



Experiment Report Form

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Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.



	Experiment title: The mechanism of N ₂ O decomposition over iron zeolites - The nature of the active surface oxygen	Experiment number: 01-01-617
Beamline: BM01b	Date of experiment: from: 20 june 2003 to: 24 june 2003	Date of report: 1 october 2003
Shifts: 9	Local contact(s): Dr. Wouter van Beek	<i>Received at ESRF:</i>

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Report:

Introduction

One of us studied the interaction of N₂O with Fe-ZSM-5 catalysts by a series of step response experiments [1]. The experiments showed that pretreatment strongly affected the catalytic activity. Catalysts, which were treated in O₂ at 400°C before reaction with N₂O, had a lower activity than catalysts, which were reduced in H₂. In the prereduced catalyst, a lot more oxygen from N₂O was incorporated into the iron oxide clusters. The higher activity of this catalyst indicates that N₂O-oxygen behaves differently from the other oxygen atoms in the cluster.

Another effect was observed after pretreatment at very high temperatures (600°C): In the first minutes of reaction with N₂O at 400°C, the catalysts had a very high decomposition activity, which slowly decayed to steady state. The transient activity was especially high after pretreatment in He at 600°C. It seems to be related to the dehydroxylation of the iron oxide clusters.

Goal of experiment 01-01-617 was to study both effects by in situ XAS.

Experimental

A new EXAFS cell was developed, which resembles a plug flow reactor. The cell has rectangular inner cross section of 15 x 6 mm and a length of 50 mm (parallel to the axis of the beam). The middle part of the cell is heated. The ends, where capton windows are placed, are cooled. The sample holder is placed in the middle of the cell and held in position by two shafts. Gas enters the cell at one end and flows through the sample pellet to the exit at the other end of the cell. Since the sample holder does not completely fill the cross section of the cell, a small by-pass cannot be avoided, but test experiments showed that only a small fraction of the feed stream passes the reactor unconverted. Experiments were performed with pellets of 25 mg of Fe-ZSM-5 prepared by sublimation of FeCl₃. The sample was pretreated in O₂ at 500°C for 1h, then cooled to room temperature. An EXAFS spectrum was recorded. Subsequently, the sample was heated in a flow of He to

600°C, kept there for 1h and cooled to 400°C. At 400°C a step from He to 5000 ppm N₂O in He was performed. The treatments were followed in situ by XANES and/or EXAFS.

A second pellet of Fe-ZSM-5 was pretreated at 400°C in H₂ and cooled to room temperature. The XANES spectrum showed that the sample was not fully reduced. Thus, reduction was repeated in a flow of 4% H₂ in He. The temperature programmed reduction was followed by XANES from room temperature to 400°C. The cell was then briefly flushed with He and a step to 5000 ppm N₂O in He was performed. EXAFS spectra were recorded of the reduced catalyst in H₂ and of the reoxidised catalyst in N₂O, both at 400°C. After reoxidation by N₂O the catalyst was also measured at room temperature.

EXAFS analysis was carried out using the IFEFFIT data analysis package. The suitability of the theoretical backscattering paths generated from FEFF 8.1 was checked by fitting the experimental spectrum of Fe₂O₃ with all single scattering paths below 4 Å, using S₀², σ² and ΔE₀ as the only fit parameters. A good fit between 1 and 3 Å was obtained for the values S₀² = 0.75, σ² = 0.003 and ΔE₀ = -4 eV. S₀² was fixed to 0.75 in the fits of the other samples.

Results and Discussion

Figure 1 shows the XANES-spectra measured during heating the O₂-treated Fe-ZSM-5 in a flow of He to 600°C. Only very little autoreduction of Fe^{III} to Fe^{II} took place even at 600°C, because the He carrier gas contained an O₂ impurity. In the subsequent step to N₂O at 400°C, a high initial N₂O decomposition activity was not observed. This can be partly ascribed to the O₂-impurity in the He carrier, but also to the different flow pattern of the in situ cell compared to a plug flow reactor filled with catalyst powder. It was therefore not possible to study the very fast, transient N₂O decomposition reaction by in situ XAS.

