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Structure and reducibility of a Fe/Al_2O_3 catalyst for selective catalytic reduction studied by Fe K-edge XAFS spectroscopy

A Boubnov[1], H Lichtenberg[1], S Mangold[2] and J-D Grunwaldt[1,*]

[1]Karlsruhe Institute of Technology (KIT), Institute for Chemical Technology and Polymer Chemistry (ITCP), Kaiserstr. 12, 76131 Karlsruhe, Germany and Institute for Catalysis Research and Technology (IKFT), Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen, Germany
[2]Karlsruhe Institute of Technology (KIT), Institute for Synchrotron Radiation (ISS), Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen, Germany

E-mail: grunwaldt@kit.edu

Abstract. EXAFS and pre-edge information from the Fe K-edge absorption spectra is used in this study to characterise the local environment and geometry of Fe-centres in a 1% Fe/Al_2O_3 model catalyst. The EXAFS results reveal clusters of 2-3 Fe oxo-moieties dispersed on the Al_2O_3-support. The Fe^{3+} centres are coordinated by 6 O-atoms in a strongly distorted octahedral geometry. This is supported by the pre-edge peak, which is far more intense than in α-Fe_2O_3 absorption data acquired for comparison. For preliminary investigations, catalytic tests for selective catalytic reduction (SCR) of NO_x by ammonia and *in situ* XANES studies of Fe/Al_2O_3 are compared with previously published data for Fe/zeolite systems. The low SCR activity of Fe/Al_2O_3 (compared to Fe/zeolite catalysts) in which the Fe^{3+} species do not change their electronic state under SCR-relevant conditions (reference temperature 250°C in our case) correlates well to the significantly higher temperatures required to reduce these species to Fe^{2+}. The difference in reducibility (and consequently in the SCR-activity) between the two systems probably results from differences in the structure and the electronic interaction of the Fe oxo-moieties and the particular catalyst support.

1. Background

Iron oxide based catalysts show a high efficiency in the selective catalytic reduction (SCR) of NO_x by ammonia and can potentially replace the environmentally harmful vanadium oxide-based catalysts [1, 2]. In order to further evaluate the potential of iron oxide-based catalysts in environmental catalysis, structure-activity relationships, i. e. correlations between structural properties and catalytic performance, have to be studied. These investigations are crucial for a fundamental understanding of the origin of catalytic activity.

This X-ray absorption spectroscopy study focuses on a model Fe/Al_2O_3 catalyst with 1% Fe loading, which was recently studied for SCR applications [3]. In Fe/Al_2O_3 systems the highly dispersed Fe^{3+} oxo-species have shown to be similar to those in previously studied Fe/zeolite catalysts [2, 4]. However, the specific catalytic activity was significantly lower [3]. First studies have also indicated that in Fe/Al_2O_3 materials the oxidation state does not change under SCR conditions, whereas Fe/zeolite catalysts show a partial reduction of Fe^{3+} to Fe^{2+} [4, 5]. Here, this issue is further addressed by identifying the structure of the Fe^{3+} clusters in the Fe/Al_2O_3 system and by studying their reducibility.

2. Experimental

The Fe/Al_2O_3 catalyst was prepared by incipient wetness impregnation of γ-Al_2O_3 with aqueous $Fe(NO_3)_3$ followed by drying and calcination at 600°C. XAFS measurements at the Fe K-edge were carried out at the ANKA synchrotron light source (Karlsruhe, Germany) at the XAS beamline using a double crystal monochromator equipped with Si(111) crystals. The monochromator was detuned to 70% of the maximum intensity for rejection of higher harmonics. The samples (catalyst and α-Fe_2O_3 as comparison reference) were mixed with cellulose, pressed into pellets, and EXAFS spectra were measured in transmission mode. For *in situ* temperature-programmed reduction (TPR) measurements, the catalyst with a sieve fraction of 100-200 µm was exposed to a flow of 5% H_2 in balance He in a capillary reactor as described previously [4-6]. Here, the XANES spectra were acquired in continuous quick-scanning XAFS mode (QXAFS, ca. 4 min/scan). XANES and EXAFS data were analysed using the Athena and Artemis extensions of IFEFFIT software [7]. The spectra were energy-calibrated and normalized. The pre-edge peak was extracted from the absorption edge by interpolating points several eV before and after the pre-edge region, similar to the method in [8]. For EXAFS data fitting the k^3-weighted EXAFS functions were Fourier-transformed in the k-range of 2.0 - 12.1 $Å^{-1}$, Fourier-filtered (R-range 1.0-2.1 Å for α-Fe_2O_3 and 1.0-3.8 Å for Fe/Al_2O_3) and fitted with single-scattering paths generated by FEFF6. In all fits an electronic amplitude reduction factor $S_0^2 = 0.86$ was used, as determined by constraining the number of O-atoms in the first shell of α-Fe_2O_3 to 6.

