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Unusual structure and stability of iron–oxygen nano-clusters in Fe-ZSM-5 catalysts

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Feng and Hall have recently reported that over-exchanged Fe-ZSM-5 materials prepared by a special route show high stability in the selective reduction of 2-methylpropane (isobutane) by NOx. We report that iron–oxygen clusters in ZSM-5 catalysts prepared by a conventional route show unexpected structural features, with significant iron–iron co-ordination and a rather short Fe–Fe interatomic distance of 2.53 ± 0.02 Å. Iron in these clusters is readily interconvertible between the (II) and (III) oxidation states, but the clusters are stable against reduction to Fe(0) even at 1250 K in hydrogen. We suggest that the clusters adopt structures similar to that of ferredoxin II, Fe_3S_4.

Keywords: SCR catalysts, Fe-ZSM-5, iron–oxygen nano-clusters, structure, stability against reduction

1. Introduction

There continues to be significant world-wide interest in catalysts for the reduction of NOx by hydrocarbons in the presence of oxygen, the so-called selective catalytic reduction or SCR reaction. Much attention has been focused on Cu-ZSM-5 materials since their introduction about five years ago by Iwamoto and others [1] although it is recognised that these materials show poor stability in high levels of water. Misono et al. have drawn attention to manganese oxide as a potentially valuable additive to cognate zeolite catalysts, to induce stability in water [2]. Now Feng and Hall (subsequently referred to as FH) claim that, through a special but undisclosed method, iron/ZSM-5 catalysts may be prepared which show high activity and selectivity in the SCR reaction, and whose catalytic performance is unaffected by the presence of high levels of water or sulphur dioxide [3].

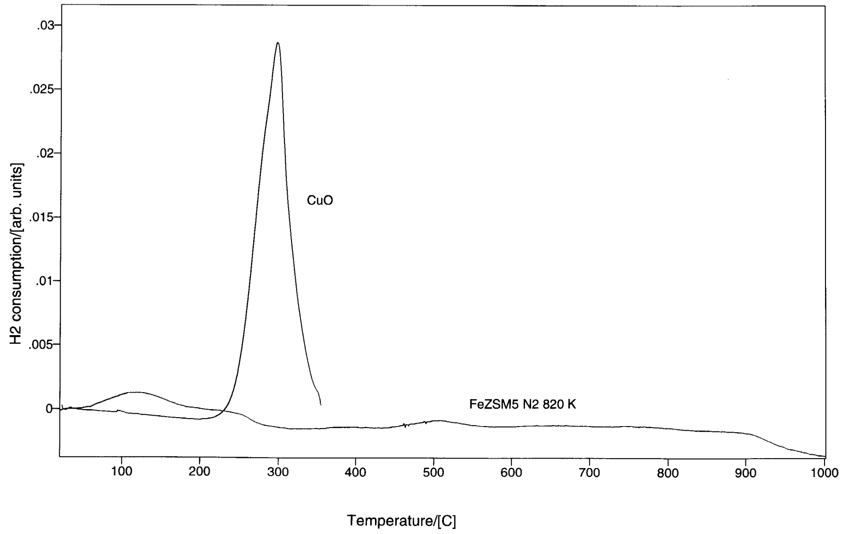

Figure 1. Temperature-programmed reduction studies of Fe-ZSM-5 pre-treated as described in the text, together with a copper(II) oxide standard.

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Table 1
EXAFS studies of Fe-ZSM-5 catalysts

Sample	Neighbour	Co-ordination number	Interatomic distance (Å)
as-synthesised	oxygen	5.9 ± 0.5	2.00 ± 0.02
	iron	1.5 ± 0.3	3.00 ± 0.05
	silicon/aluminium	1.4 ± 0.5	3.33 ± 0.05
heated in oxygen at 780 K	oxygen	1.8 ± 0.3	1.87 ± 0.03
	oxygen	3.9 ± 0.4	2.02 ± 0.02
	iron	1.9 ± 0.4	2.53 ± 0.03
	silicon/aluminium	2.2 ± 0.5	3.23 ± 0.05

These authors have used 2-methylpropane (isobutane) as the reducing gas. Because of the interest which the work of FH is likely to engender, we present a preliminary report of our studies of iron–oxygen nano-clusters in ZSM-5, which show that these possess both unusual structures, and unexpectedly high stability against reduction. A detailed account of this work will be submitted elsewhere [4].

