

K β -detected XANES of Framework-substituted FeZSM-5 Zeolites

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Introduction

Oxygen transfer reactions are very important in catalysis, as they are in nature. A wide range of transition metals are able to catalyze such reactions. The activity, selectivity, and stability of the catalytically active species depend strongly on their structure and local environment. Zeolites have proven to be good hosts for active species of transition metals. The metal elements can be introduced either during the zeolite synthesis or through post-synthesis treatments. The activation of an initially iron-framework-substituted FeZSM-5 zeolite mostly yields a very heterogeneous system. When the zeolite is heated in a flow of air or oxygen (calcination), especially in the presence of water vapor (steaming), the iron (originally in the tetrahedral sites of the zeolite structure [MFI type]) is extracted into extra-framework positions. The current techniques employed for the characterization of FeZSM-5 are not well-suited for determining the ratio of iron in a tetrahedral (framework) coordination site to iron in an octahedral (extra-framework) coordination site [1].

We use K β -detected x-ray absorption near-edge spectroscopy (XANES) to quantitatively probe the local symmetry of Fe. The pre-edge feature of the Fe K-edge x-ray absorption spectrum is sensitive to the electronic structure of the iron site. The main requirements for a quantitative determination of changes in the coordination of iron made on the basis of variations in the pre-edge features are (1) high-resolution spectra, so that characteristic features in the pre-edge are well resolved; (2) precise isolation of the pre-edge structure from the main edge, which requires a proper background subtraction; and (3) the choice of relevant parameters to describe the pre-edge characteristics.

In this work, we measure XANES pre-edge spectra by using the fluorescence emission that occurs when a 1s core hole is filled after a 1s photoexcitation (K-edge x-ray absorption). The x-ray emission upon the decay of a 3p electron to fill the 1s hole is measured with K β fluorescence spectroscopy. By using a high-resolution fluorescence detector, it is possible to measure the Fe K β region with approximately 1.0-eV resolution [3].

Methods and Materials

The K β -detected XANES spectra were measured on Bio-CAT undulator beamline 18-ID at the APS. The energy of the incoming synchrotron beam was selected by means of a Si(111) double-crystal monochromator. The incident beam passed through a slit (0.5 mm vertical by 1 mm horizontal) in front of the sample. At the iron K edge, the energy resolution was approximately 1.2 eV, and the (maximum) incident flux was 10¹³ photons/second, as monitored by an ionization chamber downstream from the slit. The fluorescence emission from the samples was collected by a crystal array spectrometer [1], by using six spherically bent Ge(620) crystals. The six analyzer crystals have a diameter of 44 mm, yielding a solid angle of ~1% of the total solid angle. A Ge solid-state detector was placed at the focus of the six crystals. To avoid unwanted x-ray photons, the energy window of the Ge detector was set to 200 eV, and an additional slit was positioned just in front of the detector. The analyzer resolution was determined to be 0.8 eV at the iron K β emission. The energy calibration was repeatedly checked with the K β emission of Fe₂O₃ and was found to constant within 0.2 eV.

The Fe/ZSM-5 samples (0.3 wt% Fe) were pressed into self-supporting wafers and placed in an in situ fluorescence cell at a 45° scattering angle with respect to the incoming beam. Spectra were recorded at 1 bar at 350°C in a flowing mixture of 7.7% O₂ in He (total flow of 100 mL/min). The K β -detected Fe XANES spectra were normalized by the average absorption intensity, calculated to be around 7200 eV. The complete spectrum was modelled by using PeakFit4 software. The normal fluorescence-yield XANES spectra were also normalized by the average absorption intensity of around 7200 eV. After normalization, the pre-edge feature was isolated by subtracting the contribution from the main Fe K absorption edge. The contribution of the main edge was calculated for the whole energy range by using a cubic spline function, while the data for several electron-volts before and after the energy position of the pre-edge were used to interpolate the main edge at the pre-edge energy position.

Results

Fe K β -detected XANES of Model Compounds

Figure 1 shows the pre-edge region of the Fe K-edge x-ray absorption spectrum of Fe_2SiO_4 (i.e., fayalite) measured in two different ways. The bottom portion of Fig. 1 shows the pre-edge as measured by conventional total fluorescence x-ray absorption spectroscopy (XAS) operated at the $\text{K}\beta$ -emission peak (solid line): fluorescence yield (FY)-XANES. The contribution of the main Fe K edge to the pre-edge was determined by using a cubic spline function, obtained by interpolating the data for several electron-volts before and after the pre-edge (dashed line). The subtraction of the modelled main-edge contribution (cubic spline) from the XANES spectrum — over the full energy range — yielded the isolated pre-edge feature (dotted line). According to the bottom portion of Fig. 1, the pre-edge intensity for the spectra measured by normal XANES depends strongly on the subtracted cubic spline function. We tried to estimate the error of this procedure by using various energy ranges around the pre-edge energy position to perform several cubic spline fits. We found that with a series of cubic spline functions (all of which were, in principle, appropriate for modelling the background), the variation in the resulting integrated pre-edge intensity amounted to 20% for compounds with a

