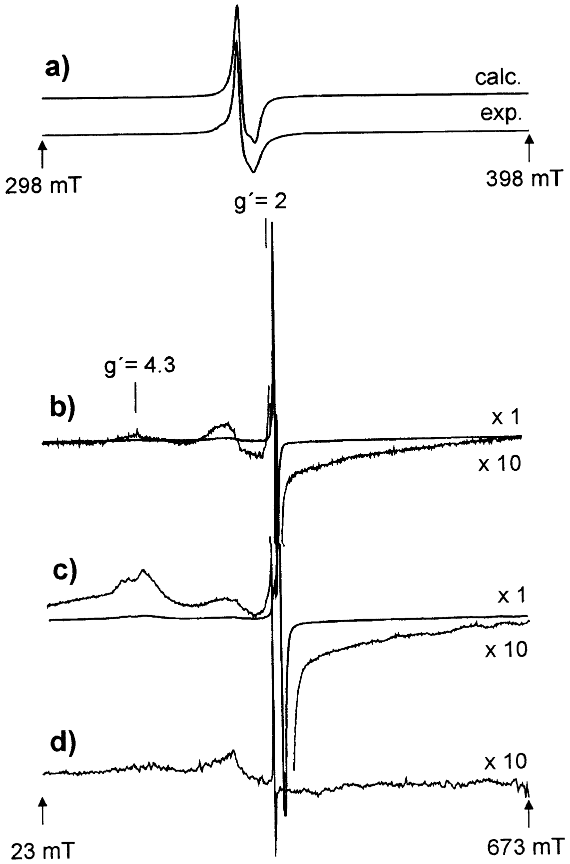

Figure 1. EPR spectra at 293 K of sample Cr-0.5: (a, b) as-synthesized; (c) after 1 h pre-treatment in flowing H_2 at 823 K without subsequent contact to air; (d) after 2 h at 773 K and 1 h at 803 K in 0.6 mol% octane/17 mol% H_2/N_2 without subsequent contact to air.

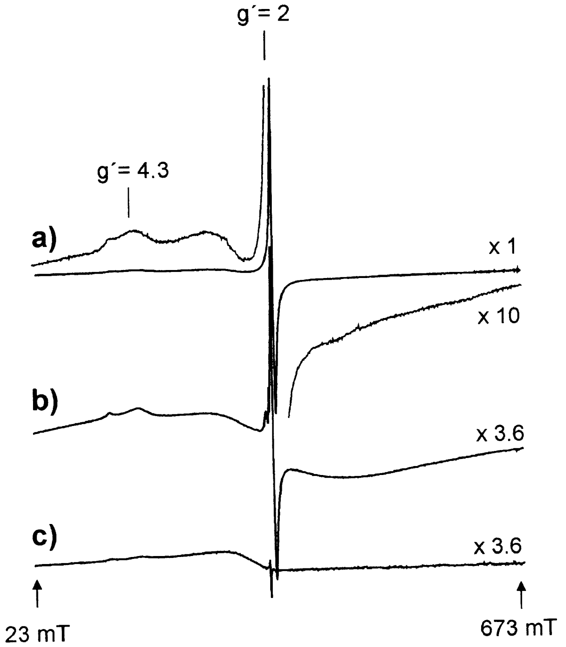

Figure 2. EPR spectra at 293 K of sample Cr-4.0: (a) as-synthesized; (b) after 1 h pre-treatment in flowing H_2 at 823 K without subsequent contact to air; (c) after 2 h reaction in 0.6 mol% octane/17 mol% H_2/N_2 at 773 K without subsequent contact to air.

