

In situ and *ex situ* XANES study of nanodispersed Mo species in zeolites used in fine chemistry catalysis

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Mo K-edge XANES experiments on Mo-containing zeolites at low Mo loading (1 and 2 wt% of Mo on H-ZSM-11, H-BETA and H-ZSM-5 catalysts), active in fine chemistry reactions, were performed *ex situ* as function of sample calcination temperature in air (in the range 773–973 K) or *in situ* at 873 and 973 K under N₂ flow. The results showed a 4-fold oxygen coordination for the incorporated Mo species in the activated (dehydrated) state. Combining these results with additional data evidences an almost total Mo exchange inside the zeolite channels.

Keywords: zeolite, Mo, xanes, fine-chemistry catalysis, methane conversion

1. Introduction

Mo-containing zeolites (crystalline aluminum silicates) are increasingly being used in different catalytic reactions (Wang *et al.*, 1993; Solymosi *et al.*, 1995; C.-L. Zhang *et al.*, 1998). In the fine chemistry catalysis field, the K3 vitamin synthesis and the ethane conversion into aromatic hydrocarbons represent successful applications of our low-content Mo-supported zeolites (Anunziata *et al.*, 1999a). The structural and electronic characterization of the Mo entity responsible of the exhibited activity in these catalysts is presently a challenge. XAFS is the technique that can provide, under suitable conditions, the nearest and second-nearest neighbours atomic coordination, electronic state and relative fractions of the Mo species. J.-Z. Zhang *et al.* (1998) applied *ex situ* EXAFS and Liu *et al.* (1999) *ex situ* XAFS to 4 and 6 wt% Mo/H-ZSM-5, respectively, prepared by the impregnation method. In the first above cited paper, the authors have not indicate the degree of dehydration of the samples during the measurements whereas the EXAFS analysis of the second one is restricted to carburized states. Recently, Li *et al.* (2000) reported more detailed *in situ* XAFS experiments in 1–3.6 wt% Mo/H-ZSM-5 (during exchange, activation and reaction), prepared from initial physical mixtures of MoO₃ and H-ZSM-5, proposing a (Mo₂O₇)²⁻ dimer as the exchanged active species.

In this work we present the first *ex situ* and *in situ* XANES results of Mo sites in low-content (1 and 2 wt%) Mo/H-ZSM-11, Mo/H-BETA, and Mo/H-ZSM-5 zeolites prepared by a unique impregnation method, measured after exchange and during activation of the catalysts (Z). There were no other previous x-ray absorption experiments reported on the two first zeolites on the Mo site; this is the first XAS characterization of the activated Mo

species in low-content Mo catalysts prepared by the impregnation method. The aim of this work is to study the effect of calcination temperature in oxidative and hydrating exchange conditions of the catalysts (*ex situ* measurements after calcinations in air) and to characterize by XANES the Mo species during real activation conditions just before reaction (*in situ* measurements in flowing N₂). We have evidenced a single Mo active species that undergoes a clear reversible evolution from a 6-fold oxygen coordination to a 4-fold coordination as function of increasing annealing temperature, in agreement with water desorption-absorption in the samples

2. Experimental

2.1. Synthesis and activation of the Mo/H-zeolites samples

Zeolites MEL, BEA and MFI (channels of 5–7 Å) with Si/Al ratio of 15 were prepared using sol-gel technique (Anunziata *et al.*, 1999b). The materials were characterized by XRD, FTIR, BET and TAPD. Mo/H-zeolites were prepared by impregnating NH₄-zeolites with aqueous ammonium heptamolybdate solutions (Anunziata *et al.*, 1999a). Finally, the samples were dried at 383 K, calcined at 773 K under N₂ flow and then under an oxidizing atmosphere (air) for 20 h to obtain the Mo-exchanged samples. The activation of the catalysts is done under N₂ flow at 773–973 K.

2.2. X-ray absorption experiments

X-ray absorption transmission experiments were performed at the Mo K-edge, in all the samples and all the conditions described below, on the XAS13 station of the DCI storage ring at LURE. XANES spectra were recorded with 1 eV step in the 19920–20200 eV range, using a Si331 channel-cut single crystal monochromator, vertical beam aperture 0.8 mm, obtaining simultaneously a reference spectrum of a Mo foil. The second inflexion point on the K-edge XANES of the Mo foil was used as calibration and set as 20000 eV. Pressed pellets of commercially

