EXAFS Studies of Mo-Y-Zeolite Catalysts

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Introduction

In recent years there has been an increasing interest in molybdenum containing zeolite catalysts as effective bifunctional catalysts.[1-4] Different techniques have been used to prepare and characterize the Mo-zeolites. It is difficult to exchange the cations of a zeolite for molybdenum ions directly because high valence cationic molybdenum can only exist in very acidic solution where ion-exchange equilibria are unfavourable and many zeolites are unstable. Ion exchange with neutrial and anionic species results in a large amount of surface loading. In order to overcome the difficulties of aqueous ion exchange, molybdenum is introduced into zeolites by the solid-ion axchange method. A special procedure was developed recently for initiating controlled immigration of $MoO_2(OH)_2$ into the zeolite pore of HY with MoO_3 in the presence of water vapor.[5]

EXAFS is an effective physical method for determination of the local structure of specific atoms in complex sytems such as highly dispersed supported metal catalysts. It has been successfully applied to some metal zeolite catalysts: viz. Pt-Y-zeolite[6], Cd-Y-zeolite[7] and Ni, Mo-Y-zeolite[8] and other bimetallic catalysts[9-10]. However, an EXAFS study of Mo-zeolite prepared with solid-ion exchange method has not been published. In this work, we studied by EXAFS the change of the local environment around Mo in the preparation of Mo-Y-zeolite directly to see if is Mo incorprated into the framework of Y-zeolites. As prepared, reduced and dehydrated samples were studied.

Experimental

Samples

The HNaY zeolite was prepared by exchange of NaY with 0.1 N NH_4NO_3 solution at 365K for 1 hour, followed by a direct calcination at 823K for 5.5 hours in a closed vessel. The modified solid ion exchange was performed as following: a mixture of 27 g HNaY and 1.2g MoO_3 was ground in a mortar

(hereafter denoted as MoHY), placed in a quartz tube and then calcined at 723K, water vapor at 323K (118 torr) was carried through the mixture using H_2 as the vector gas with a flow of 45ml/min. The sample obtained after calcination was then denoted as MoHYR. This sample then underwent dehydration at 673K (MoHYRD). The contents of the samples were then analyzed by AAS, Na contents were detemined by ICP, and X-ray powder diffraction measurements were made using a Cu-target x-ray tube.

X-ray absorption measurement

X-ray absorption experiments were performed on beam line X-11A of the National Synchrotron Light Source (NSLS), Brookhaven National Laboratory. The X-ray absorption spectera for Mo K-edge were recorded with the ring operating at 2.5 GeV beam energy and a beam current of 40-180 mA. The pressed powder samples were mounted on the holder and measured at liquid nitrogen temperature in the transmission mode.
Data analysis was carried out with using standard methods[11] and the fitting was done using experimentally determined Mo-O (from ZnMoO4), Mo-Mo (from metallic Mo) and theoretically calculated Mo-Si (using FEFF)[12] phase shifts and backscattering amplitudes. Both single or multiple shell models were assumed for fitting the various filtered Fourier transform (FT) peaks.

Results and Discussion

1. XAS of Mo-Y-zeolites

The normalized X-ray absorption curves of MoO_3, MoHY, MoHYR, MoHYRD and Mo metal are shown in Fig.1. The high pre-edge peak on the MoHY curve provides strong evidence for the presence of a short M=O bond characterizing MoO_3 in the mixture of MoO_3 and HY.[13] This feature of MoO_3 almost disappears after calcination of the mixture at 723K in the presence of water vapour which means that the incorporation of Mo from MoO_3 into zeolite has taken place. XRD measurement also showed that MoO_3 diffraction peaks located at d=6.907, 3.801 and 3.255Å were absent in these samples.[14] Further changes of the spectrum occurred when the sample was calcined in H_2 (MoHYR) and then dehydrated (MoHYRD). The comparison between $k^3\chi(k)$ of MoO_3 and MoHYRD (see Fig.2) indicates that a great change of the environment around Mo in them clearly takes place because of the solid-ion exchange process. Further comparison of the Fourier transforms as shown in Figure 3 also show significant changes but no strong evidence for the formation of the metallic phase. From these comparisons

we assume that there is no significant change of the oxidation state of Mo after incorporation of MoO_3 into the zeolite.

2. Fitting results

Fitting to the Fourier isolated shells in each sample was done using the reference compounds cited above. A summary of the results are listed in Table 1 for the three catalysts studied as well as MoO_3. For the first three shells in MoHY, a good fit was only obtained with a short Mo=O bond along with two Mo-O bonds. Any other combination of Mo oxygen bonds had variances at least a factor of two greater than the resulted shown here. It is also consistent with the observation of the absorption profiles (Fig.1) and Fourier transforms (Fig.3) where the first Mo=O peak changed.

