Catalysis Letters 8 (1991) 193–200

DETERMINING THE ENVIRONMENT OF TRANSITION METAL IONS IN ZEOLITIC CATALYSTS: A COMBINED COMPUTATIONAL AND SYNCHROTRON-BASED STUDY OF NICKEL IONS IN ZEOLITE-Y

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Received 26 November 1990; accepted 18 December 1990

Computer modelling techniques are used to investigate the local structure of the zeolite framework around Ni^{2+} ions in the S_I sites of Ni exchanged zeolite-Y. Our calculations show that there are pronounced inward relaxations (0.4 Å–0.6 Å) of the surrounding oxygen ions. The results allow a detailed rationalisation of recent EXAFS and diffraction studies on this zeolite.

Keywords: Zeolitic catalysts, transition metal ions, nickel; computation, environment, EXAFS, modelling catalysts

1. Introduction

How is one to locate the precise position of catalytically active metal ions in a zeolitic catalyst? One method would be to use synchrotron radiation and a special in-situ cell which permits the recording of both X-ray powder diffractograms and X-ray absorption spectra under the actual reaction conditions. Although we have demonstrated [1,4] the feasibility of doing just this, and of the extraction of atomic coordinates for Ni^{2+} ions from both Rietveld refinement of powder diffraction patterns and extended X-ray absorption fine structure (EXAFS), it remains difficult to carry out a definitive, in-situ, experiment capitalising on the combined use of these two approaches. But even with the most detailed diffraction studies such as EXAFS data, it is still desirable to achieve yet higher resolution and greater structural insight by invoking supplementary methods. In particular, computational studies, of the kind we describe in this letter, should prove invaluable. Such studies can reveal subtle changes in the local atomic environment at active sites in the large family of uniform heterogeneous catalysts.

We focus our attention here on nickel-exchanged zeolite-Y catalysts such as those examined previously in this laboratory in other in-situ (rotating-anode X-ray) studies of the cyclotrimerization of acetylene. Full reports of the results of the joint X-ray powder diffraction and EXAFS studies have been given elsewhere

[1,4]. Briefly, the EXAFS work yields a Ni-O bond length of 2.02 Å and a coordination number of 4^{+}-1 for the metal ion (Ni^{2+}) in the S_I site, whereas Rietveld analysis locates the Ni^{2+} at the S_I site, coordinated to 6 framework oxygen atoms at 2.28 Å. We interpreted this apparent contraction in terms of the flexibility, and in particular, the relaxation of the framework structure surrounding the Ni^{2+} in the S_I site. As there is only fractional occupancy (by Ni^{2+} ions) of the S_I site (estimated at 0.75) we interpreted the observed bond length determined by diffraction to be the weighted average of the relaxed bond lengths (i.e. that determined by EXAFS) and the unrelaxed length.

This computational study sets out specifically to determine, independently, the magnitude of the structural relaxation around the S_I site occupied by Ni^{2+} ions, and, more generally to lay the foundation of more sophisticated studies of structural rearrangement in the vicinity of active sites and under a variety of environmental conditions.

It is to be noted that Ni^{2+} ions situated at the S_I site, upon which we focus in this communication are not themselves catalytically active under reaction conditions, at least in the trimerization of acetylene [3,4]. The experimental evidence indicates that migration from these sites takes place during activation, and the Ni^{2+} ions are closer to S_{II} sites in the catalytically active state. Future computational studies will take into consideration this fact.

2. Computational procedure

We use the energy minimization techniques available in the CASCADE code, which performs a full minimization on a spherical region of the lattice; with the polarization of more distant regions being calculated by approximate methods based on the procedure, developed by Mott and Littleton [5], the methodology and application of which are discussed in detail in ref. [6]. All calculations employed a region radius of 7.5 Å as this gave an acceptable balance between computational cost and accuracy. The potentials employed were those used by den Ouden et al. [7] in a previous study of Ni containing zeolites.

In the first set of calculations we examined a purely siliceous faujasite, before progressing to attempt a crude simulation of the incorporation of Al by modifying the effective charge of the tetrahedral atoms which were reduced from 4 to 3.69 corresponding to a Si : Al ratio of 2.25. A modification of this approach retained a purely siliceous matrix but adjusts the average tetrahedral charge in the 12 Si atoms of the six-rings comprising the hexagonal prism.

The next stage of sophistication was to replace explicitly a number of Si by Al ions, which is a far more realistic model for the real structure. Thus into the inner region of the simulation one included an Al ion distribution around the double hexagonal prism; Na^{+} ions were also added to achieve electroneutrality (after inclusion of Ni^{2+}) The Al ions were distributed according to Loewenstein's rule in which Al-O-Al bridges are forbidden.

Into these host structures an Ni^{2+} cation was placed and anchored at the centre of the S_I site; the surrounding zeolite cage was then allowed to relax.

3. Results and discussion

Both relaxed and initial Ni^{2+} framework atomic distances are given in table 1 for each of the types of calculation discussed above.

