

On the Presence of Fe(IV) in Fe-ZSM-5 and FeSrO_{3-x}—Unequivocal Detection of the 3d⁴ Spin System by Resonant Inelastic X-ray Scattering

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The contribution of a 3d⁴ spin configuration to the valence electronic structure of Fe compounds can be probed via spin-selective Fe K-pre-edge absorption spectra, using resonant inelastic X-ray scattering (RIXS). The 3d⁴ configuration of Fe(IV) can be unequivocally detected even in a mixture with the high-spin 3d⁵ configuration of Fe(III). This is demonstrated on the perovskite FeSrO_{3-x} with formal oxidation state Fe(IV). When the technique was applied to an Fe-ZSM-5 catalyst during reaction with N₂O, no 3d⁴ configuration was detected. The formation of Fe(IV) upon reaction of Fe-ZSM-5 with N₂O can, therefore, be ruled out.

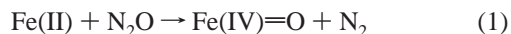
Introduction

High oxidation states of iron play an important role in biological systems.¹ Oxoiron(IV) species are found in heme enzymes, and Fe(IV) intermediates are important parts of the catalytic cycles of methane monooxygenase and of ribonucleotide reductase. The high oxidation states of iron in biological systems (and in synthetic Fe(IV) or Fe(V) complexes) are stabilized by electron-donating nitrogen ligands.² In solid-state chemistry, high oxidation states of iron are less common. The best known examples for a material with formal oxidation state Fe(IV) are the perovskite FeSrO_{3-x} and related materials with similar composition. They play an important role in catalysis,³ gas sensors,⁴ electrochemistry,⁵ and solid-state physics.⁶

The spectroscopic identification of Fe(IV) is elusive. Fe(IV) is a 3d⁴ spin system with *S* = 1 or *S* = 2. Since the zero field splitting of both configurations is very large,⁷ Fe(IV) is EPR silent. In Mössbauer spectra of ⁵⁷Fe-enriched samples, Fe(IV) can be identified on the basis of its isomer shift and electric quadrupole splitting.^{8,9} The XANES spectra of metalorganic Fe(IV) complexes are characterized by an increased intensity of the pre-edge peak and a shift of the Fe K-edge to higher energies.⁹ In the XANES spectra of FeSrO_{2.86}, however, only a small shift of the Fe K-edge was observed.¹⁰ The electronic ground state of FeSrO_{3-x} is a mixed high-spin 3d⁴ + 3d⁵ \bar{L} configuration where \bar{L} corresponds to a hole on the oxygen ligand.¹¹ The strong admixture of a 3d⁵ configuration is because the energy of a sextet spin multiplicity is lowered by exchange-

like interactions within the 3d shell (Hund's rule). Thus, a pure 3d⁴ configuration is not easily achieved, and due to the strong ligand-to-metal charge transfer, only a small edge shift can be observed.

An important scientific case where the role of high oxidation states of iron is the subject of an intense debate is the Fe-ZSM-5 system. The involvement of Fe(IV) species was invoked to explain the high activity and selectivity of Fe-ZSM-5 catalysts in the oxidation of benzene to phenol.¹² The reaction of N₂O with Fe(II) sites in ZSM-5, generated by autoreduction at high temperatures, creates a highly reactive surface oxygen species, which selectively oxidizes benzene at moderate temperatures. The generation of the active surface oxygen species can be written as



Depending on how the electrons are distributed between Fe and O, the Fe(IV)=O species can also be described as an Fe(III)–O^{•−} radical anion.¹³ Experimental proof of the existence of Fe(IV) in Fe-ZSM-5 has not yet been given. The iron sites in ZSM-5 are in a highly irregular environment, and a mixture of different sites is present. A spin-Hamiltonian analysis of the Mössbauer spectra, as commonly applied for metal–organic complexes, is therefore not possible. One has to rely on a phenomenological interpretation of the line shifts in Mössbauer and XANES¹⁴ spectra, which is often ambiguous for strongly covalent systems and therefore inconclusive. Hence, the identification of the oxidation state of iron in Fe-ZSM-5 asks for an alternative solution.

