Towards advanced structural analysis of iron oxide clusters on the surface of γ-Al$_2$O$_3$ using EXAFS

Alexey Boubnov [a,b], Andreas Roppertz [c], Matthew D. Kundrat [d], Stefan Mangold [e], Boris Reznik [f], Christoph R. Jacob [d,g], Sven Kureti [c], Jan-Dierk Grunwaldt [a,b,*]

[a] Institute for Chemical Technology and Polymer Chemistry, Karlsruhe Institute of Technology, Kaiserstr. 12, D-76131 Karlsruhe, Germany
[b] Institute of Catalysis Research and Technology, Karlsruhe Institute of Technology, Hermann-von-Helmholtz-Platz 1, D-76344 Eggenstein-Leopoldshafen, Germany
[c] Institute of Energy Process Engineering and Chemical Engineering, Chair of Reaction Engineering, Technical University of Freiberg, Fuchsmuehlenweg 9, D-09599 Freiberg, Germany
[d] Center for Functional Nanostructures and Institute of Physical Chemistry, Karlsruhe Institute of Technology, Kaiserstr. 12, D-76131 Karlsruhe, Germany
[e] Institut für Beschleunigerphysik und Technologie (IBPT), Karlsruhe Institute of Technology, Hermann-von-Helmholtz-Platz 1, D-76344 Eggenstein-Leopoldshafen, Germany
[f] Institute of Applied Geosciences, Karlsruhe Institute of Technology, Kaiserstr. 12, D-76131 Karlsruhe, Germany
[g] Institute of Physical and Theoretical Chemistry, TU Braunschweig, Hans-Sommer-Str. 10, D-38106 Braunschweig, Germany

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ABSTRACT

Iron oxide centres are structurally investigated in 0.1% Fe/γ-Al$_2$O$_3$, which is known as highly active catalyst, for instance in the oxidation of CO. The sample was characterised by using X-ray absorption spectroscopy (XAS) in terms of X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS), Mössbauer spectroscopy, X-ray diffraction (XRD) and transmission electron microscopy (TEM). These analyses evidenced high dispersion of the iron oxide entities without significant presence of bulk-like aggregates associated with the low Fe content of the catalyst. A library of structural models of Al$_2$O$_3$-supported surface Fe was created as input for EXAFS fitting. Additionally, several model structures of Fe substituting Al ions in bulk γ-Al$_2$O$_3$ were created with optimised geometry based on density-functional theory (DFT) calculations. From EXAFS refinement of the best 8 out of 24 models, it was found that the trivalent Fe ions are coordinated by 4–5 oxygen atoms and are located on octahedral lattice sites of the exposed surfaces of γ-Al$_2$O$_3$. These iron oxide species exist mainly as a mixture of monomeric and binuclear species and due to the low concentration represent suitable model systems as alternative to single crystal systems for structure-function relationships.

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1. Introduction

Harmful emissions from vehicles and industry can be reduced by using catalytic after-treatment processes. Iron oxide-based zeolite-supported catalysts are commercially applied for the abatement of nitric oxide (NO) and nitrogen dioxide (NO$_2$) from lean-burn engines [1–7] and decomposition of nitrous oxide (N$_2$O), e.g. from nitric acid production [8].

Due to their high efficiency, low cost and low environmental impact during production alumina-supported iron oxide catalysts (Fe/Al$_2$O$_3$) are prospective candidates for exhaust gas after-treatment. Fe/Al$_2$O$_3$ catalysts are active in the removal of NO$_x$ according to the selective catalytic reduction (SCR) with NH$_3$ but also alternative reducing agents like ethanol [9,10]. Additionally, Fe/Al$_2$O$_3$ catalysts are known to be effective for the oxidation of CO [11,12] with substantial activity for aggregated iron oxide entities [13,14]. Also, strongly clustered iron oxides are reported as active catalysts for soot oxidation [15]. However, for practical long-term performance, the susceptibility of Fe/Al$_2$O$_3$ to sulphur poisoning has to be taken into account; the desulphurisation of such catalysts seems feasible [16,17].