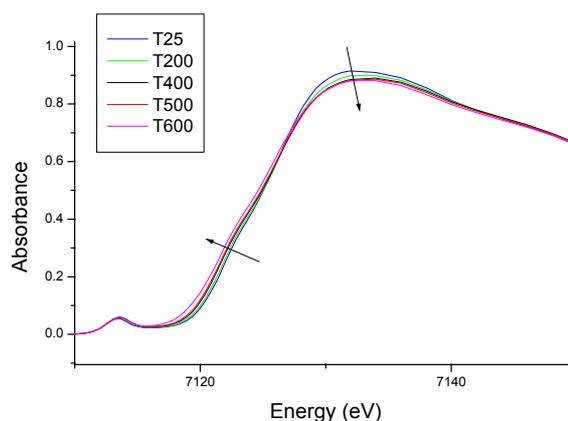
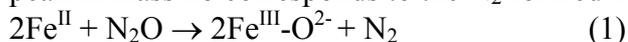


Figure 1 XANES spectra of Fe-ZSM-5 (pretreated in O₂) during heating in a flow of He.

The second experiment addressed the question why a catalyst, which was prereduced in H₂, exhibited a higher steady-state activity in N₂O decomposition. The catalytic behaviour suggests that atoms originating from N₂O behave differently from the other oxygen atoms in the iron oxide cluster. These structural differences should be detectable by EXAFS. Thus, Fe-ZSM-5 was reduced in H₂, reoxidised with N₂O and compared with the original material treated in O₂.

Figure 2 shows the XANES spectra measured during reduction of Fe-ZSM-5 in a stream of H₂/He. Before the start of the in situ experiment the catalyst had already been partly reduced “offline”, i.e. without measuring XAS. The XANES spectrum measured at room temperature showed a mixture of Fe^{II} and Fe^{III} species: The preedge peak had a shoulder at lower energies and the energy at half height of the edge was at 7120.7 eV, compared to 7122.7 eV for the fully oxidised catalyst. During heating from room temperature to 200°C, the intensity of the white line decreased and the edge became flatter (not shown), indicating the desorption of H₂O from iron sites. Above 200°C reduction of Fe^{III} to Fe^{II} set in. The position of the edge shifted to lower energies and in the preedge the peak at 7113.5 eV decreased, while the peak at 7111 eV increased. After 10 min at 400°C reduction was complete. The sample was left another hour at 400°C in H₂-flow while 2 EXAFS scans were recorded.

After this the cell was flushed with He and a step to N₂O was performed. Figure 3 shows that already during flushing with He a slow reoxidation of the catalyst took place, due to the presence of an O₂ impurity. After the step to N₂O oxidation was completed very rapidly. Figure 3b shows the corresponding MS-signals. The peak in mass 28 corresponds to the N₂ formed in the reoxidation of Fe^{II} to Fe^{III}:



The reoxidation reaction was nearly complete when the first XANES scan after the switch to N₂O was measured. After reaching steady state in N₂O decomposition, 2 EXAFS scans of the working catalyst were recorded. Table 1 compares the fit parameters of the reduced and N₂O-treated catalyst at 400°C, Table 2 the fit parameters of the original O₂-treated catalyst and the catalyst after reduction and N₂O-treatment, measured at room temperature.