2. Experimental

A Fe-ZSM-5 catalyst was prepared from H-ZSM-5 with a framework ratio $Si/Al = 36$ (determined by ^{29}Si MAS NMR), by ion exchange at room temperature with an 0.01 molar solution of iron(III) nitrate (Aldrich Chemical, $> 99.99\%$ pure). The iron content was 0.70 wt%, determined by atomic absorption spectroscopy, and the materials were characterised by temperature-programmed reduction (TPR), in situ X-ray absorption spectroscopy (EXAFS and XANES), and infrared spectroscopy. For TPR, 50 mg of catalyst was pre-heated to 820 K in flowing, dry air for 1 h, cooled to room temperature and then heated in a 40 ml min^{-1} flow of 5% hydrogen in argon at 5 K min^{-1}. Hydrogen uptake was measured by a thermal conductivity detector. X-ray absorption spectroscopy was carried out at beamline 9.3 at the CCRL Daresbury Laboratory in an in situ cell to be described in detail elsewhere [5] and interpreted using standard data analysis procedures [6]. For infrared spectroscopy, samples were pressed into thin self-supporting wafers, and measurements were performed using an ATI RS1 Fourier transform spectrometer equipped with an in situ stainless steel cell with calcium fluoride

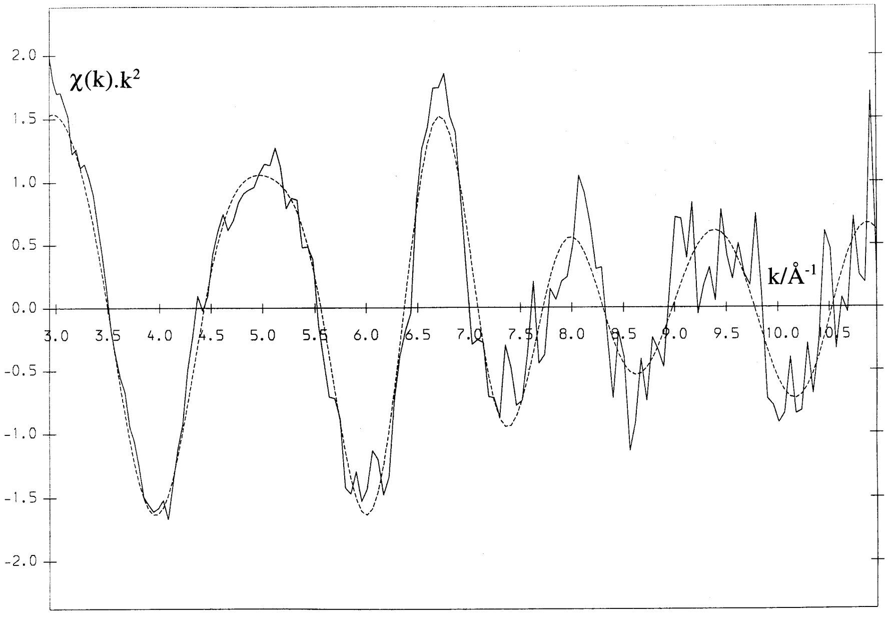

Figure 2. Experimental (solid lines) and calculated EXAFS (dotted lines) for Fe-ZSM-5 treated in oxygen, as described in the text.