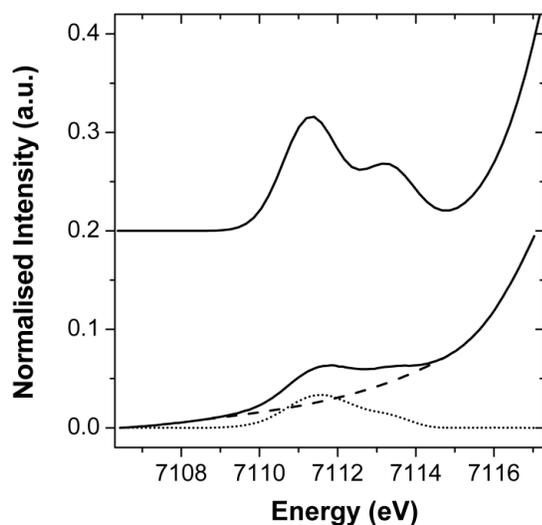


FIG. 1. Fe K pre-edge feature of Fe_2SiO_4 (fayalite: Fe^{II} , O_h). Bottom lines show the FY-XANES spectrum (solid line), the cubic spline function used to model the background (dashed line), and the isolated pre-edge (dotted line). The analysis was done according Wilke et al. [4]. Top line shows the $\text{K}\beta$ -detected XANES spectrum, with no background subtracted. In both spectra, the pre-edge is normalized to the average absorption intensity, calculated to be around 7200 eV.

weak pre-edge (i.e., with an octahedral oxygen coordination). To overcome this disadvantage of normal XANES, we measured the spectra by means of $\text{K}\beta$ -detected XANES.

The top portion of Fig. 1 shows the Fe_2SiO_4 spectrum measured by $\text{K}\beta$ -detected constant emission energy (CEE) scans, denoted as $\text{K}\beta$ -detected XANES. The small fluorescence energy window selected by the high-resolution detector used in this experiment prevented a high background contribution, as indicated by the almost flat signal before the pre-edge. Therefore, no background was subtracted from the $\text{K}\beta$ -detected XANES. The peaks in the pre-edge feature measured by $\text{K}\beta$ -detected XANES are resolved much better and display a significantly higher intensity relative to the main edge, which also was normalized at the absorption of around 7200 eV.

Activation of Framework-substituted FeZSM-5 Zeolites

The influence of the activation treatments on the oxidation state and local geometry of iron in framework-substituted FeZSM-5 was probed by $\text{K}\beta$ -fluorescence-detected XANES. All of the samples were measured at 350°C in a moderate oxygen atmosphere (i.e., 7.7% in He). Figure 2 presents the changes in the centroid position and its integrated pre-edge intensity for framework-substituted FeZSM-5 samples after template decomposition (template-free or tf-FeZSM-5), calcination, ion exchange, and again calcination (hydrogen or H-FeZSM-5) and steaming (both mild steaming [ms-FeZSM-5] and hard steaming [hs-FeZSM-5]). The characteristics of the reference iron oxide compounds with known valences and local coordinations of iron are also plotted in the graph (filled squares). The position of the centroid does not differ much for the FeZSM-5 samples but does deviate from the position of the Fe^{III} references by about 0.2 eV to higher energy.

Discussion

The influence of activation treatments on the iron in framework-substituted FeZSM-5 is clearly visible from the $\text{K}\beta$ -detected XANES results. The integrated pre-edge intensity previously identified as a characteristic of the pre-edge shows a downward trend. The centroid position of the pre-edge hardly changes from the energy position for Fe^{III} compounds. The removal of the synthesis template out of the zeolite channels and cages causes the distortion from the tetrahedral framework coordination for incorporated iron atoms. By using the hydrothermal synthesis method, Fe can be built in the silica matrix of MFI, yielding Fe-silicalite or — in case of the presence of Al — FeZSM-5. Because of its larger dimensions, the incorporation of a Fe atom most likely induces a local