We demonstrate here that RIXS spectroscopy^{15,16} can unequivocally prove or disprove the presence of the high-spin 3d⁴ spin system of Fe(IV). The strong spin–spin (exchange) interaction between an unpaired electron in the Fe 3p shell and the valence shell spin can be used to record spin-selective absorption features at the Fe K-edge.¹⁷ This gives a clear and

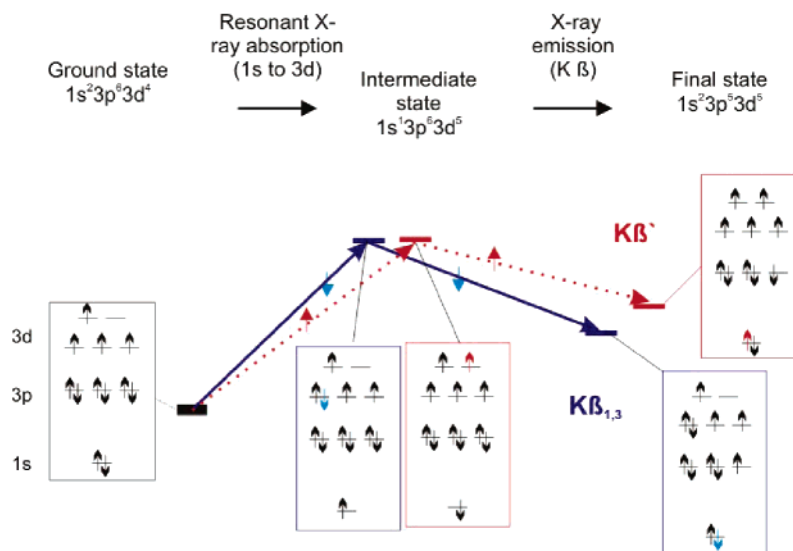
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SCHEME 1. Schematic Representation of the RIXS Process for Fe⁴⁺

unique signature of a high-spin 3d electron configuration with less than five electrons. The method is tested on a system that is known to have a 3d⁴ contribution (SrFeO_{2.89}) and then used to investigate Fe-ZSM-5.

Principle of RIXS Spectroscopy

The principle of RIXS is shown in Scheme 1. The iron sample is irradiated with X-rays in the energy range of the 1s–3d transition, the so-called pre-edge peak in conventional X-ray absorption spectroscopy. A 1s core hole is created and refilled by the decay of an electron from a 3p shell upon concomitant emission of an X-ray photon (X-ray fluorescence). The energy of the 3p⁵ final state is split by the strong exchange interaction between the 3p hole and the spin-unpaired 3d electrons of iron. The Kβ fluorescence spectrum thus separates into a sharp line (Kβ_{1,3}) at ~7059 eV and a broader, weaker line (Kβ') at lower energies.^{15a} The Kβ' feature represents an almost pure antiparallel orientation between the 3p hole and the 3d spin.¹⁷ The spin orientation of the core hole relative to the valence electrons is preserved during the transition. Fe⁴⁺ has only four d-electrons. Scheme 1 shows that spin-up and spin-down 1s electrons can be resonantly excited to the 3d shell, and hence, both spin alignments are possible in the final state. The occurrence of a Kβ' emission line after resonant excitation is therefore a unanimous proof for the existence of unoccupied levels in the Fe 3d spin-up density of states, which corresponds to a 3d⁴ configuration and, thus, an oxidation state higher than Fe(III). With high-spin Fe³⁺ or high-spin Fe²⁺ systems, only a spin-down electron can be excited into the 3d shell, which necessarily results in a parallel alignment of the 3p and 3d spins in the final state. Therefore, there will be no Kβ' line in the fluorescence spectrum.

Experimental Section

Fe-ZSM-5 with an iron loading of 0.36% was prepared by ion exchange of NH₄-ZSM-5 (Zeochem, PZ-2/40) with an aqueous solution of FeCl₂·4H₂O, at 353 K for 5 h. The sample was extensively washed, calcined at 773 K in air, treated in a 300 mbar steam at 873 K for 5 h, and finally in flowing He at 1218 K for 2 h. The synthesis and characterization of FeSrO_{2.89} was performed according to literature and is described in the Supporting Information.

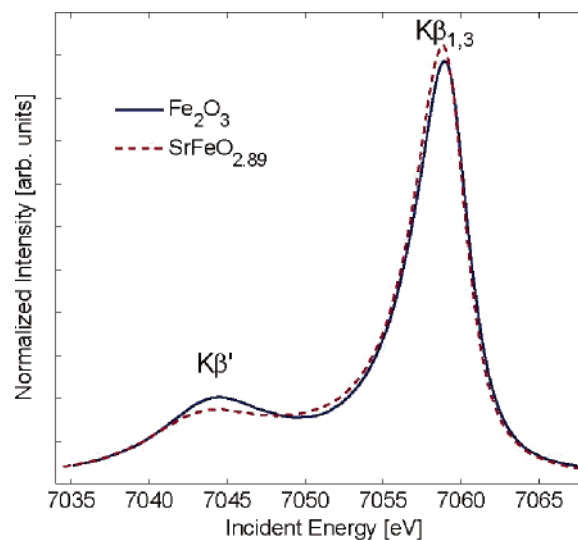


Figure 1. Kβ main lines in Fe₂O₃ (solid) and FeSrO_{2.89} (dashed).