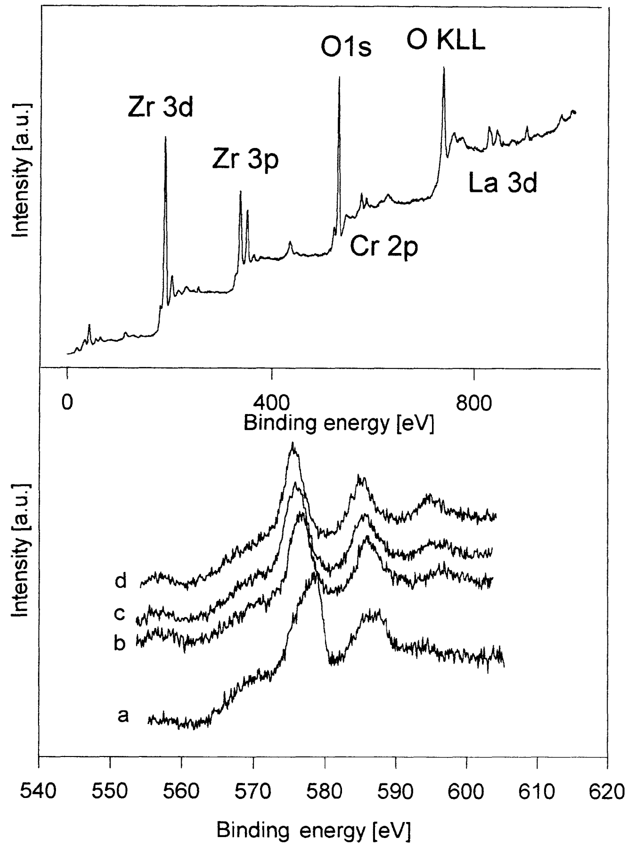

Figure 3. Overall *in situ* XPS spectrum of sample Cr-4.0 after 1 h pre-treatment in flowing H_2 at 823 K (above) and *in situ* XPS spectra of the Cr 2p signals (below): (a) as-synthesized; (b) after 1 h pre-treatment in flowing H_2 at 823 K; (c) after 2 h at 873 K in 11.5 mol% octane/N_2; (d) after 8 h at 873 K in 11.5 mol% octane/N_2.

in the g-tensor values $g_{||} = 1.959$ and $g_{\perp} = 1.978$ which agree well with those found for Cr^{5+} on CrO_x/ZrO_2 catalysts [11]. The γ-signal intensity is approximately inversely proportional to the temperature, as expected according to the Curie–Weiss law for pure paramagnetic behaviour. Besides the γ-signal of Cr^{5+}, two broad lines can be seen in the EPR spectra of both as-synthesized samples Cr-4.0 and Cr-0.5 after suitable amplification at $g = 2$ (β-signal) and $g' = 4.3$ (δ-signal) (figures 1(b) and 2(a)). They are assigned to magnetically interacting Cr^{3+} ions in Cr_2O_3 clusters and to isolated coordinatively unsaturated Cr^{3+} ions on the surface, respectively [6,14]. After deconvolution of the chromium peaks in the XPS spectrum of the as-synthesized sample Cr-4.0 (figure 3(a)) it turned out that the total chromium content on the surface consists of 61% Cr^{6+} evidenced by a $2p_{3/2}$ binding energy of 578.7 eV (table 1). The remaining 39% are due to low-valent Cr species (mainly Cr^{3+}), as indicated by a binding energy of 576.6 eV [9]. This is compatible with the EPR spectrum

Table 1
Results of the *ex situ* XPS measurements of sample Cr-4.0.

Treatment	Signal	Binding energy (eV)	Surface (at%)
As-synthesized	Cr $2p_{3/2}$	576.6, 578.7	2.3
	Zr $3d_{5/2}$	188.6	19.6
	O 1s	530.5	74.2
After EPR experiment (figure 5)	Cr $2p_{3/2}$	577.4	0.61
	Zr $3d_{5/2}$	182.7	15.9
	O 1s	530.5	51.4
	C 1s	285.1	30.2

