Synthesis, structure, and reactivity of iron–sulfur species in zeolites

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Previous studies have shown that a variety of iron-oxo species, including nanoclusters and dimers, can be formed within the pore structure of ZSM-5 and other porous materials. We report that these species can readily be sulfided by exposure to hydrogen sulfide at 623 K when formed in ZSM-5, mordenite, and MCM-41. The iron–sulfur entities produced have been characterized by XPS and EXAFS spectroscopy. Iron is in the oxidation state +2 and the nearest neighbor iron–sulfur interatomic distance is ~2.25 Å, which is close to that in iron(II) sulfide. Sulfidation appears to be at least 90% complete. In ZSM-5 the same iron–sulfur species, which contains isolated iron atoms or very small clusters, is formed irrespective of whether the iron was introduced by aqueous exchange or chemical vapor deposition. The sulfided ZSM-5 material is found to be weakly active for the hydration of acrylonitrile to acrylamide in tetrahydrofuran solution at 338 K, with the best materials achieving about 0.5 turnovers per iron species per day.

KEY WORDS: synthesis of iron–sulfur species; zeolites; acrylonitrile hydrolysis to acrylamide.

1. Introduction

A variety of oxo-species are produced when iron is introduced by different methods into the channels of microporous and mesoporous materials. The formation of oxo-bridged iron dimers is claimed to occur in ZSM-5 when a chemical vapor deposition route is used [1], while monomeric species in which the iron nearest neighbors are, of course, oxygen predominate in MCM-41 [2]. When aqueous exchange is the method of introduction, we have reported extensive evidence that unusual oxo-nanoclusters are formed in ZSM-5 [3] and there is also evidence for some clustering when iron is introduced into zeolite beta by this method [4]. The average iron oxo-cluster in ZSM-5 contains four iron atoms and a similar number of oxygen atoms. Clusters are characterized by Fe–O distances in the range 1.93–2.10 Å, and also by unusually short iron–iron distances of ~2.55 Å. Because of these short iron–iron distances, we have drawn analogies between these and the structures of both natural and synthetic small sulfur-containing clusters, specifically with high-potential iron proteins (HIPIP) [5] and ferredoxins [6]. It is thus of interest to study whether any of the iron-containing materials can be sulfided, and whether sulfided entities are able to mimic the enzyme nitrile hydratase in *Pseudomonas chlororaphis*, which is thought to contain Fe–S entities as its active site. This enzyme catalyses the hydration of acrylonitrile ($CH_2=CH–CN$) to acrylamide ($CH_2=CH–C(O)NH_2$) [7], which is also catalyzed on an industrial scale by Raney copper [8].

2. Experimental

The frameworks studied were ZSM-5 (Si/Al = 25), MOR (Si/Al = 10), and siliceous MCM-41 (mean pore size 30 Å). Zeolite samples were obtained from Catal Ltd, Sheffield, UK, while the MCM-41 was synthesized in house. The exchange procedures have been fully described [2,3], and samples were also prepared by chemical vapor deposition, using the method first described by Chen and Sachtler [9]. The iron content varied with the framework and method of introduction, and typical values are given in table 1. Sulfiding was carried out by heating 500 mg of each sample to 373 K in helium overnight, followed by exposure to hydrogen sulfide (Air Products, >99.9% pure, 5% in helium) at 623 K and 20 ml min^{-1} for 2 h. The samples, which were originally yellow-brown, almost colorless, or gray in color, were found to be black after sulfiding.

The sulfided materials were characterized by X-ray photoelectron spectroscopy (XPS) using a VG ESCA-3 spectrometer, and at the Daresbury, UK, synchrotron radiation source by *in situ* iron K edge X-ray absorption fine structure spectroscopy (EXAFS) with fluorescence detection. Standard experimental and data analysis methods were employed for both of these techniques, which have been fully described previously [3]. The

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Table 1
XPS results

Material	Sulfur 2p binding energy (eV)	Iron $2p_{3/2}$ binding energy (eV)	Fe/S ratio
Prepared by sublimation			
2.45% Fe-ZSM-5	163.6 and 170.6	710.8	1.2
4.2% Fe-MOR	162.9	710.9	1.4
Prepared by exchange from solution			
1.11% Fe-ZSM-5	163.6 and 170.1	710.1	1.4
2.9% Fe-MCM-41	162.9	709.9	0.8
Reference material			
Iron(II) sulfide [a]	162.5	710.0	1.2

[a] BDH Technical Grade.

statistical significance of each contribution to the EXAFS analysis has been confirmed [10]. EXAFS results are available only for sulfided ZSM-5 materials.

