

The nature of the active site in the Fe-ZSM-5/N₂O system studied by (resonant) inelastic X-ray scattering

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Abstract

Resonant inelastic X-ray scattering (RIXS) was applied to investigate whether the iron–oxygen species created upon reaction of Fe-ZSM-5 with N₂O have a (partial) 3d⁴ configuration, i.e. oxidation state Fe(IV). Fe-ZSM-5 samples with low iron loading were pre-treated at high temperatures before reaction with N₂O. Then Fe K-edge XANES spectra were recorded either by selecting the fluorescence of the main Kβ_{1,3} line or the satellite Kβ' line in the Kβ emission spectrum. The experiments were performed in situ and imitated the experiments performed in the laboratory reactor. The absence of a pre-edge in the Kβ' line spectrum proves that the configuration of the active iron–oxygen species is purely 3d⁵. The result was confirmed for several differently treated Fe-ZSM-5 catalysts. The high reactivity of Fe-ZSM-5 is therefore not due to the formation of high oxidation states of iron, but must be ascribed to the particular oxygen species that is created by the reaction of N₂O with the catalyst.

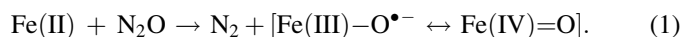
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1. Introduction

Due to high stability of the benzene ring it is difficult to design appropriate catalysts that achieve a high selectivity and at the same time sufficient conversion for the direct oxidation of benzene to phenol. Current industrial routes for the production of phenol from benzene are therefore indirect, i.e. they involve the formation of other intermediates whose oxidation to phenol is easier. Some time ago it was discovered that Fe-ZSM-5, in combination with N₂O as oxidant, may be a suited catalyst for the direct oxidation of benzene, since it is almost 100% selective [1,2]. The best Fe-ZSM-5 catalysts contain very low concentrations of Fe. In addition, a special high-temperature pre-treatment is required to activate the catalyst [2–6]. The nature of the active species has been the subject of intensive research. The decisive question is how N₂O deposits its oxygen atom onto the catalyst surface and which oxygen species is so

reactive and at the same time selective. Proposals for the active sites include Fe(III)–O[−] radical anions [3] or Fe(IV)=O ferryl species [6], formed by the reaction



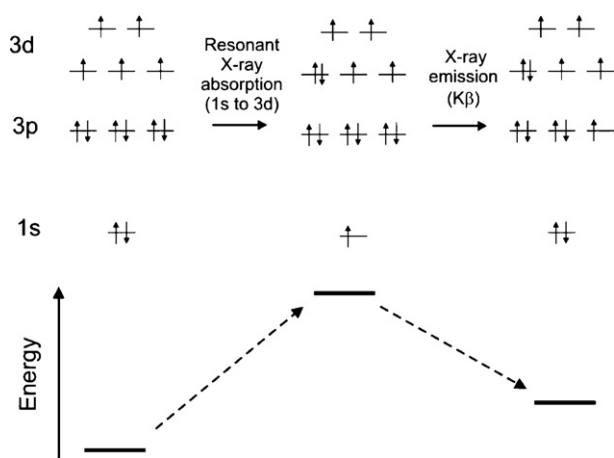
Fe(III)–O^{•−} and Fe(IV)=O are mesomeric forms of the same species and can in that sense not be distinguished. It is, however, valid to ask the question whether the active species is closer to the Fe(III) radical anion or to the Fe(IV) oxo mesomer. The Fe(III)–O^{•−} species was proposed on the basis of Mössbauer data [3], which indicate that the oxidation state of the active species is +III. The presence of the oxygen radical anion could, however, not be confirmed by ESR spectroscopy [7]. The coupling of the spin on the oxygen radical with the spin of Fe makes the detection of the oxygen radical difficult. Until now, no direct experimental proof has been given for a Fe(IV)=O component of the active species. A Fe(IV) component should lead to a shift of the Mössbauer lines to lower energies. Mössbauer spectra of homogeneous Fe(IV) and Fe(III) complexes show that the range of typical isomer shifts of the two oxidation states are not clearly separated [8]. The interpretation of Mössbauer line shifts is therefore ambiguous.

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The same holds true for the shift of the Fe K-edge, measured in XANES spectra. Position and shape of the absorption edge do not only depend on the oxidation state, but also on covalence, band structure, geometry, etc.