Furthermore, different synthesis procedures such as wet impregnation and flame spray pyrolysis [11,18] as well as load of Fe strongly affect the distribution of the iron sites onto the Al$_2$O$_3$ support, which drives the catalytic performance. For instance, high loadings of Fe result in haematite-like aggregates with high surface area, whereas low contents of iron lead to highly dispersed

iron oxide entities [9]. For SCR, it is well-known that the catalytic activity is closely related to the number of Fe sites with high dispersion, particularly isolated centres and oligonuclear clusters [19,20], whereas strongly aggregated moieties reveal rather little activity [4,10]. Furthermore, the interaction of the Fe sites with respective substrate also affects catalytic efficiency, for instance in low- and high-temperature SCR [21]. However, exact locations of highly-dispersed active iron centres on the support are poorly known.

The structure of iron oxide entities can be unravelled by X-ray absorption fine structure (EXAFS) by determining bond distances and coordination numbers. Analysis is typically based on standards of bulk crystalline substances [22] or molecular coordination compounds [23,24], where models are constructed to resemble the local atomic arrangement of the sample studied. However, for supported heterogeneous catalysts, individual molecular models must be considered to account for metal ions immobilised on the substrate.

Nevertheless, the local atomic order of highly-dispersed iron oxide moieties present in catalysts, e.g. Fe/ZSM-5 [1,25–29], Fe/MCM-41 [30] and Fe/Al$_2$O$_3$ [31,32], is often modelled by using bulk oxides such as α-Fe$_2$O$_3$ neglecting the interaction of Fe with the support. As a consequence, large and strongly varying correction terms (such as the ΔE_0) are required to obtain a statistically reliable EXAFS fit. The use of bulk oxides is well-justified if only the first Fe-O shell is analysed [19]. Contrary, more accurate structural models are reported for Fe/ZSM-5 zeolite by combination of EXAFS analysis with density functional theory (DFT) calculations suggesting the existence of monomeric and dimeric Fe oxo clusters [33,34]. Additionally, the interaction of Fe sites with the support is also discussed for Fe/Al$_2$O$_3$ samples based on EXAFS studies [35].

Therefore, the present paper deals with the systematic development of structural models of the iron oxide species present in Fe/Al$_2$O$_3$ to elucidate their structure and preferential locations on the γ-Al$_2$O$_3$ support. For this purpose, a library of structures is constructed by DFT calculations assuming the exchange of lattice Al ions by Fe as well as iron oxide clusters placed on exposed alumina surfaces. The Fe species on the catalyst surface are systematically characterised by X-ray diffraction (XRD), transmission electron microscopy (TEM), X-ray absorption near-edge structure (XANES) and Mössbauer spectroscopy. Basically, iron oxide clusters can be deposited on single crystal Al$_2$O$_3$ surfaces [36], but in this work high dispersion has been achieved by preparing a Fe/Al$_2$O$_3$ sample with low Fe content using a wet impregnation method.

2. Experimental

2.1. Catalyst synthesis

The 0.1% Fe/Al$_2$O$_3$ catalyst was prepared by incipient wetness impregnation of γ-Al$_2$O$_3$ powder (Sasol, calcined at 600 °C; BET surface area: 184 m^2/g) with an aqueous solution of ferric nitrate nonahydrate (Sigma-Aldrich) resulting in a total Fe loading of 0.1 wt.%. The powder samples were dried and calcined at 500 °C in air. In order to produce a sample for ^{57}Fe Mössbauer spectroscopy the synthesis protocol was repeated with an iron nitrate precursor prepared by dissolving ^{57}Fe (enrichment $\geq$90%, Campro Scientific) in nitric acid. This sample is denoted as 0.1% ^{57}Fe/Al$_2$O$_3$.