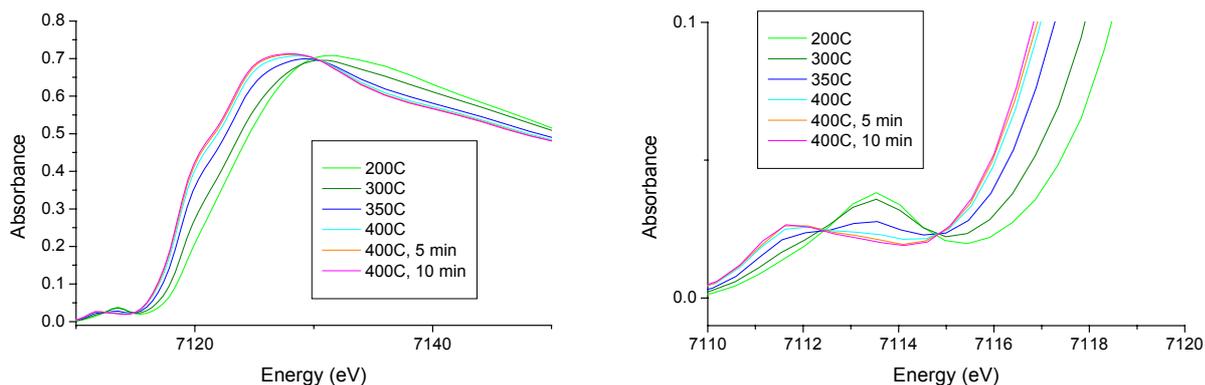


Figure 2 XANES spectra of Fe-ZSM-5 during heating in H₂/He

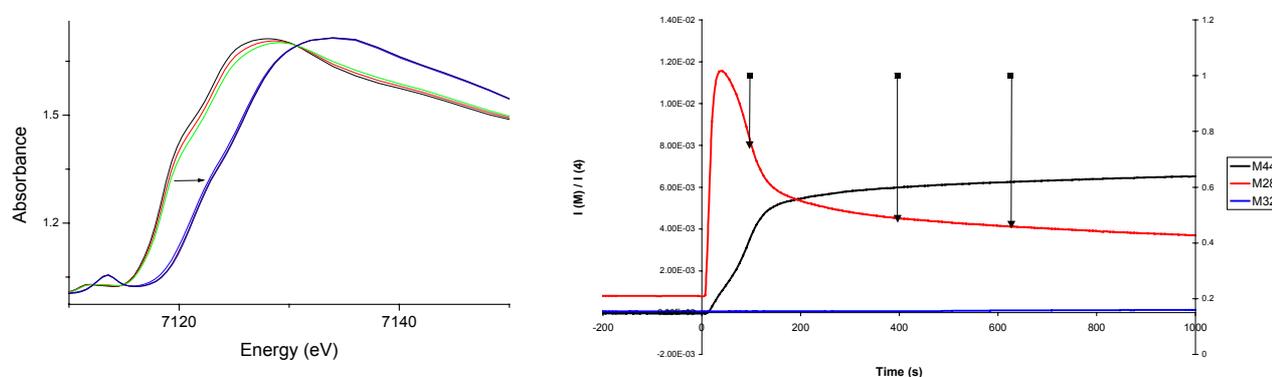


Figure 3 (a) XANES spectra of Fe-ZSM-5 before and after the step to N₂O at 400°C. (b) MS signal of $m/e = 44, 28$ and 32 after the step to N₂O. Arrows indicate the time at which a spectrum was measured.

Comparison of the spectra in H₂ and N₂O shows that the total coordination number of the Fe-O shells increased from 3.0 to 3.3 upon oxidation with N₂O. The Fe-O bond lengths decreased by about 0.1 Å. If the spectra were fitted with only one oxygen shell, its coordination number increased from 3.2 to 3.7. The expected difference is $\Delta CN = 1.0$. The smaller increase of the coordination number observed in our experiments is explained by the fact that the reduced iron oxide clusters bind some of the water formed during the reduction.

The Fe-Fe coordination was close to 2.0 in all the spectra of the oxidised catalyst, at room temperature as well as at 400°C. Only in the reduced state a Fe-Fe coordination number of 1.0 was found. This indicates that reduction breaks the iron clusters into smaller, binuclear units. A model where a cluster or a chain of four iron atoms is split upon reduction, fits well with the coordination numbers obtained from the EXAFS fit. Note that the Debye-Waller factor of the Fe-Fe shell was very high, indicating a large spread of Fe-Fe distances, i.e. a high structural disorder. In view of the high Debye-Waller factors we attempted to fit the spectra with two Fe-Fe shells. The shells converged to distances of 2.95 and 3.11 Å in the oxidised catalyst. The sum of the coordination numbers was the same as in the fit with only one single iron backscattering shell.