Catalytic experiments were performed under reflux at 338 K in tetrahydrofuran (THF), with analysis by off-line gas chromatography. Typically 12 g of a solution of 8.3% acrylonitrile and 8.5% water in THF contained 0.13 g of catalyst. Experiments were also carried out without solvent in the temperature range 338–368 K, using ~13 g of a 6.1% solution of acrylonitrile in water and 0.3 g of catalyst. The limited solubility of acrylonitrile in water prevents the use of more concentrated aqueous solutions. Blank experiments showed that there was no reaction in the absence of a catalyst.

3. Results and discussion

The structures and composition of the iron-containing materials before sulfidation are in good agreement with previous reports. Figures 1(a) and (b) show iron K edge EXAFS spectra, respectively, of Fe-ZSM-5 samples prepared by chemical vapor deposition (CVD) [9] and by aqueous exchange; the fitting parameters used are listed in table 2. It is worth noting that these two different preparation procedures result in quite different iron local environments. As we have reported previously, aqueous exchange leads to very short iron–iron distance of ~2.51 Å. These are not found in the CVD-prepared sample, which instead shows a much more routine iron–iron distance of ~3.1 Å with a coordination number close to one, which has been interpreted as indicating the preponderance of iron oxo-dimers in these materials [1,11]. The spectrum of the CVD sample shown in figure 1(b) closely resembles that reported first by Prins *et al.* [1] and then by Koningsberger *et al.* [11]. Our analysis of this spectrum is also similar to that made by both those groups of authors and we do indeed observe the iron–iron distance that has been ascribed to dimers. There are differences in detail and infrared spectroscopic evidence that leads us to believe that this material contains a mixture of isolated iron ions and clusters larger than dimers, the clusters having a structure more closely resembling that of an iron oxide, possibly wustite. The EXAFS coordination number is of course only an average, and we believe that its agreement with the value of unity (used as evidence for the presence of dimers) is simply a coincidence.

A color change from yellow-brown to black on exposure to hydrogen sulfide was observed for all materials. The color change suggests that sulfidation has taken place, and this is confirmed both by XPS and by EXAFS. Some XPS binding energies are given in table 1, which also lists the iron content of the samples studied. All show a sulfur 2p peak near to 163 eV, while some also have a feature at ~170 eV. The iron binding energies observed are characteristic of Fe(II), and the iron/sulfur ratios within the region of the material sampled by XPS show that all samples have an approximately 1 : 1 Fe/S stoichiometry.

The presence of sulfur is confirmed by EXAFS, which crucially demonstrates that it is bound to the iron in the zeolite pores. Figures 1(c) and (d) show typical iron K edge EXAFS spectra for samples prepared by CVD and ion exchange, after sulfiding; again, these figures also shows spectra calculated using parameters listed in table 2. Spectra of both materials are dominated by an iron–sulfur interatomic distance of 2.24 ± 0.03 Å, with a coordination number of 2.5 ± 0.4. There are also two other shells of neighbors that contribute to the calculated EXAFS in a statistically significant manner at much more than the minimum level (10). There is a shell at 3.6–3.7 Å which may reflect Fe–Al or Fe–Si interatomic distance, and an Fe–Fe contribution at the relatively short distance of <2.85 Å, with a low coordination number. In attempting to model the experimental spectra we have tested a wide range of possible models, and have found no others that give reasonable descriptions of the experimental data. We therefore believe that our results represent unique solutions, although with EXAFS the possibility always remains that there are other solutions of which we have not thought.

The EXAFS results show that, although the structures around iron in the two oxo samples are quite different before sulfiding, after reaction with H_2S they are the same within experimental error. The observed Fe–S distance of 2.24 Å is close to the iron–sulfur nearest neighbor distance in iron(II) sulfide (2.23 Å). The EXAFS results show, however, that the iron–sulfur species present are mainly isolated ions or very small clusters, since the iron–iron shells of neighbors (although statistically significant) have coordination numbers of 0.5 or lower. The relatively short iron–iron interatomic distance suggests that any clusters formed may indeed resemble cubanes or ferredoxins [12,13]. The absence of any iron–oxygen contribution to the EXAFS after sulfiding indicates that the iron species are now bonded