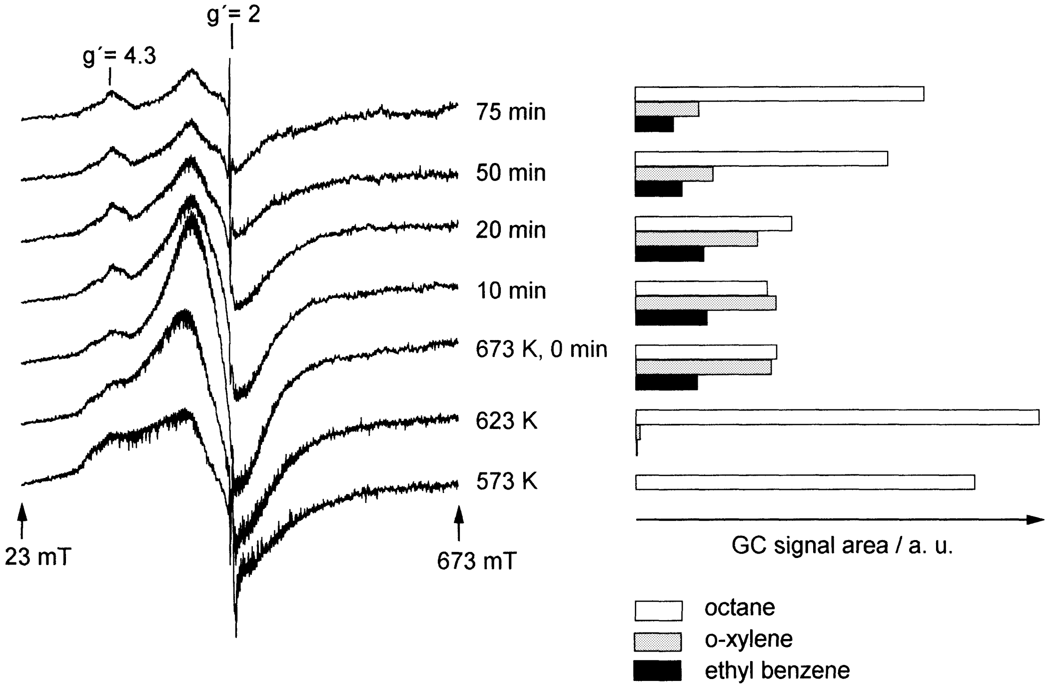

Figure 4. EPR spectra of sample Cr-0.5 during the catalytic reaction in 0.6 mol% octane/N_2 and on-line GC signal areas of the product mixture (for more clarity only the GC signal areas of octane and the two main products *o*-xylene and ethylbenzene are shown).

of as-synthesized Cr-4.0 confirming the presence of Cr^{3+} and traces of Cr^{5+} (figure 2(a)).

Upon heating sample Cr-0.5 in a flow of 0.6 mol% octane/N_2 the EPR γ-signal of Cr^{5+} disappears immediately above 533 K and β- and δ-signals increase markedly indicating the formation of Cr^{3+} species (figure 4). The intensity of the β-signal passes a maximum at the very beginning of the catalytic reaction. This can be seen from the comparison of the spectra with the respective on-line GC signal areas. The β-signal diminishes again with time on stream accompanied by an increase of the GC signal of unreacted octane, pointing to gradual deactivation of the catalyst. A similar behaviour is observed, too, for sample Cr-4.0 (figure 5). The deactivation of the catalysts goes along with the deposition of carbon on the surface. This can be seen from the XPS spectrum of sample Cr-4.0 taken after the EPR experiment (table 1). Moreover, deactivated samples are black and show a narrow EPR signal at $g' = 2.003$ which is characteristic for coke radicals (figures 1(d) and 2(c)). Furthermore, it is evident from figure 2(c) and table 1 that the catalyst Cr-4.0 deactivated in the EPR flow reactor contains only Cr^{3+} species and a markedly lower Cr : Zr atomic ratio (Cr : Zr = 0.04) in comparison to the as-synthesized sample Cr-4.0 (Cr : Zr = 0.17).