3. Results and Discussion

The similarity of the overall shapes of the XANES spectra of α-Fe_2O_3 and the 1% Fe/Al_2O_3 catalyst (figure 1A) indicate similar electronic structures. The coinciding positions of the absorption edges reveal that the catalyst contains trivalent iron. The pre-edge peak in the spectra corresponds to the dipole-forbidden $1s \rightarrow 3d$ transition. It gains intensity through the deviation from centrosymmetric geometry and from $3d$-$4p$ orbital mixing; its position indicates the oxidation state of iron in the sample [9]. The inset of figure 1A shows this feature in greater detail. In this case, the low intensity of the pre-edge peak for α-Fe_2O_3 matches well the slightly distorted octahedral coordination (the high-energy tail corresponds to other transitions which will not be considered [8]). The main pre-edge peak position (7114 eV) is consistent with trivalent Fe in both α-Fe_2O_3 and the catalyst. The high intensity of the pre-edge peak for the catalyst indicates either a very high degree of distortion of octahedral FeO_6-moieties or tetrahedrally-coordinated Fe^{3+} [8].

Figure 1B shows Fourier-transformed EXAFS spectra of α-Fe_2O_3 and the 1% Fe/Al_2O_3 catalyst. Both samples show Fe-O shells in the region of 1-2 Å. Further contributions appear in the interval 2-4 Å. For α-Fe_2O_3 they primarily arise from the strong backscattering of the Fe neighbours in the crystal, whereas the catalyst only shows weak features in this range: the expected neighbours at these distances would be Al atoms, which are significantly weaker backscatterers than Fe atoms. Possibly there is a smaller number of Fe atoms in this coordination shell compared to α-Fe_2O_3. Note that Fe was introduced into the system by impregnation, i.e. the Fe atoms should be mostly located on the surface of the Al_2O_3 crystallites and thus mainly have metal neighbours on one side. The formation of aluminates cannot be excluded but is usually expected at higher temperatures [10].

A derivation of the atomic structure is provided by the EXAFS data analysis presented in Table 1. Concerning the structure of α-Fe_2O_3, the focus is on the distorted octahedral FeO_6-moiety and therefore the analysis of further shells was omitted. The two calculated Fe-O bond distances at 1.92 Å and 2.07Å both with a coordination number of 3, are close to the expected values based on crystallographic data. The two Fe-O shells refined from the spectrum of the 1% Fe/Al_2O_3 catalyst summed up to a coordination number of 4.7 O, suggesting a mixture of tetrahedral and octahedral coordination. The second Fe-O bond distance (2.45 Å) differs significantly from that for α-Fe_2O_3, indicating a highly distorted geometry of the FeO_6-moieties. This is in accordance with the information provided by the pre-edge peak discussed above. Further EXAFS contributions in the 1% Fe/Al_2O_3 are assigned to Fe-Al and Fe-Fe shells (table 1). The Fe-Al contributions in the catalyst data indicate that Fe_xO_y clusters are well dispersed on or partly incorporated into the Al_2O_3 surface (Fe-Al coordination numbers of 1.9, note the rather weak backscattering). A Fe-Fe coordination number of 1-2 suggests that the clusters are likely a mixture of binuclear and oligonuclear clusters. This is also supported by UV-vis measurements [3]. A binuclear cluster which might be present among other structures derived from the EXAFS analysis is shown in figure 1C. The large variation of the Fe-O bond distances may originate from the fact that some of the O-atoms form bonds between the metal ions (Fe, Al), while others point away from the Al_2O_3 surface as oxo- or hydroxyl-groups.

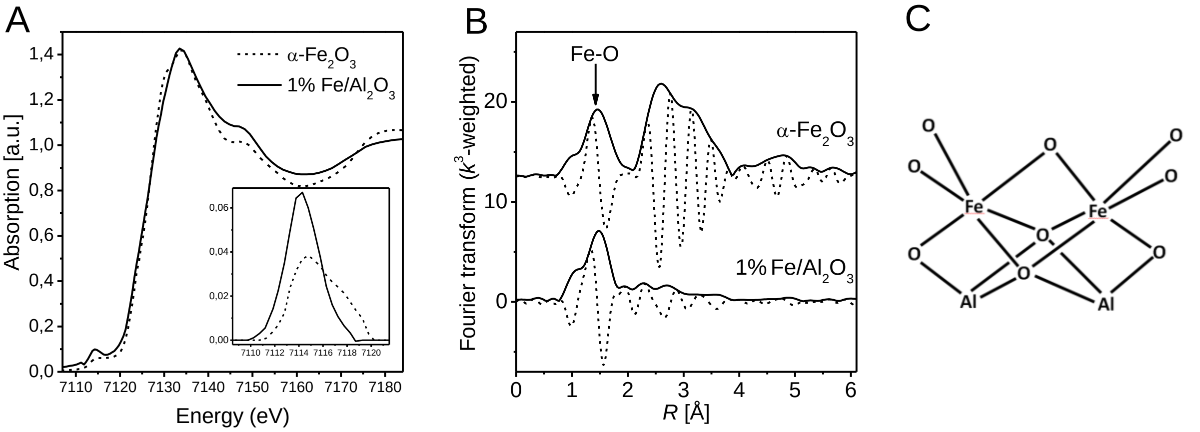

Figure 1. (A) XANES spectra of α-Fe_2O_3 and 1% Fe/Al_2O_3 catalyst with extracted pre-edge feature as inset. (B) Corresponding Fourier transformed EXAFS spectra. Solid line: magnitude; dashed line: imaginary part. (C) Suggested structure of a binuclear iron oxo-cluster based on the EXAFS analysis of 1% Fe/Al_2O_3.