The RIXS experiment was performed on beamline ID26 of the European Synchrotron Radiation Facility (ESRF). The energy of the incoming beam was selected by means of a pair of cooled Si crystals with a (220) orientation. Higher harmonics were suppressed by three mirrors operating in total reflection. The emission spectroscopy was performed using a spherically bent analyzer crystal (Si (531)) that was arranged with sample and X-ray detector in a Rowland geometry. The reaction of Fe-ZSM-5 with N₂O was performed in a quartz capillary micro-reactor (see Supporting Information).

Nonresonant X-ray emission spectra were recorded by setting the incident energy above the K absorption edge at 7160 eV. The nonresonant X-ray emission scans of Fe₂O₃ and of FeSrO_{2.89} are shown in Figure 1. The spectra are normalized to the spectral area. The shift in the Kβ_{1,3} line is indicative of the smaller spin in the valence shell of SrFeO_{2.89} compared to Fe₂O₃, due to the higher oxidation state of Fe in SrFeO_{2.89}. Spin-selective XANES spectra of the Fe K-edge were then recorded by setting the emission energy on the maximum of the Kβ_{1,3} emission line (7059 eV, spin-down transition) and on the Kβ' line (7045 eV, spin-up transition), respectively, and scanning the incident energy (see Supporting Information for more details).

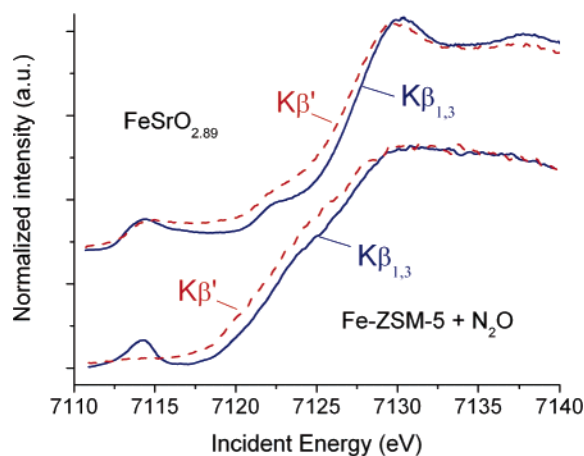


Figure 2. XANES spectra of the Fe K-edge of $\text{FeSrO}_{2.89}$ and of Fe-ZSM-5 after reaction with N_2O (bottom), recorded on the $\text{K}\beta_{1,3}$ and the $\text{K}\beta'$ fluorescence channel.

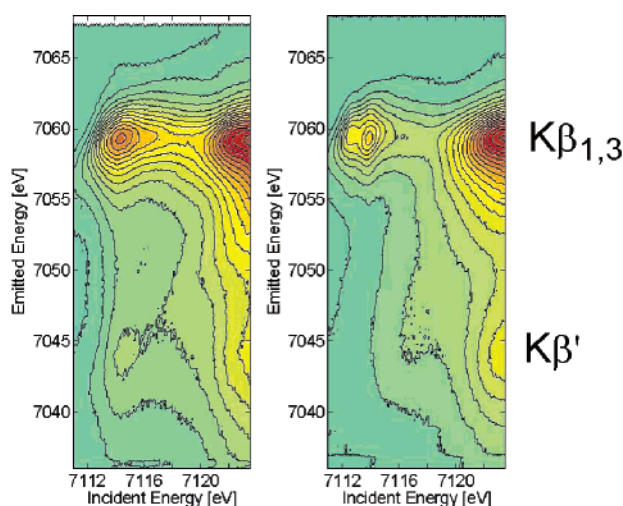


Figure 3. RIXS planes of $\text{FeSrO}_{2.89}$ (left) and Fe_2O_3 (right).