Generally, the deactivation is enhanced with increasing reaction temperature and percentage of octane in the educt

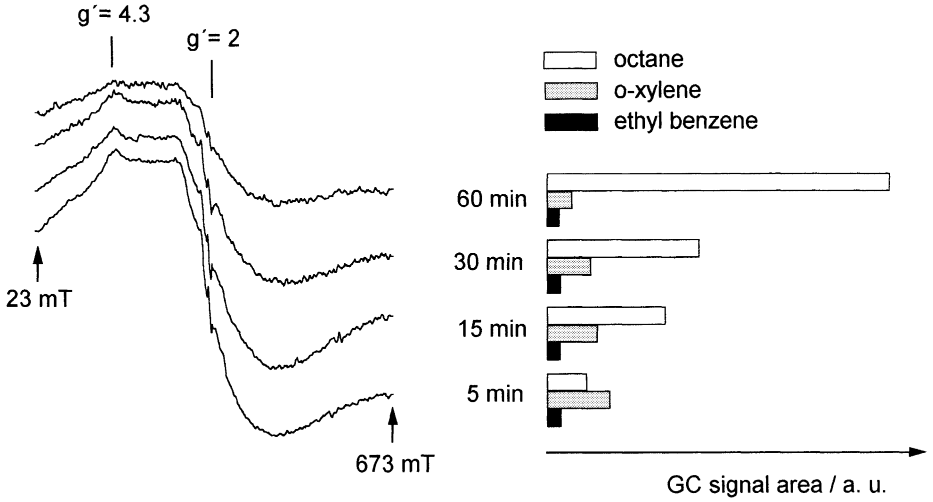

Figure 5. EPR spectra of sample Cr-4.0 during the catalytic reaction in 0.6 mol% octane/N_2 and on-line GC signal areas of the product mixture (for more clarity only the GC signal areas of octane and the two main products o-xylene and ethylbenzene are shown).

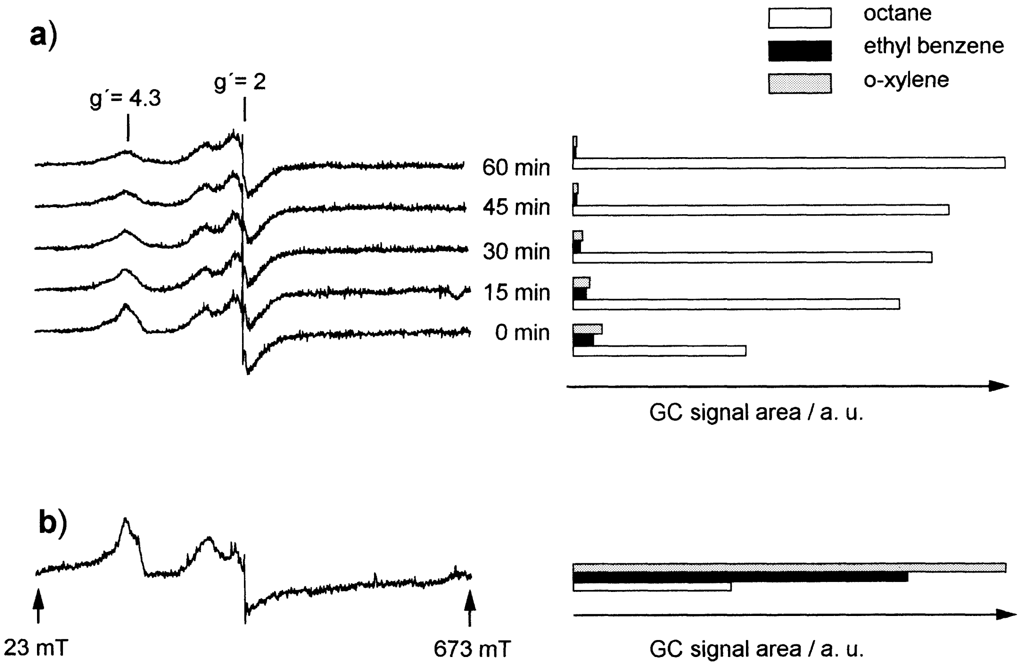

Figure 6. EPR spectra of sample Cr-0.5 and on-line GC signal areas: (a) after heating in 7.4 mol% octane/N_2 to 773 K and isothermal hold for 1 h; (b) after 2 h at 823 K in 0.6 mol% octane/82 mol% H_2/N_2.