When Mo is incorporated into the supercages of the zeolite, fitting shows that two new longer Mo-O bonds, 2.03-2.05 Å and 2.66-2.67 Å, are formed instead of 1.70 and 1.96Å bonds in MoO_3. For the first two peaks in the FT of MoHYRD, the isolated $k^3\chi(k)$ and the fitting curve with two longer Mo-O models are overplotted in Fig.4. The agreement is excellent. It was observed previously that the longer metal-oxygen bond around 2.6 Å can be present in metal-Y-zeolites.[15] The Mo-Mo interaction fitting results (see CN and R for Mo-Mo in Table 1) show that initially when Mo has been exchanged with the cationic ions in zeolite the Mo-Mo coordination is relatively large with an average Mo-Mo bond about 3.40Å but that this is significantly changed after reduction and dehydration. The Mo coordination number decreases from 6 (MoHY) to 1 (MoHYRD). This means that Mo was dispersed into the supercages of Y-zeolite, probably in octahedral clusters as [-Si-MoO_4-MoO_4-Si-] . Also a new third coordination shell around Mo in MoHYR and MoHYRD develops which is a combination of both Mo and Si(or possibly Al). The fitting of the third Fourier transform peaks in MoHYR and MoHYRD with both Mo-Mo and Mo-Si models greatly reduces the fitting variation between the experimental and calculated EXAFS data by up to 10-15 times compared to those with Mo or Si only as the neighbor. From Fig. 5 and 6, it can be seen that the two shell fitting gives the best results. The presence of Si around Mo from the zeolite framework, the decrease of the Mo-Mo coordination and the appearance of a long Mo-O bond all support the hypothesis that the solid-ion exchange method produces a Mo-substituted zeolite.

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Table 1. Mo Coordination Shells in Mo-Y-Zeolites and Mo Trioxide

MoHY					MoO3			
Model	CN	R(Å)	DWF.10^2	d-E_0(eV)	CN	R(Å)	DWF.10^2	d-E_0 (eV)
Mo=O	1.1±.1	1.58±.01	-0.59±.03	12.8±.5	1.0±.1	1.63±.01	-0.35±.03	12.0±1.0
Mo-O	3.4±.3	1.77±.01	-0.24±.06	-2.1±.2	2.5±.2	1.78±.01	0.27±.02	-7.0±.7
Mo-O	2.4±.2	1.98±.01	-0.56±.09	-2.1±.2	1.5±.1	1.97±.01	-0.68±.06	-2.0±.2
Mo-Mo	5.7±.2	3.36±.02	0.73±.01	3.2±.3	8.9±.8	3.48±.02	0.18±.02	-7.7±.8
Mo-O	2.5±.2	3.92±.02	-0.84±.08	-8.9±.8	7.6±.5	3.90±.02	-0.57±.05	-8.9±.9

MoHYR					MoHYRD			
Model	CN	R(Å)	DWF.10^2	d-E_0(eV)	CN	R(Å)	DWF.10^2	d-E_0(eV)
Mo-O	2.5±.2	2.03±.01	-0.27±.02	-7.9±.6	2.7±.2	2.05±.01	-0.23±.01	-6.7±.7
Mo-O	1.3±.1	2.67±.01	-0.52±.05	2.0±.2	1.3±.1	2.65±.01	-0.72±.01	6.6±1.0
Mo-Si	1.6±.1	3.45±.02	-0.27±.01	-10.7±.8	0.7±.1	3.45±.01	1.10±.01	-7.7±1.0
Mo-Mo	1.8±.1	3.75±.02	-0.28± 02	-5.6±.5	1.1±.1	3.75±.01	-0.22±.01	0.9±.1

Note: The experimental standardmdata are used for fitting: Mo-O (CN=4,R=1.78Å) from $ZnMoO_4$ and Mo-Mo (12,2.73Å) from metal Mo foil.

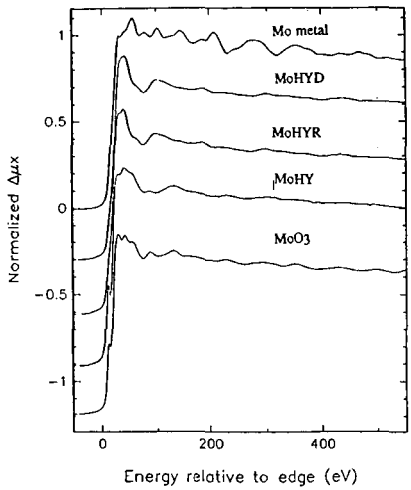

Figure 1. The normalized x-ray absorption spectrum versus energy for Mo metal, Mo in Y-zeolite which has been reduced and dehydrated as described (MoHYRD), Mo in Y-zeolite which has been reduced (MoHYR), Mo in Y-zeolite as prepared (MoHY) and MoO_3. The enrgy scale is relative to the binding enrgy of the Mo 1s state (20,000 eV).