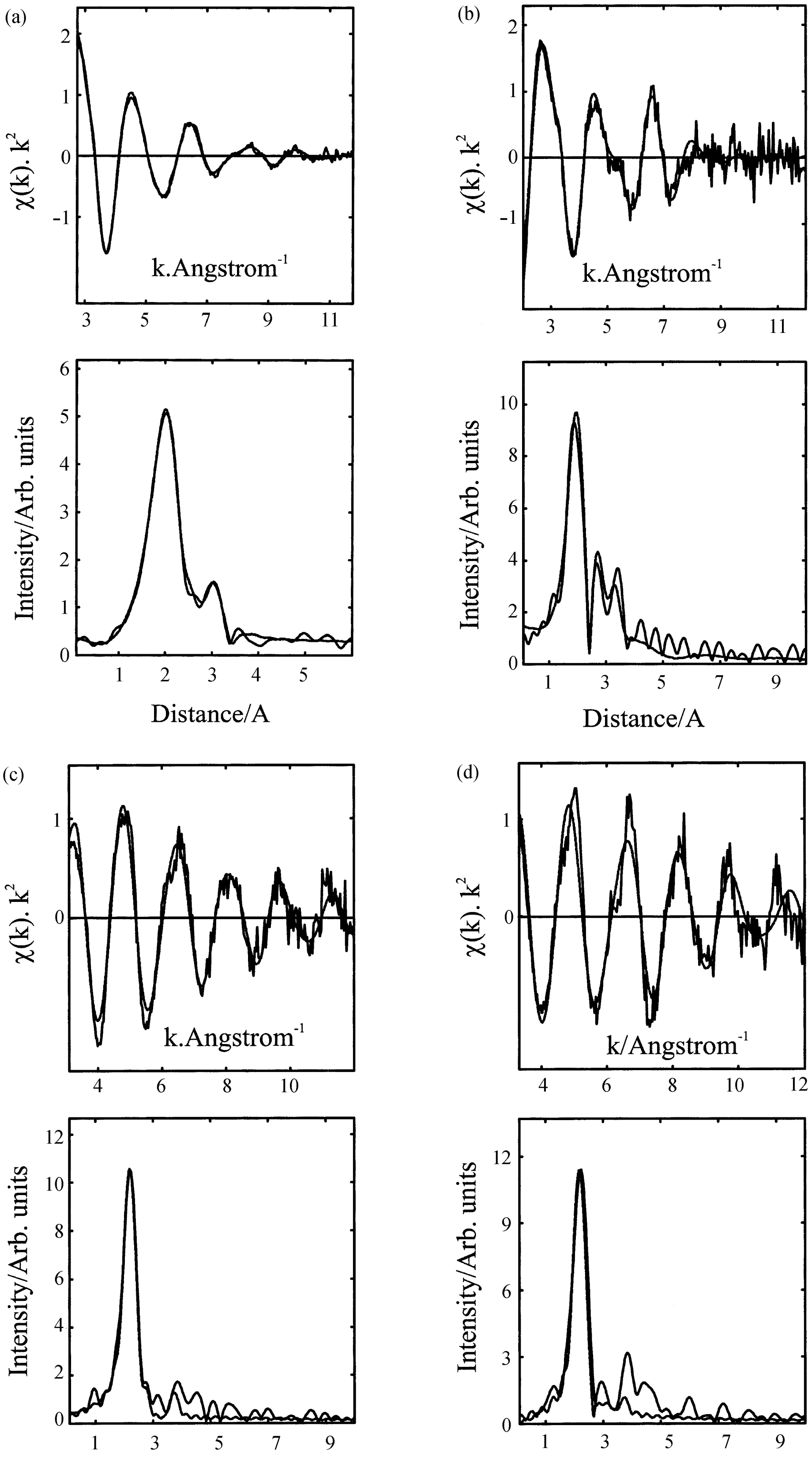

Figure 1. Experimental (solid line) and calculated (dotted line) iron K edge EXAFS spectra. In each case the upper panel shows the EXAFS spectra in reciprocal space, while the lower panel shows the Fourier transforms. For details see the text, and for the parameters used to generate the calculated spectra see table 1. (a) Unsulfided material, prepared by CVD; (b) unsulfided material, prepared by aqueous exchange; (c) CVD sample after sulfiding; (d) aqueous exchange sample after sulfiding.

Table 2
Parameters used to model the experimental EXAFS spectra shown in figure 1. The experimental errors in the dominant shell(s) are typically ±0.02 Å and in coordination numbers ±15%

Neighbor	Interatomic distance (Å)	Coordination number	Debye–Waller factor (Å^2)
(A) Unsulfided sample prepared by chemical vapor deposition, *R* factor = 10.9			
Oxygen	1.91	1.1	0.015
Oxygen	2.05	3.0	0.014
Iron	3.06	0.9	0.024
(B) Unsulfided sample prepared aqueous ion exchange, *R* factor = 29.5			
Oxygen	2.01	4.1	0.027
Iron	2.51	2.1	0.026
Aluminum	3.24	3.5	0.023
(C) CVD sample after sulfiding and heating in nitrogen at 573 K, *R* factor = 27.9			
Sulfur	2.25	2.5	0.010
Iron	2.72	0.5	0.022
Aluminum	3.67	1.0	0.003
(D) Aqueous exchange sample after sulfiding and heating in nitrogen at 573 K, *R* factor = 36.6			
Sulfur	2.23	2.5	0.008
Iron	2.83	0.3	0.005
Aluminum	3.60	0.8	0.003

to the zeolite through sulfur or thiol (–SH) species. The precise details of this bonding are unclear.