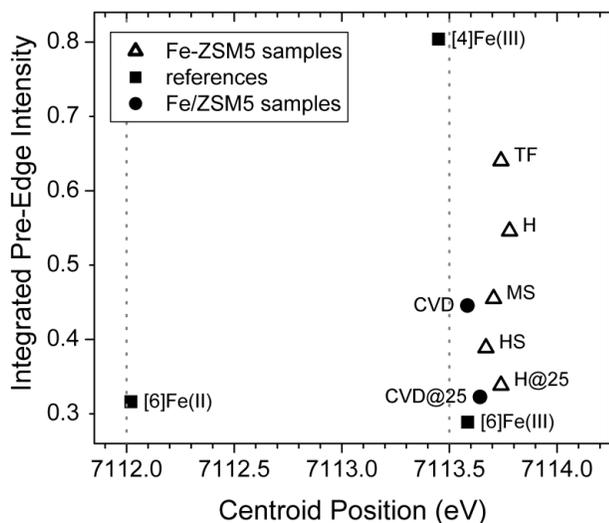


FIG. 2. Integrated pre-edge intensity versus centroid position for Fe in different ZSM-5 zeolite samples. All ZSM-5 samples were measured in a flow of 7.7% O₂ in He at 350 °C except where @25 is shown, which indicates a temperature of 25 °C. TF = tf-FeZSM-5 = sample after template removal; H = H-FeZSM-5 = proton form of sample after calcination of ammonium-exchanged sample; MS = ms-FeZSM-5 = mild-steamed sample; and HS = hs-FeZSM-5 = hard-steamed sample. The pre-edge characteristics are also given for iron model compounds: FePO₄ = [4]Fe(III), α-Fe₂O₃ = [6]Fe(III), and Fe₂SiO₄ = [6]Fe(II).

stress on the Si-O-Si bonds of the zeolite framework. The relaxation effect of the template, resulting in the tetrahedral framework coordination, perished upon template removal. This effect is even more pronounced for samples treated further (H-FeZSM-5).

The influence of the purposeful disruption of Si-O-Fe bonds (by heating in a helium stream containing water vapor [steaming]) on the iron coordination was investigated for H-FeZSM-5. For the steamed samples, the changes in the pre-edge are discussed as modifications in the percentage of Fe^{III} that occupies T_d sites. In this case, the integrated intensity of steamed FeZSM-5 samples is considered to be a linear combination of two Fe^{III} references. We assumed that the iron symmetries in FePO₄ and in Fe₂O₃ represent the extremes for the possible coordination of iron species in FeZSM-5 (i.e., isomorphous substitution for silicon in the T_d sites of the zeolite framework, or fully extracted and hence sixfold coordinated by oxygen). We chose FePO₄ as a model for Fe^{III} in tetrahedral oxygen coordination, and we chose Fe₂O₃ as a model for Fe^{III} slightly distorted from octahedral oxygen coordination.

Hard steaming causes a considerable amount of iron to be extracted from the framework, so that just 19% is left in it. We performed a separate mild steaming procedure. In that case, 68% of the iron was present in extra framework positions, compared to 81% for the hard-steamed sample. Therefore, the decrease in the amount of Fe^{III} that occupies tetrahedral sites in the MFI-type zeolite is related to the duration and severity of the steaming procedure, where the pre-edge intensity is lower for hard-steamed (hs) samples than for mild-steamed (ms) samples.

This study on the nature of Fe sites in FeZSM-5 zeolites is a good example for showing the strengths of selective x-ray absorption techniques, such as Kβ-detected XANES. New ways of quantitatively determining the oxidation state and coordination of transition-metal ions in catalysts have been made possible. Certain qualities of Kβ-detected XANES, such as high-resolution spectra with a small background and a good separation of the pre-edge feature from the main edge, make it an invaluable tool for conducting research on the catalysis and chemistry of corresponding biological systems.

Acknowledgments

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References

- [1] W.M. Heijboer, A.A. Battiston, A. Knop-Gericke, M. Hävecker, H. Bluhm, B.M. Weckhuysen, D.C. Koningsberger, and F.M.F. de Groot, *Phys. Chem. Chem. Phys.* **5**, 4484-4491 (2003).
- [2] U. Bergmann and S.P. Cramer, *Proc. SPIE-Int. Soc. Opt. Eng.* **3448**, 198-209 (1998).
- [3] W.M. Heijboer, P. Glatzel, K.R. Sawant, R.F. Lobo, U. Bergmann, R. Barrea, D.C. Koningsberger, B.M. Weckhuysen, and F.M.F. de Groot, *J. Am. Chem. Soc.* (submitted, 2003).
- [4] M. Wilke, F. Farges, P.E. Petit, G.E. Brown, and F. Martin, *Am. Mineral.* **86**, 714 (2001).