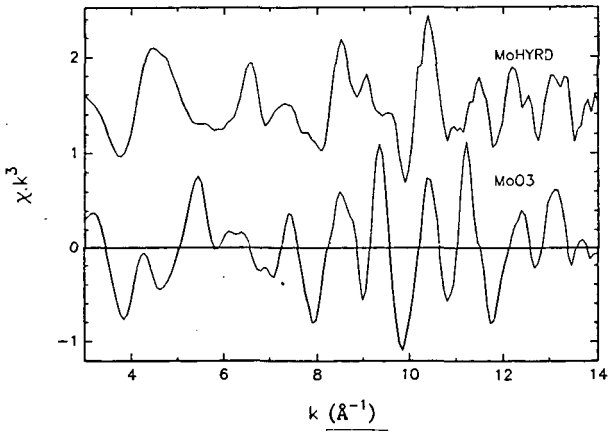

Figure 2. A comparison of the weighted spectra $k^3\chi(k)$ versus k of MoHYRD and MoO_3.

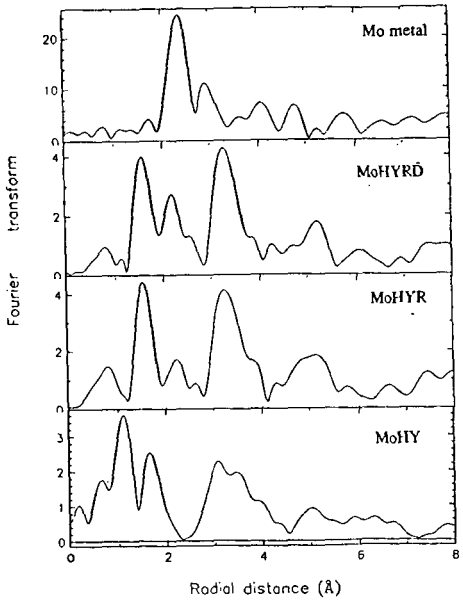

Figure 3. A comparison of the magnitudes of the Fourier transforms of the weighted EXAFS for Mo metal, MoHYRD, MoHYR, and MoHY versus R. The transforms are all of $k^3\chi(k)$ and taken over a k-space range of 3-14 $Å^{-1}$.

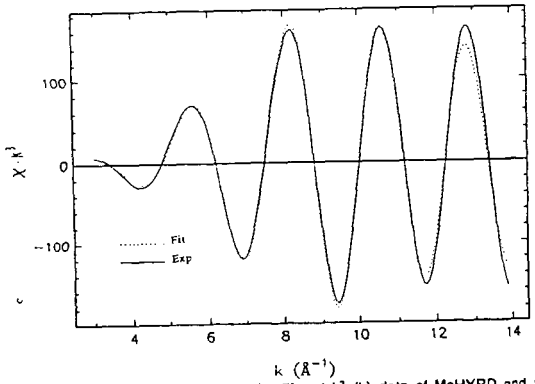

Figure 4. An overplot of the Fourier filtered $k^3\chi(k)$ data of MoHYRD and the best fitting results (see Table 1) versus r. The filtering range was from 1 to 2.8 $Å^{-1}$. The fitting included two Mo-O bonds only.

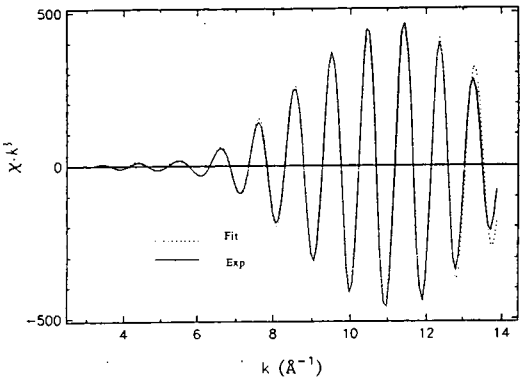

Figure 5. An overplot of the Fourier filtered $k^3\chi(k)$ third shell data of MoHYR and the best fitting results (see Table 1) versus R. The filtering range was from 2.8 to 4.1 Å^{-1}. The fit included both Mo-Mo and Mo-Si contributions.

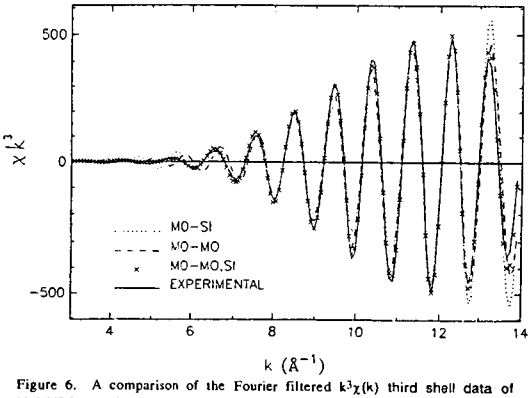

Figure 6. A comparison of the Fourier filtered $k^3\chi(k)$ third shell data of MoHYRD and fits containing Mo-Mo only (---), Mo-Si only (· · ·), and Mo-Mo and Mo-Si (xxx) versus R. The filtering range was from 2.8 to 4.1 Å^{-1}.