Structure and reducibility of a Fe/Al₂O₃ catalyst for selective catalytic reduction studied by Fe K-edge XAFS spectroscopy

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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/Al₂O₃ model catalyst. The EXAFS results reveal clusters of 2-3 Fe oxo-moieties dispersed on the Al₂O₃-support. The Fe³⁺ 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-Fe₂O₃ absorption data acquired for comparison. For preliminary investigations, catalytic tests for selective catalytic reduction (SCR) of NOₓ by ammonia and in situ XANES studies of Fe/Al₂O₃ are compared with previously published data for Fe/zeolite systems. The low SCR activity of Fe/Al₂O₃ (compared to Fe/zeolite catalysts) in which the Fe³⁺ 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 Fe²⁺. 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 NOₓ 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/Al₂O₃ catalyst with 1% Fe loading, which was recently studied for SCR applications [3]. In Fe/Al₂O₃ systems the highly dispersed Fe³⁺ 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/Al₂O₃ materials the oxidation state does not change under SCR conditions, whereas Fe/zeolite catalysts show a partial reduction of Fe³⁺ to Fe²⁺ [4, 5]. Here, this issue is further
addressed by identifying the structure of the Fe$^{3+}$ clusters in the Fe/Al$_2$O$_3$ system and by studying their reducibility.

2. Experimental

The Fe/Al$_2$O$_3$ catalyst was prepared by incipient wetness impregnation of γ-Al$_2$O$_3$ 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$_2$O$_3$ 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 $k^2$-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$_2$O$_3$ and 1.0-3.8 Å for Fe/Al$_2$O$_3$) 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$_2$O$_3$ to 6.

3. Results and Discussion

The similarity of the overall shapes of the XANES spectra of α-Fe$_2$O$_3$ and the 1% Fe/Al$_2$O$_3$ 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$_2$O$_3$ 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$_2$O$_3$ 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$_2$O$_3$ and the 1% Fe/Al$_2$O$_3$ 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$_2$O$_3$, 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$_2$O$_3$. 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$_2$O$_3$ 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$_2$O$_3$, 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 2.07 Å 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$_2$O$_3$ 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$_2$O$_3$, 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/Al₂O₃ are assigned to Fe-Al and Fe-Fe shells (table 1). The Fe-Al contributions in the catalyst data indicate that Fe₃O₄ clusters are well dispersed on or partly incorporated into the Al₂O₃ surface (Fe-Al coordination numbers of 1.9, note the rather weak backscattering). A Fe-Fe bond distance 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 Al₂O₃ surface as oxo- or hydroxyl-groups.

![Figure 1.](image)

**Figure 1.** (A) XANES spectra of α-Fe₂O₃ and 1% Fe/Al₂O₃ 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/Al₂O₃.

| Sample       | Path | d [Å] | CN  | σ² [Å²] | ΔE₀ [eV] | R-factor |
|--------------|------|-------|-----|---------|---------|----------|
| α-Fe₂O₃      | Fe-O | 1.92  | 3   | 0.005   | -5.1 eV | 0.029    |
|              | Fe-Fe| 2.08  | 3   | 0.008   |         |          |
| 1% Fe/Al₂O₃  | Fe-O | 1.92  | 2.8 | 0.004   | -9.5 eV | 0.17     |
|              | Fe-Fe| 3.28  | 1.9 | 0.008   |         |          |

The in situ XANES spectra during the TPR of the 1% Fe/Al₂O₃ 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 Fe³⁺ to Fe²⁺. 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. Fe³⁺ species are mainly reduced to Fe²⁺-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/Al₂O₃ 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$_2$O$_3$), accompanied by half of the Fe in a reduced state (Fe$^{2+}$) at this temperature.

![Figure 2](image)

Figure 2. (A) Rapid in situ XANES spectra of the 1% Fe/Al$_2$O$_3$ 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$_2$O$_3$ 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$_2$O$_3$ system is significantly lower than that in known Fe/zeolite systems, possibly due to the tight attachment to the Al$_2$O$_3$ 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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