2.2. Catalytic activity

The CO oxidation activity of the 0.1% Fe/Al$_2$O$_3$ catalyst was exemplarily studied. The tests were made on a laboratory bench using a fixed-bed quartz glass tube reactor (ID = 8 mm). The feed consisted of 500 ppm CO, 5% O$_2$, 5% H$_2$O and N$_2$ as balance and was adjusted at a total flow rate of 500 mL/min (space velocity: 25,000 h^{-1}), while using a catalyst mass of 1.0 g. Two K-type thermocouples located directly in front of and behind the catalyst bed ensured isothermal conditions. The reactor effluents were continuously checked by a FTIR gas analyser (Multigas 2030, MKS Instruments), whereas the concentrations were recorded under stationary conditions. The catalytic tests showed starting CO oxidation at 200 °C with a CO conversion of 10%, while total conversion was observed at 250 °C and above. The 0.1% Fe/Al$_2$O$_3$ catalyst was used in present work, since its Fe sites reveal highest turnover frequencies in CO oxidation as derived from a systematic study implying Fe loads from 0.02 to 25 wt.%.

2.3. X-ray diffraction

X-ray powder diffraction (XRD) patterns were acquired on a Bruker D8 Advance diffractometer with Ni-filtered CuKα radiation (λ = 1.54 Å). The analyses were made in 2θ range from 20 to 80° at an acceleration voltage of 40 kV and an anode current of 35 mA. The (440) reflection of the γ-Al$_2$O$_3$ substrate was fitted with a Lorentzian shape peak function for determining the lattice spacings d_{hkl} and the average crystallite sizes D_{ave} according to Bragg's law $d_{hkl} = \lambda/(2\sin\theta)$ and the Debye-Scherrer equation $D_{ave} = 0.9 \cdot \lambda/(\beta\cos\theta)$ respectively, where λ is the wavelength of the X-rays, 2θ the scattering angle, and β is the FWHM of the reflection in radians. The scattering angle and FWHM of the 5 other reflections were calculated from the parameters obtained using the (400) reflection. The shape of the reflections was approximated as pure Lorentzian due to the fact that the diffractometer is able to resolve peaks much narrower than those characteristic for γ-Al$_2$O$_3$.

2.4. Transmission electron microscopy

The structure and morphology of the γ-Al$_2$O$_3$ support were studied by transmission electron microscopy (TEM) using a Philips CM200 FEG microscope operated at 200 kV acceleration voltage. The powder sample was dispersed in acetone in an ultrasonic bath and deposited on a lacy carbon copper TEM grid. High resolution TEM (HRTEM) images were recorded with a CCD camera at a magnification corresponding to pixel resolution of 10 pixels per Å. The images were processed using the ImageJ software [37]. Several well-resolved particles were selected and a fast Fourier transform was applied to analyse the periodicity and direction of the lattice planes visible in the image. From the lattice distances determined in Fourier-space the lattices were identified in terms of their Miller indices.

2.5. Mössbauer spectroscopy

Mössbauer spectra were recorded under ambient conditions using a conventional spectrometer equipped with a ^{57}Co source (3.7 GBq) in a Rh matrix. The sample was inserted inside an Oxford Instruments Mössbauer-Spectromag 4000 Cryostat, where temperatures as low as 3 K could be achieved by pumping the sample space. The spectra were recorded in constant-acceleration mode in the velocity range between −11 mm/s and +11.0 mm/s at 3 K, 200 K and 300 K. Isomer shifts are given relative to α-Fe at room temperature.

2.6. X-ray absorption spectroscopy

X-ray absorption spectra at the Fe K-edge (7112 eV) were recorded at the ANKA synchrotron light source (Karlsruhe, Germany) at the XAS beamline using a double crystal monochromator equipped with Si(111) crystals. The ANKA storage ring is operated at an electron energy of 2.5 GeV and currents of 80–160 mA. The monochromator was detuned to 70% of the maximum intensity for rejection of higher harmonics. X-ray absorption