We present here a different method that gives an unequivocal proof for the presence of Fe(IV) or, more precisely, of a $3d^4$ spin system, that is, resonant inelastic X-ray scattering (RIXS). A good introduction into the theory of RIXS is given, for example, in refs. [9,10]. Inelastic X-ray scattering refers to the fluorescence radiation emitted upon absorption of an X-ray photon. The fluorescence is inelastic because the emitted X-ray has a lower energy than the absorbed X-ray. The term “resonant” means that the absorbed X-ray photon transfers an electron from an inner shell to an unoccupied orbital close to the Fermi level instead of to the continuum. In the case of the Fe K-edge, the sample is irradiated with X-rays in the energy range corresponding to the $1s$ – $3d$ transition, i.e. the so-called pre-edge peak in conventional X-ray absorption spectroscopy. The subsequent X-ray fluorescence, which results from the transfer of a $2p$ or $3p$ electron to the $1s$ core hole, is spectrally analyzed. For our purpose the $3p$ – $1s$ ($K\beta$) fluorescence line is more suitable, since the exchange interaction of the $3p$ with the $3d$ orbitals is stronger than of the $2p$ orbitals. The $K\beta$ emission can be resolved into a main emission line ($K\beta_{1,3}$) and a satellite ($K\beta'$) at lower energies. $K\beta_{1,3}$ corresponds to a parallel and $K\beta'$ to an antiparallel alignment of the spins in the $3d$ and the $3p$ orbital [11]. The energy of these two final states is different because of the $3d$ – $3p$ exchange energy. Since the electron spin is conserved during the electron transfers $1s \rightarrow 3d$ and $3p \rightarrow 1s$, the spin orientation of the final state reflects the spin orientation of the $1s$ electron that was resonantly excited into the $3d$ shell. With high spin Fe^{3+} ($3d^5$) only a spin-down electron can be transferred and the alignment of $3d$ and $3p$ spins in the final state is parallel (see Scheme 1). Hence, no $K\beta'$ line is expected. With Fe^{4+} ($3d^4$) a spin-up or a spin-down electron can be transferred. Parallel and antiparallel alignment of the $3d$ and $3p$ spins is possible in the final state and resonant excitation leads to a $K\beta_{1,3}$ and a $K\beta'$ emission line. This difference between high spin $3d^5$ and $3d^4$ is exploited in our experiments.



Scheme 1. Schematic representation of the RIXS process for Fe(III).

2. Experimental

2.1. Preparation of Fe-ZSM-5

NH_4 -ZSM-5 was obtained by three-fold ion exchange of PZ2-40 (Zeochem, Si/Al = 24) with 1 M NH_4NO_3 solution at room temperature. A diluted aqueous solution of $FeCl_2 \cdot 4H_2O$ was used for the ion exchange, which was carried out at 353 K for 5 h in an atmosphere of N_2 , to avoid oxidation of Fe^{2+} to Fe^{3+} . After filtration, washing and drying all samples were calcined in air at 773 K for 5 h. The calcined samples were subjected to a high temperature treatment in a flow of He, at 1173 or 1218 K, for 2 h (Table 1). The Fe and Al content of the samples was determined by AAS. UV–vis spectra were recorded on a Cary 400 spectrometer under ambient conditions using a Praying Mantis sample holder from Harrick. The samples are coded as Fe-ZSM-5(wt% Fe), with the suffix HT if a treatment at high temperatures was applied. Part of sample Fe-ZSM-5(0.4) was additionally steamed at 873 K for 5 h before the high temperature treatment in He. This sample is coded Fe-ZSM-5(0.4)st-HT.

2.2. Deposition of active oxygen atoms

50 mg of Fe-ZSM-5 was loaded in a laboratory quartz reactor of 4 mm inner diameter, treated at 873 K in He (purity 99.996%) for 1 h and then cooled to 523 K. A step from He to 5000 ppm N_2O in He was performed and the amount of N_2 released after the step was quantified by a mass spectrometer. It corresponds to the amount of oxygen atoms deposited on the catalyst.

2.3. Setup for operando X-ray experiments

X-ray absorption and scattering measurements were performed under conditions as close as possible to the experiments described above, i.e. using a plug flow reactor, a narrow sieve fraction of Fe-ZSM-5, and the same gas feeding device. 5–6 mg of Fe-ZSM-5 (sieve fraction 100–150 μm) was placed in a quartz capillary of 1 mm diameter and 10 μm thickness, which served as micro reactor, as described in refs. [12,13]. The capillary was placed on top of a gas blower (provided by ESRF), supplied with N_2 or Ar, which heated the sample. In order to assure a homogenous temperature distribution around the sample, a cap was placed on top of the capillary and wrapped with Al foil during the high temperature treatments and with Kapton foil during the X-ray measurements. The cap was constructed from

Table 1
Iron loading of the samples and conditions of the high temperature treatment

	wt% Fe	Fe/Al	T(HT) [K]
Fe-ZSM-5(0.1)	0.13	0.04	–
Fe-ZSM-5(0.1)-HT	0.13	0.04	1173
Fe-ZSM-5(0.4)	0.36	0.12	–
Fe-ZSM-5(0.4)-HT	0.36	0.12	1218
Fe-ZSM-5(0.4)st-HT	0.36	0.12	1218

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