Table 1 Fit parameters of the spectrum of Fe-ZSM-5 measured at 400°C in H₂ and in N₂O flow. The k²-weighted χ -data in the range from 2.9 to 14.8 Å⁻¹ were transformed and fit in R-space from 1.0 to 3.0 Å.

Shell	R	CN	σ^2	ΔE_0
H ₂ , 400°C				
Fe-O	1.94	1.5 ± 0.4	0.005	-6.4
Fe-O	2.07	1.5 ± 0.3	0.005	
Fe-Fe	3.01	1.0 ± 0.6	0.012	
N ₂ O, 400°C				
Fe-O	1.83	1.6 ± 0.2	0.003	-6.4
Fe-O	1.98	1.7 ± 0.2	0.003	
Fe-Fe	2.98	1.7 ± 1.3	0.017	

Table 2 Fit parameters of Fe-ZSM-5 measured at room temperature, after treatment in O₂ at 500°C and after reduction in H₂ at 400°C, followed by reoxidation with N₂O. The k²-weighted χ -data from k = 2.9 to 15.6 Å⁻¹ were transformed and fit in R-space from 1.0 to 3.0 Å.

Shell	R	CN	σ^2	ΔE_0
O ₂				
Fe-O	1.86	1.75 ± 0.2	0.002	-7.0
Fe-O	1.99	2.1 ± 0.3	0.002	
Fe-Fe	2.98	2.2 ± 0.6	0.013	
N ₂ O				
Fe-O	1.86	1.75 ± 0.2	0.003	-6.1
Fe-O	2.00	2.3 ± 0.2	0.003	
Fe-Fe	3.00	2.4 ± 1.3	0.015	

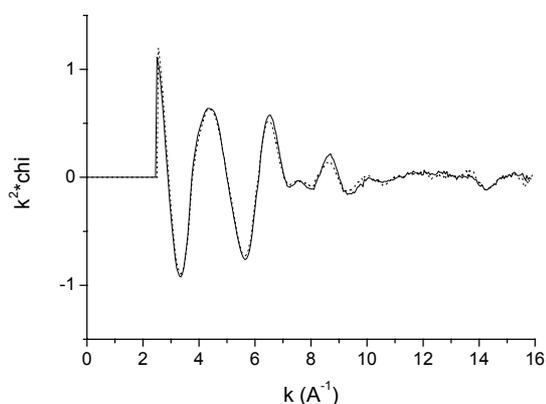


Figure 4 χ -data of Fe-ZSM-5, measured at room temperature after pretreatment in O₂ at 500°C and after reduction in H₂ at 400°C, followed by reoxidation with N₂O at the same temperature.

Conclusions

Sublimation of FeCl₃ followed by washing and calcination forms small iron oxide cluster in ZSM-5, whose size is estimated to be in the range of three to five atoms. The large Debye-Waller factor of the Fe-Fe shell indicates high disorder, i.e. a mixture of different structures. Reduction splits the clusters into smaller (binuclear) units. Incorporation of oxygen from N₂O into the iron oxide cluster does not lead to significant changes in the oxygen coordination number and distance.

Comments

The quality of the spectra was very good this time. For the in situ experiments it would be very helpful to install a gas distribution system, which allows to feed high purity gas into the EXAFS cell. For systems, which are very sensitive to air impurities, improvised gas connections with plastic or teflon tubes are not sufficient because air permeates through them.

Reference:

¹ G.D. Pirngruber, J. Catal. 219 (2003) 456.

The χ -data of the O₂- and N₂O-treated catalyst were nearly identical (see Figure 4). The two spectra could be fitted with very similar parameters. By isotope labelling we showed that the oxygen atoms, which N₂O deposits on the catalyst surface, exchange rapidly with the other oxygen atoms of the iron oxide cluster. EXAFS indicates that the oxygen atoms, which N₂O incorporates into the iron oxide clusters, do not have a distinctly different bond length and do not affect the average coordination number. The oxygens originating from N₂O only distinguish themselves by their high mobility on the catalyst surface.