Table 1. EXAFS analysis results α-Fe_2O_3 (only first shell analysis for α-Fe_2O_3) and of 1%Fe/Al_2O_3 (Debye-Waller factor of Fe-Al was constrained to 0.008)

Sample	Path	*d* [Å]	CN	σ^2 [$Å^2$]	ΔE_0, R-factor
α-Fe_2O_3	Fe-O	1.92	3	0.005	-5.1 eV, 0.029
	Fe-O	2.08	3	0.008	
1% Fe/Al_2O_3	Fe-O	1.92	2.8	0.004	-9.5 eV, 0.17
	Fe-O	2.45	1.9	0.004	
	Fe-Al	3.28	1.9	0.008	
	Fe-Fe	3.42	1.1	0.010	

The *in situ* XANES spectra during the TPR of the 1% Fe/Al_2O_3 catalyst are shown in figure 2A. The noise level in these spectra is higher since they were acquired in the QXAFS mode. Nevertheless they clearly reveal the trends of interest. The shift of the pre-edge peak (inset of figure 2A) from 7114 eV to 7112 eV and the absorption edge shift by 5 eV to lower energy are evidence of the reduction of Fe^{3+} to Fe^{2+}. The presence of isosbestic points at *e.g.* 7130 eV and 7155 eV indicates that only two types of species are involved in this transformation. The metallic state of Fe is not observed in this experiment (absorption edge of metallic Fe is at 7112 [11]), supporting the observation of the Fe oxo-clusters being well-dispersed and stabilised against sintering and therefore full reduction.

The results of linear combination fitting (figure 2B; reference spectra: first and last spectrum of the series) illustrate the reduction profile, with the onset of significant structural changes taking place above ca. 350°C. Fe^{3+} species are mainly reduced to Fe^{2+}-species. This temperature range is much higher than the reduction temperatures reported for Fe/zeolite systems [4, 5], which can be correlated to the significantly lower SCR-activity of the Fe/Al_2O_3 system at 250°C compared to Fe/zeolite. The reduction profile in terms of the Fe^{3+}-fraction of a Fe/BEA zeolite studied in [4] is also shown in figure 2B to support this hypothesis. The turnover frequency of selective catalytic reduction of NO at ca. 250°C was more than an order of magnitude higher over Fe/BEA (compared to Fe/Al_2O_3), accompanied by half of the Fe in a reduced state (Fe^{2+}) at this temperature.

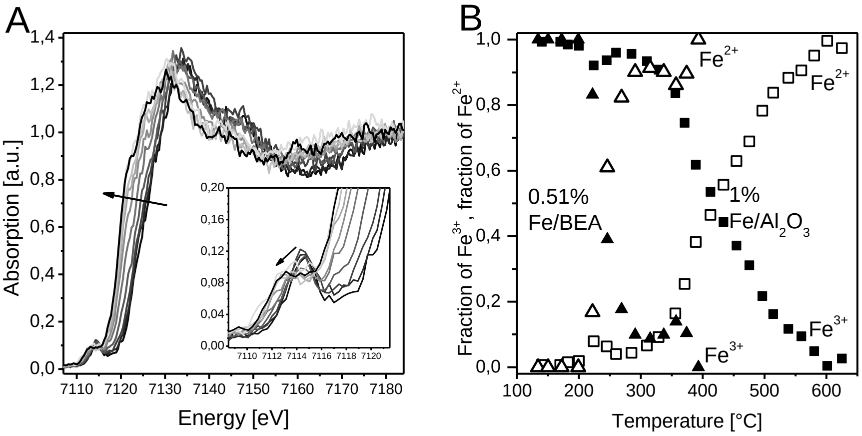

Figure 2. (A) Rapid *in situ* XANES spectra of the 1% Fe/Al_2O_3 catalyst during hydrogen-TPR: selected spectra collected in the temperature range 130°C-625°C. Inset shows details of the pre-edge feature from the same spectrum series (not extracted). (B) Results of linear combination fitting (1% Fe/Al_2O_3 and 0.51% Fe/BEA zeolite for comparison) of the initial and final XANES spectra in the series (cf. text).

4. Conclusion

This study shows that the reducibility of Fe in the present Fe/Al_2O_3 system is significantly lower than that in known Fe/zeolite systems, possibly due to the tight attachment to the Al_2O_3 matrix. The structure of iron on alumina was analysed in detail using XANES and EXAFS spectroscopy. The SCR-activity seems to be strongly influenced by the attachment of iron (and the support itself).

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