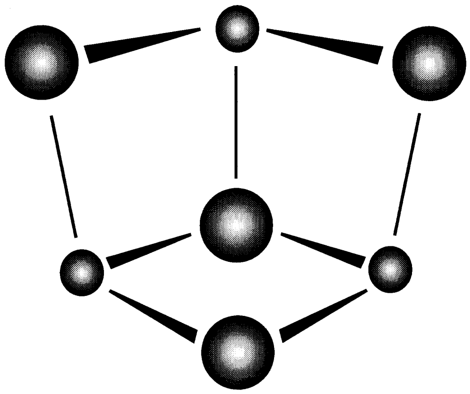

Figure 3. Possible structure of the iron–oxygen clusters in the zeolite, by analogy to ferredoxin II (after ref. [11]): larger circles, oxygen; smaller circles, iron.

windows, capable of a base pressure $< 10^{-7}$ mbar. Catalytic measurements were carried out in a flow apparatus and using conditions that have also been described previously [7].

3. Results and discussion

The temperature-programmed reduction behaviour of the Fe-ZSM-5 catalyst is shown in figure 1, which also indicates the result obtained with a standard of copper(II) oxide. As can be seen, there is very little reduction of Fe-ZSM-5, the hydrogen uptake peaks at 400–500 K being sufficiently large only to account for reduction from Fe(III) to Fe(II). No significant further reduction was observed, even at the maximum temperature of > 1250 K. High resistance to reduction has also been reported for iron exchanged into faujasite [8], although reduction to Fe(0) did occur at 1200 K, probably as a consequence of zeolite lattice breakdown. The reductive stability of Fe-ZSM-5 is in marked contrast to Cu-ZSM-5 catalysts, where facile reduction starts at 500 K in hydrogen [9].

Examination of the as-prepared catalyst by X-ray absorption indicates that each iron atom is co-ordinated to ca. 6 oxygen atoms at a distance of 2.00 ± 0.03 Å, and ca. 1.5 iron atoms at a distance of 3.00 ± 0.05 Å, as indicated in table 1. Both iron–oxygen and iron–iron distances are characteristic of iron in an edge-sharing octahedral environment, as found for example in FeOOH. On heating in He/O_2 to about 780 K, however, marked changes occur, and both the experimental and calculated EXAFS spectra are shown in figure 2, with the parameters used in the fit again being tabulated. The local environment of the iron atoms in the zeolite is well described by four shells of neighbours: two sets of oxygen atoms respectively at distances of 1.87 and 2.02 Å, two iron neighbours at the relatively short distance of 2.53 Å, and a shell due to silicon or aluminium at about 3.23 Å. (Because of the similarity of their backscattering power for X-rays, EXAFS cannot differentiate between aluminium and silicon as neighbours.) The range of iron–oxygen distances is similar to that observed when iron is tetrahedrally co-ordinated to oxygen, for example in Na_5FeO_4 and $Na_8Fe_2O_7$ [10]. The Fe–Fe distances observed are different from those present in the bulk iron oxides FeO, Fe_3O_4, and Fe_2O_3. The Fe–Fe distance of 2.53 Å is close to the nearest-neighbour distance in metallic iron, although the TPR result, the XANES observations and the high Fe–O co-ordination number clearly show that this material is not fully reduced. The spectrum is also very different from that observed when iron is incorporated into the silicalite framework [11],