As can be seen from table 1B the purely siliceous zeolite distorts symmetrically, unlike all the other systems which contain some resemblence of aluminium character, and distort asymmetrically. For the pure SiO_2 system, the O atoms relax inwards by 0.5 Å. In contrast, those calculations where an average tetrahedral atom with a reduced charge was used (table 1C), the O atoms relax inwards by 0.3 Å indicating such models are less satisfactory. When the reduced tetrahedral change is localised, inward O relaxation is once more simulated (table 1D) with an asymmetrical inner distortion.

When Al ions were added explicitly, the first configuration comprised an Al, in the six-ring and another in a sodalite cage; hence the Ni defect is only close to one Al. The results (table 1E) indicate a sharp drop in the minimum Ni-O distance; but the other oxygen atoms are not significantly pulled towards the defect site.

Next, two Al ions were included in the two six-rings and these were positioned at opposite sites in the rings, in order to minimise the Al-Al interactions. Again, as seen in table 1F, the O atoms relax towards the Ni^{2+} ion; but the minimum Ni-O distance is seen to be greater than that for the one Al system, although more oxygens have been pulled closer. Thus, there is an overall increase in the inward relaxation of the six-ring.

In the preceding systems the Si/Al ratio is not close to that experimentally observed; an increase to four Al ions in the double six-ring yields a ratio of 2 : 1 which is near the ratio used in the experimental study of Dooryhee et al. [1]. It was necessary to add to this system two additional cations, hence two Na^+ were placed at the S_{II} site, which is the experimentally observed occupancy site for Na^+ [1]. There are many possible combinations of four Al ions between twelve atoms; but due to the highly symmetric structure and the restrictions due to Loewenstein's rule, only a few combinations are possible. These combinations were simulated and the results are given in table 2; the Al ion distributions used are indicated in fig. 1. As can be seen the resulting relaxation distances depend upon the Al configuration, but overall the oxygen shell is drawn closer to the Ni^{2+}.

The anti-symmetric splitting of the shells can also be seen in the Ni-Si distances; the shell is symmetric in the purely siliceous system but is distorted in

Table 1

A. Initial distances from the defect site to the surrounding framework

Co-ordination number	Ni-O distance (Å)	Co-ordination number	Ni-Si distance (Å)
6	2.845	12	3.607
6	3.77		
12	5.184		

B. Relaxed geometries for the purely siliceous system

Co-ordination number	Ni-O distance (Å)	Co-ordination number	Ni-Si distance (Å)
6	2.361	12	3.41

C. Relaxed geometries for an effective tetrahedral charge of 3.69

Co-ordination number	Ni-O distance (Å)	Co-ordination number	Ni-Si distance (Å)
2	2.531	2	3.587
2	2.593	4	3.615
2	2.65	6	3.68

D. Relaxed geometries for effective tetrahedral charged 3.69 ion in T sites in the double hexagonal prism

Co-ordination number	Ni-O distance (Å)	Co-ordination number	Ni-Si distance (Å)
2	2.301	2	3.397
2	2.317	4	3.405
2	2.334	4	3.420
		4	3.428

E. Relaxed geometries for a calculation based on explicit inclusion of one aluminium in the six-ring

Co-ordination number	Ni-O distance (Å)	Co-ordination number	Ni-Si distance (Å)	Ni-Al distance (Å)
1	2.11	1	3.29	3.549
1	2.24	1	3.35	
4	2.40	1	3.377	
		2	3.38	
		2	3.412	
		2	3.432	
		2	3.472	

F. Relaxed geometries for a calculation based on explicit inclusion of two aluminium atoms in the six-ring

Co-ordination number	Ni-O distance (Å)	Co-ordination number	Ni-Si distance (Å)	Ni-Al distance (Å)
2	2.137	2	3.315	3.493
1	2.38	1	3.38	3.503
2	2.42	3	3.404	
1	2.44	1	3.438	
		1	3.455	
		2	3.474	

Table 2
Relaxed geometries calculated when four aluminium ions are included explicitly in the simulation

Arrangement A

Coordination number	Ni-O distance (Å)	Co-ordination number	Ni-Si distance (Å)	Ni-Al distance (Å)
1	2.18	2	3.29	3.447
2	2.20	1	3.34	3.462
1	2.24	1	3.38	3.498
1	2.46	3	3.448	3.52
1	2.49			

Arrangement B

Coordination number	Ni-O distance (Å)	Co-ordination number	Ni-Si distance (Å)	Ni-Al distance (Å)
1	2.16	1	3.283	3.414
1	2.17	1	3.31	3.458
1	2.20	1	3.326	3.478
1	2.23	1	3.333	3.519
1	2.48	1	3.458	
1	2.53	1	3.482	
		1	3.56	
		1	3.51	

Arrangement C

Coordination number	Ni-O distance (Å)	Co-ordination number	Ni-Si distance (Å)	Ni-Al distance (Å)
2	2.196	2	3.294	3.43
1	2.227	2	3.315	3.49
1	2.257	1	3.46	3.46
1	2.45	1	3.47	3.51
1	2.48	2	3.482	