Results and Discussion

$\text{FeSrO}_{2.89}$, which is formally composed of a mixture of 80% Fe(IV) and 20% Fe(III), was used to validate the method. The $\text{K}\beta_{1,3}$ - and $\text{K}\beta'$ -detected absorption-like line spectra of $\text{FeSrO}_{2.89}$ in Figure 2 closely resemble each other. The pre-edge peak below 7115 eV is clearly visible in the spectra recorded on the $\text{K}\beta_{1,3}$ as well as on the $\text{K}\beta'$ emission line. The full RIXS plane¹⁶ illustrates the spin selectivity in the pre-edge region (Figure 3). The strong spin-down and weaker spin-up spectral features are centered around 7059 and 7045 eV emission energies, respectively. The spin-up feature is absent in high-spin $3d^5$ configurations, for example, in Fe_2O_3 (Figure 3).¹⁸ The presence of unoccupied levels in the Fe $3d$ spin-up density of states, which corresponds to a partial Fe $3d^4$ configuration, can be unequivocally detected by recording the pre-edge spin-selectively. Due to the strong ligand-to-metal charge transfer, the contribution of a $3d^4$ configuration is only about 30% in SrFeO_3 .¹¹ This contribution is even less in $\text{SrFeO}_{2.89}$ (formally 78% Fe(IV) and 22% Fe(III)). Nevertheless, we find a clear signature of a $3d^4$ configuration in the RIXS spectra. The technique is thus sufficiently sensitive to detect Fe(IV) species even in a mixture with other iron sites.

In a next step, RIXS was applied to Fe-ZSM-5 under working conditions. The concentration of active iron sites in Fe-ZSM-5, which presumably react with N_2O to give Fe(IV), is low, on the order of 0.01 mmol/g.^{12,13,19} The active sites are generated

by treatment of the sample at high temperatures. We used an Fe-ZSM-5 sample with an iron loading of 0.36 wt % and treated it in steam at 873 K and finally in He at 1218 K. After this treatment, the majority of the iron sites should react with N_2O either to Fe(IV) or to $\text{Fe(III)-O}\cdot^-$, according to eq 1. After an in situ dehydration of the sample at 890 K and cooling to 533 K, a step from He to 5000 ppm N_2O was performed. The Fe K-edge shifted by ~ 0.8 eV to higher energies, demonstrating that the Fe(II) sites, which had been generated by the pretreatment at high temperatures, were oxidized by N_2O . The final edge position indicated an oxidation state of Fe(III). A full oxidation of Fe(II) to Fe(III) would lead to an edge shift of ~ 3 eV. From the measured edge shift, we can estimate that one-third of the iron sites were in oxidation state Fe(II) before the step to N_2O . Mass spectroscopic analysis of the reactor effluent showed that 0.5 N_2/Fe was released directly after the step, i.e., the same amount of oxygen was deposited on the catalyst. This corresponds to the deposition of at least one oxygen atom per Fe(II) site. To prove or disprove whether the oxidized iron sites can be described by a (partial) $3d^4$ configuration, the spin-selective $\text{K}\beta_{1,3}$ - and $\text{K}\beta'$ -detected fluorescence spectra were recorded. In contrast to $\text{FeSrO}_{2.89}$, the $\text{K}\beta'$ -detected spectrum exhibited no pre-edge peak. The oxidized Fe-ZSM-5, thus, has a pure high-spin $3d^5$ configuration, without a measurable $3d^4$ component. RIXS cannot prove whether the oxygen atom from N_2O is really deposited in the form of an $\text{Fe(III)-O}\cdot^-$ radical anion (the formation of that species only follows from stoichiometry of reaction 1), but we can safely state that we cannot observe any electron transfer from Fe to O beyond the $3d^5$ configuration. A high-spin $3d^5$ configuration is very stable due to exchange-like interactions, and a strong force is required to yield a charge higher than $3+$ on the Fe atom. In a solid, this force can be provided by the Madelung potential.²⁰ In oxide catalysts with isolated iron sites, these long-range effects are missing, and the formation of high-valence Fe species is therefore very unlikely.

Conclusions

RIXS unequivocally proves that Fe(IV) species with a $3d^4$ spin configuration are not formed during the catalytic reaction of Fe-ZSM-5 with N_2O . The partial $3d^4$ configuration of the perovskite $\text{FeSrO}_{2.89}$, on the other hand, is clearly detected. The difference between the two systems is ascribed to the Madelung potential, i.e., to long-range effects in the solid. The asset of RIXS compared to other techniques is that it gives a straightforward yes/no answer to the question of whether high oxidation states of iron are present in a sample, without recourse to spectral fitting. The method is especially useful in the analysis of samples containing a mixture of different species, as, for example, in Fe-ZSM-5. An additional advantage is that RIXS can be employed in operando measurements of working catalysts because it makes use of hard X-rays. The presented technique can be exploited for transition metals other than Fe.

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Supporting Information Available: Detailed description of the sample preparation and the RIXS experiments. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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