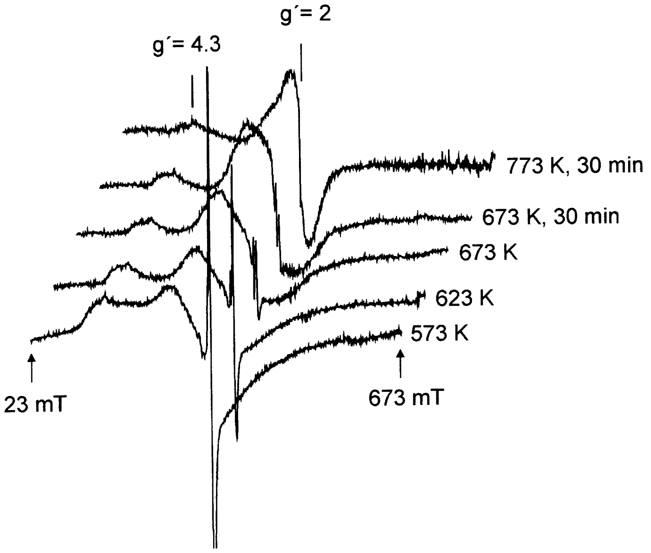

Figure 7. EPR spectra of sample Cr-0.5 during pre-treatment in flowing H_2.

feed mixture. It can be partially suppressed by excess hydrogen. Thus, the catalyst Cr-0.5 is almost completely deactivated after 1 h at 773 K in 7.4 mol% octane/N_2, while it is still working properly after 2 h at 823 K in 0.6 mol% octane/82 mol% H_2/N_2 (figure 6). Under octane-rich feed, deactivation is already dominant just after reaching 773 K and almost complete after 1 h at 773 K. It is interesting to note that the EPR β-signal of Cr_2O_3 clusters virtually does not change during this time while the δ-signal for isolated Cr^{3+} surface species decreases step by step as the catalyst also loses its residual activity (figure 6(a)). In contrast to this behaviour, the δ-signal remains well visible when the activity of the catalyst is preserved by the presence of hydrogen (figure 6(b)). Besides the addition of H_2 to the feed, pre-treatment of the catalysts in flowing hydrogen in the range $773 < T < 823$ K is another possibility to slow down the deactivation under reaction conditions. The EPR spectra of sample Cr-0.5 recorded during the pre-treatment procedure (figure 7) show similar changes as in the initial period of the catalytic reaction (figure 4). Enhancement of β- and δ-signals indicates the formation of Cr^{3+} species. However, in comparison to the δ-signal, the increase of the β-signal is more pronounced. This suggests that Cr^{3+} is preferentially arranged in the form of Cr_2O_3 clusters.

In addition to *in situ* EPR experiments, the Cr species on the surface of sample Cr-4.0 have been studied by a series of subsequent *in situ* XPS measurements. The results are summarized in figure 3. After pre-treatment in flowing H_2 (2 h, 823 K, 1.5 $\mathrm{l\,h^{-1}}$), the Cr $2p_{3/2}$ peak position is shifted to 576.4 eV. This indicates that Cr^{6+}, which is predominantly present in the as-synthesized sample Cr-4.0, has been reduced to Cr^{3+}. To stimulate deactivation, sample Cr-4.0 was then treated at 873 K in a flow of 11.5 mol% octane/N_2. In the gas mixture leaving the reaction chamber *o*-xylene and ethylbenzene besides other products were detected by off-line GC indicating that the catalyst was working. By subsequent XPS measurements after 2 and 8 h time on stream, increasing amounts of carbon were detected and the Cr $2p_{3/2}$ peak was shifted to 575.8 and 575.4 eV, respectively (figure 3 (c) and (d)). At the end of the reaction period, octane was the only component detected by off-line GC in the product mixture pointing to deactivation of the catalyst.