The main sulfur 2p binding energy observed in XPS, ~163 eV, is also consistent with the presence of sulfide. The higher sulfur XPS binding energy observed is believed to be the result of atmospheric oxidation to sulfate during transfer to the spectrometer, indicating the lability of the sulfur species present. Similar behavior has previously been observed in studies of sulfided chromia catalysts [14]. The thermodynamic driving force for sulfidation is considered to be the formation of water:

$$\mathrm{Fe{-}O} + \mathrm{H_2S} \longrightarrow \mathrm{Fe{-}S} + \mathrm{H_2O}$$

This reaction is favorable for (bulk) iron(II) oxide ($\Delta H_\mathrm{o}^{298} = -91\,\mathrm{kJ\,mol^{-1}}$), but not for $\mathrm{Fe_2O_3}$, since iron(III) sulfide is unstable.

The sulfided materials have been found to have limited activity for the hydration of acrylonitrile to acrylamide, the best results being obtained with a ZSM-5 catalyst where the iron was introduced by the CVD method. An acrylonitrile conversion of ~2% was observed after 185 h reflux in THF at 338 K, indicative of about 4 turnovers per iron species. No other products were detected, so that selectivity to acrylamide is 100%. These results are still some way away from mimicking the performance of the enzyme of *P. chlororaphis*, which achieves its saturation yield of 45% acrylamide after a few hours at 20 °C [7].

The hydration of acrylonitrile has also been studied in aqueous solution (1 ml acrylonitrile in 12.5 ml water) at temperatures in the range 338–368 K over about 180 h. The activity was very poor, with a maximum yield representing only about 0.4 turnovers per iron atom at 368 K, the equivalent of about 0.5 turnovers per site per day. However, the catalyst gradually lost sulfur at reaction temperature in water, as indicated by the loss of its black color over a period of a few hours and by XPS studies after reaction. It is therefore possible that the reaction *is* catalytic (i.e. producing more than one turnover per possible active site), but that the catalyst is destroyed by hydrolysis during reaction. In dry air the sulfided catalysts are unreactive with oxygen, even after many hours at 373 K.

Other iron-containing materials that we tested showed even lower activity. With the unsulfided iron-containing zeolites in aqueous solution, the maximum yield found was <0.1 turnover and no activity at all was found with powdered iron sulfide.

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References

[1] P. Marturano, L. Drozdova, A. Kogelbauer and R. Prins, J. Catal. 192 (2000) 236.

[2] M. Stockenhuber, M.J. Hudson and R.W. Joyner, J. Phys. Chem. B 104 (2000) 3370.

[3] R.W. Joyner and M. Stockenhuber, J. Phys. Chem. B 103 (1999) 5963.

[4] M. Stockenhuber, R.W. Joyner and G.S. Paine, unpublished results.

[5] See e.g. S.P. Cramer, in: *X-ray Absorption, Principles, Applications and Techniques of EXAFS*, eds. D.C. Koningsberger and R. Prins (Wiley, New York, 1988), and references therein.

[6] C.R. Kissinger, E.T. Adman, L.C. Sieker and L.H. Jensen, J. Am. Chem. Soc. 110 (1988) 8721.

[7] H. Yamada and M. Kobayashi, Biosci. Biotech. Biochem. 60 (1996) 1391.

[8] M.S. Wainwright, in: *Catalysis of Organic Reactions*, ed. R.E. Malz Jr. (Marcel Dekker, New York, 1996), p. 213.

[9] H.-Y. Chen and W.M.H. Sachtler, Catal. Today 42 (1998) 73.

[10] R.W. Joyner, K.J Martin and P. Meehan, J. Phys. C (Solid State Phys.) 20 (1987) 4005.

[11] A.A. Battiston, J.H. Bitter and D.C. Koningsberger, Catal. Lett. 66 (2000) 75.

[12] M.R. Antonio, B.A. Averill, I. Moura, J.J.G. Moura, W.H. Orme-Johnson, B. Teo and A.V. Xavier, J. Biolog. Chem. 257 (1982) 6646.

[13] N. Okazaki, S. Osada and A. Tada, Appl. Surf. Sci. 121/122 (1997) 396.

[14] B.W.L. Southward, G.J. Hutchings, R.W. Joyner and R.A. Stewart, Catal. Lett. 68 (2000) 75.