Arrangement D

Coordination number	Ni-O distance (Å)	Co-ordination number	Ni-Si distance (Å)	Ni-Al distance (Å)
1	2.19	1	3.2896	3.457
1	2.23	1	3.316	3.472
2	2.245	2	3.322	3.474
2	2.458	1	3.44	3.497
		1	3.460	
		1	3.477	
		1	3.482	

Table 2 (continued)

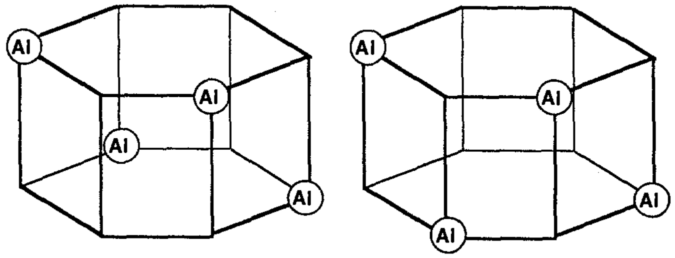
Arrangement: 3 aluminiums in one six-ring

Coordination number	Ni-O distance (Å)	Co-ordination number	Ni-Si distance (Å)	Ni-Al distance (Å)
1	2.19	1	3.30	3.477
2	2.204	1	3.31	3.483
1	2.24	2	3.329	3.485
2	2.46	1	3.411	3.506
		1	3.434	
		1	3.44	
		1	3.48	

the Al containing systems. The relaxation of the hexagonal prism, illustrated in fig. 2 is typical of all the calculations.

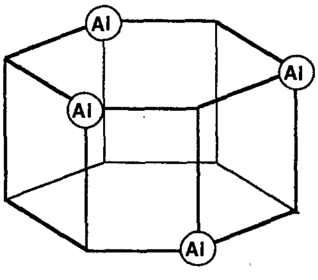
The magnitude of the relaxations tie in well with the information from the EXAFS spectra, which showed inward movement of the Ni-O bonds of 0.5 Å and indicate a complex range of Ni-O spacings, a result which is well reproduced by our calculations based on four Al substitutients.

Simulations of the EXAFS spectra using our calculated models for the framework structure around the Ni^{2+} are being calculated at present.

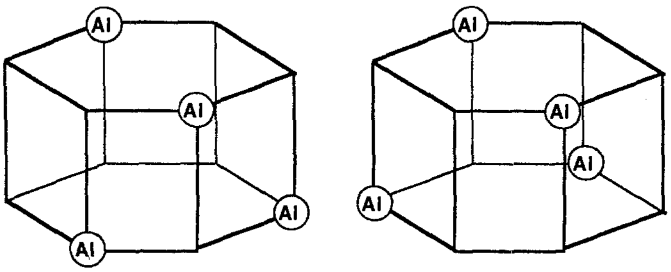


Arrangement A

Arrangement B



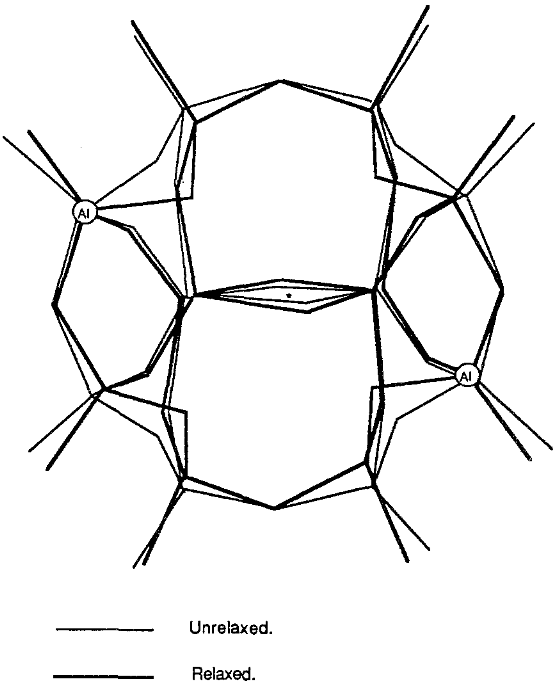
Arrangement of three aluminiums in one six-ring.



Arrangement C

Arrangement D

Fig. 1. Arrangement of aluminiums around the hexagonal prism.



The Ni^{2+} ion has been excluded from the diagram for clarity, and should appear in the (*) position.

Fig. 2. An overlay of the relaxed and the unrelaxed framework for 2 Al in the hexagonal prism.

4. Conclusion

Overall the results demonstrate the flexibility of zeolite frameworks and the ability of extra framework cations to effect extensive perturbations of the framework structure. Moreover the possibility of simulating these subtle effects by computational methods is clearly demonstrated by our study. Such methods are clearly an invaluable tool in these complex structural studies.

Acknowledgements

We are indebted to the Science and Engineering Research Council for general support and a quota studentship (to A.R.G.)

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