4. Discussion

In the as-synthesized sample Cr-4.0, the Cr content amounts to 4.0 wt% corresponding to 10 at% (based on CrO_3). Assuming that the majority of the Cr ions, due to the preparation method, is located on the support surface, a surface chromium content higher than 10 at% would have to be expected. However, the experimental value of 2.3 at% derived from XPS data is markedly lower. This indicates that only a minor part of the chromium ions is accessible on the surface. Possible reasons are diffusion into the bulk of the support or low dispersion of the chromium oxide particles. Furthermore, it is evident from the XPS results (figure 3, table 1) that the surface of the as-synthesized catalyst Cr-4.0 contains Cr^{6+} and Cr^{3+} in approximately equal amounts. However, it has to be noted that the XPS method is sensitive only to a few upper layers of the sample. Thus, conclusions concerning the overall Cr^{6+}/Cr^{3+} in sample Cr-4.0 cannot be derived by XPS. Indeed, it has been found by temperature-programmed reduction experiments that the major chromium percentage in sample Cr-4.0 is comprised by Cr^{6+} [15].

From the relative intensity of the Cr^{3+} EPR signals (figures 1(b) and 2(a)) it can be derived that a minor part of three-valent chromium is present as isolated, coordinatively unsaturated Cr^{3+} ions on the surface (δ-signal, $g' = 4.3$) while the majority of Cr^{3+} forms Cr_2O_3 clusters (β-signal, $g' = 2$). The small linewidth of the γ-signal in the spectra of both as-synthesized samples Cr-4.0 and Cr-0.5, the resolution of the g anisotropy as well as the Curie-like behaviour of the temperature dependence of the line intensity indicate that the Cr^{5+} ions responsible for this signal are well isolated from other paramagnetic species and, hence, can exist in small amounts only. This may be the reason why they do not give rise to a separate peak in the XPS spectrum of the as-synthesized sample Cr-4.0 (figure 3, table 1).

When the catalysts are heated in reducing atmosphere, i.e., either in the reactant mixture (figure 4) or in H_2 (figure 7) the initial stage of the reduction seems to be governed by the formation of both isolated (δ-signal) and cluster-like Cr^{3+} species (β-signal). As the reduction continues, only the β-signal intensity increases indicating further formation of Cr_2O_3 clusters presumably by agglomeration of isolated chromium species. In contrast to Cimino et al. [11], who proposed the redox couples Cr^{5+}/Cr^{3+} and Cr^{6+}/Cr^{2+} on the surface of ZrO_2, we have to conclude from our results that the main pathway for the formation of Cr^{3+} is the reduction of Cr^{6+}. The area of the initial Cr^{5+} signal is negligible in comparison to that of the Cr^{3+} signals formed by reduction (figures 1 and 2). Thus, it is obvious that the major part of Cr^{3+} is formed from Cr^{6+}. Moreover, the Cr^{5+} signal is still present after pre-treatment in hydrogen (figures 1(c) and 2(b)) and disappears only in the presence of octane (figures 1(d) and 2(c)). The fact that, despite its detection by EPR, Cr^{5+} is not visible as a separate peak in the XPS spectrum of sample Cr-4.0 after pre-treatment in H_2 (figure 3(b)) is another evidence for its low concentration.

With time on stream, especially at high reaction temperatures and octane percentages as well as in the absence of H_2, gradual deactivation of the catalysts takes place. This can be seen from the on-line GC signal areas showing an increasing percentage of unreacted octane in the product mixture (figures 4, 5 and 6(a)). Simultaneously, coke is deposited on the catalyst surface as indicated by the black colour of deactivated catalysts, the narrow EPR signal at $g' = 2.003$ (figures 1(d) and 2(c)) and the appearance of C 1s peaks in the XPS spectra (table 1). From table 1 it is also evident that the relative chromium content of the surface diminishes as the carbon content rises. This suggests, besides agglomeration of chromium species, that carbon is preferentially deposited on the chromium sites, thus preventing them from detection by XPS.