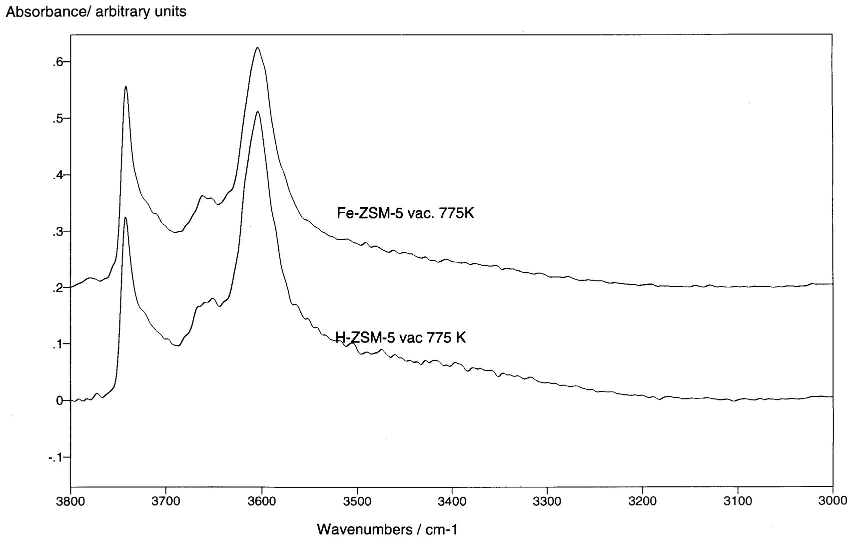

Figure 4. Infrared spectra of the O–H stretching region for Fe-ZSM-5 and the parent H-ZSM-5 zeolite after in situ activation in vacuum at 775 K.

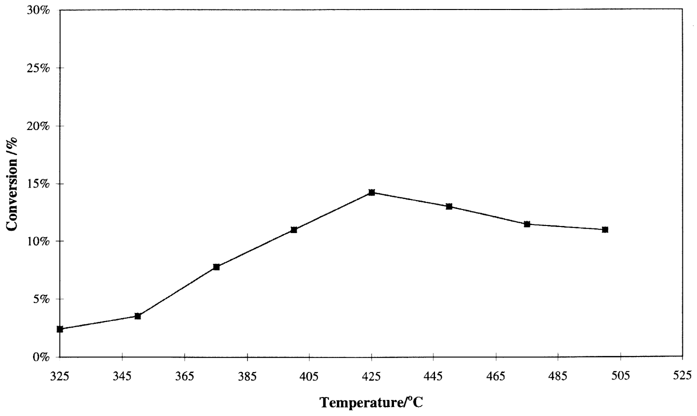

Figure 5. NO conversion over Fe-ZSM-5 as a function of temperature, under the conditions described in the text.

and different in character from that of copper in Cu-ZSM-5 catalysts. In over-exchanged Cu-ZSM-5, a much longer copper–copper interatomic distance of ca. 2.96 Å is observed, the value expected for clusters resembling copper oxides [9].

Our experimental results provide no information on the extent to which the stable iron–oxygen clusters observed are mono-disperse. However, the short Fe–Fe interatomic distances and the stability against reduction suggest the presence of unusual, and perhaps largely monodisperse species. On the basis of the EXAFS interatomic distances and co-ordination numbers, and by comparison with the active site from ferredoxin II, Fe_3S_4 [12], we propose that the iron clusters in the zeolite could adopt a similar structure to that shown in figure 3. The differences in bond lengths compared to ferredoxin, for both Fe–O and Fe–Fe distances, simply reflect the difference in the size of the oxygen and sulfur ions. Calculation of the Fe–Fe bond distance by substitution of sulphur by oxygen and our experimental Fe–O bond distance of 2.02 Å into the ferredoxin II structure, leads to a Fe–Fe bond distance of 2.46 Å, which compares reasonably with the Fe–Fe bond length observed here, 2.53 Å. The short iron–oxygen distance observed thus reflects bonding of the iron of the cluster to framework oxygen of the zeolite.

The influence of iron on the Brønsted acidity of the parent zeolite can be seen in figure 4, which is the O–H stretching region of the infrared spectrum. In comparison to Cu-ZSM-5, where exchange leads to suppression of Brønsted acidity [13], ca. 70% of Brønsted acid sites still remain after introduction of iron, compared to the expected value of $< 20\%$. The presence of iron, however, influences the *strength of acidity*, as shown by a reduction of ca. 50 K in the temperature at which we have found that ammonia desorbs from Fe-ZSM-5, compared to the parent H-ZSM-5 zeolite. There is also a slight blue shift of the O–H stretching frequency of the remaining Brønsted acid sites, which is in line with decreased acidity in the Fe-ZSM-5 [14].

We have measured the activity and selectivity of our catalyst in the SCR reaction using propene as reductant, and the results are shown in figure 5. As reported by others [15], we find that the iron-containing material is *less effective* than Cu-ZSM-5 catalysts, although active over a similar temperature range. With propene, the maximum SCR activity is observed at ca. 700 K, compared with a value of > 800 K reported by FH using 2-methylpropane as reductant.

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