From the *in situ* XPS spectra (figure 3 (b)–(d)) it can further be seen that a shift of the chromium signals to lower binding energies occurs with increasing time on stream and, thus, gradual carbon deposition. After 8 h treatment in a stream of 11.5 mol% octane/N_2 at 873 K the binding energy of the Cr $2p_{3/2}$ signal is close to the value which has been published previously for Cr^{2+} [16]. The rather symmetric line shape of the signal suggests that it arises from a single type of species. However, from the EPR spectrum of the deactivated sample Cr-4.0 it is known that even after marked coking the Cr^{3+} signals do not vanish completely (figures 2(c), 5 and 6(a)). Thus, one should expect asymmetric XPS signals after deactivation pointing to the presence of different chromium species. This is, however, not the case and at least two possible explanations can be given for this phenomenon: (i) During the deactivation process coke is deposited on top of the Cr_2O_3 particles and reduces a certain part of the Cr^{3+} ions to Cr^{2+}. Reduction of Cr^{3+} by coke has been observed too with chromia–alumina catalysts [17]. Thus, the oxide layer just below the carbon deposit is assumed to contain mainly Cr^{2+} ions. It is probable that Cr^{3+} ions in deeper layers which are not exposed to reduction by carbon are no longer detected by XPS but by EPR since this method comprises the whole sample volume and not only the surface. (ii) On the other hand, electronic interaction between carbon and neighbouring Cr^{3+} ions can enhance the electron density of the latter leading in turn to a gradual change of their binding energy and, accordingly, also to a decrease of the EPR signal amplitude caused by line broadening. In any case, the results reveal a strong interaction of carbon and chromium species.

The changes of the EPR β-signal in figure 4 have been interpreted in terms of the formation of Cr_2O_3 clusters (intensity increase) and their subsequent reduction by coke (intensity decrease). It is interesting to note that the changes of the δ-signal arising from isolated Cr^{3+} surface species are markedly less pronounced. This can be seen by inspection of figures 4 and 6(a). The δ-signal decreases more slowly than the β-signal. Thus, it seems likely that cluster-like chromium oxide particles act as favoured sites for coke formation and are, therefore, more easily poisoned. This conclusion is also supported by the observation that the deactivation rate increases with the chromium loading of the catalysts. Residual catalytic activity after 75 min at 673 K in 0.6 mol% octane/N_2 (figure 4) might be mainly governed by isolated Cr^{3+} species. This interpretation is also supported by comparing the EPR spectrum of the properly working catalyst Cr-0.5 in 0.6 mol% octane/82 mol% H_2/N_2 at 823 K (figure 6(b)) with that of the deactivated one in 7.4 mol% octane/N_2 at 773 K (figure 6(a)). The δ-signal for isolated Cr^{3+} surface species is well present in the former while it disappears gradually in the latter with the loss of residual activity (figure 6). The fact that the β-signal of Cr_2O_3 clusters in figure 6(a) does not change suggests that these sites are covered by carbon deposits already in the initial stage of deactivation and are, thus, excluded from further participation in the catalytic reaction.

5. Conclusions

In properly working chromia–zirconia catalysts there exist two types of Cr^{3+} sites; Cr_2O_3 clusters and isolated, coordinatively unsaturated Cr^{3+} surface species. Probably both are constituents of active sites. In contrast, Cr^{6+} and Cr^{5+} ions present in the as-synthesized catalysts can be ruled out as active species in the aromatization of octane since they are reduced to Cr^{3+} ions at the very beginning of the reaction which are responsible for catalytic activity.

With increasing time on stream, at high reaction temperatures and high octane partial pressures and, especially in the absence of hydrogen, deposition of coke on the Cr^{3+} sites leads to gradual deactivation of the catalysts. Strong interaction of chromium and carbon species has been detected by XPS and by *in situ* EPR which can also be interpreted in terms of partial reduction of Cr^{3+} species. The deactivation is slowed down by pre-heating the catalysts in flowing hydrogen or by admixing a certain amount of hydrogen to the feed. Cluster-like Cr_2O_3 species seem to be more sensitive against poisoning by coke deposition than isolated Cr^{3+} species, which are assumed to govern residual catalytic activity.

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