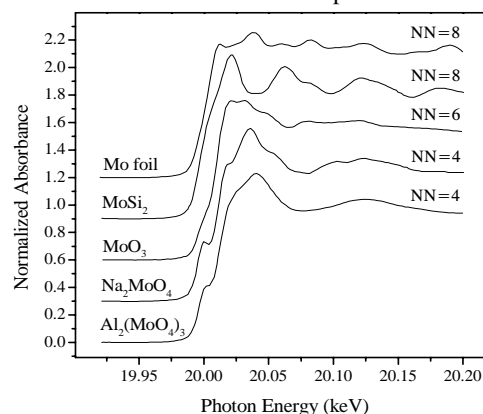


Figure 1 Mo K-edge XANES spectra of Mo compounds used as standards. The number of Mo nearest neighbours (NN) is quoted.

obtained MoSi₂, MoO₃ and Na₂MoO₄ powders, and prepared Al₂(MoO₄)₃ (modifying the method of Harrison *et al.*, 1988), were measured at RT as standards. Already-exchanged Mo/H-zeolites catalytic samples were divided in two identical starting sets: the first consists in pressed pellets calcined in air at 773, 873 and 973 K (one sample for each annealing); few days later they were dried in air for more than 1.5 h at 473 K (to take out physisorbed water) and sealed in kapton tape in air just before

measurement at RT (*ex situ*). Three months later after the last 973 K treatment, some of them were dried in air for more than 2 h at 473 K and measured. The second set consists in powders, pressed inside a NB crucible with graphite windows, which underwent the *in situ* cumulative measurements in flowing N_2 (20–30 ml/min) at 873 and 973 K (rise time 30 K/min). Mo/H-ZSM-5 samples, after reaching RT in flowing N_2 , were afterwards measured *ex situ* (in air at RT) 10 days later without drying. All the others were subjected also to this program but 2 months later. Mo(2%)/H-BETA underwent also the same program after the 873K step but 10 days later. This became the starting sample for the *in situ* 973 K step. XANES spectra were pre-edge subtracted then normalised in the mean height of the first EXAFS oscillation ($\cong 20098$ eV). It is worthy to be note that the experiments test each annealing condition independently, except the second *in situ* step, since the annealing treatments are not cumulative.

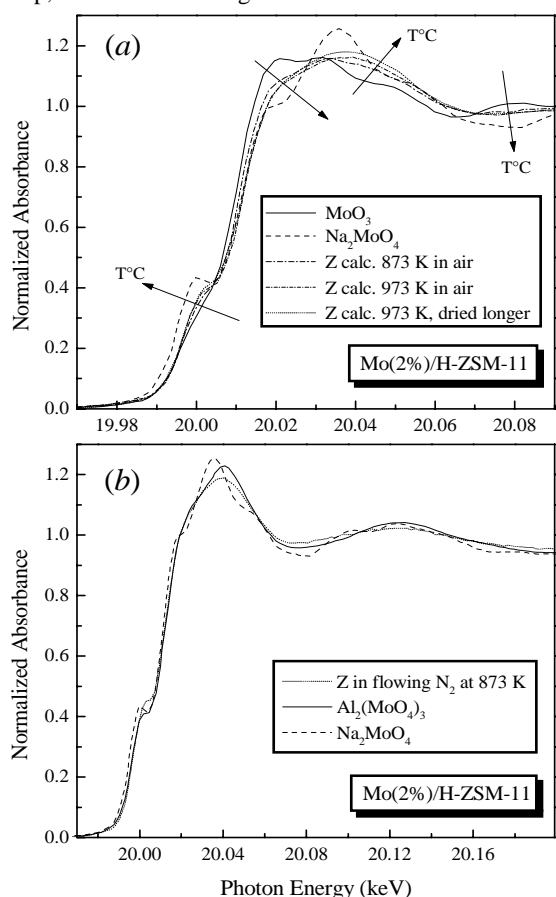


Figure 2
Comparison with standards of Mo K-edge XANES of Mo(2%)/H-ZSM11 catalyst (Z) measured at (a) RT in air and (b) in flowing N_2 at 873K.

3. Results and discussion

In Fig. 1, XANES spectra of Mo compounds used as standards are shown. Na_2MoO_4 and $Al_2(MoO_4)_3$ have tetrahedral sites for Mo. The first compound has 2 second nearest oxygen neighbours and 6 Na ones; the more abundant of the two Mo sites in the second one has 3 Al before the second oxygen shell. Figure 2(a) shows selected spectra of the Mo(2%)/H-ZSM-11 calcination series in air: the spectra seem to be a combination of the MoO_3 and Na_2MoO_4 spectra, evolving from the first to the second as function of increasing calcination temperature, but also of “drying time”. But Fig. 2(b) clearly shows that the Mo species

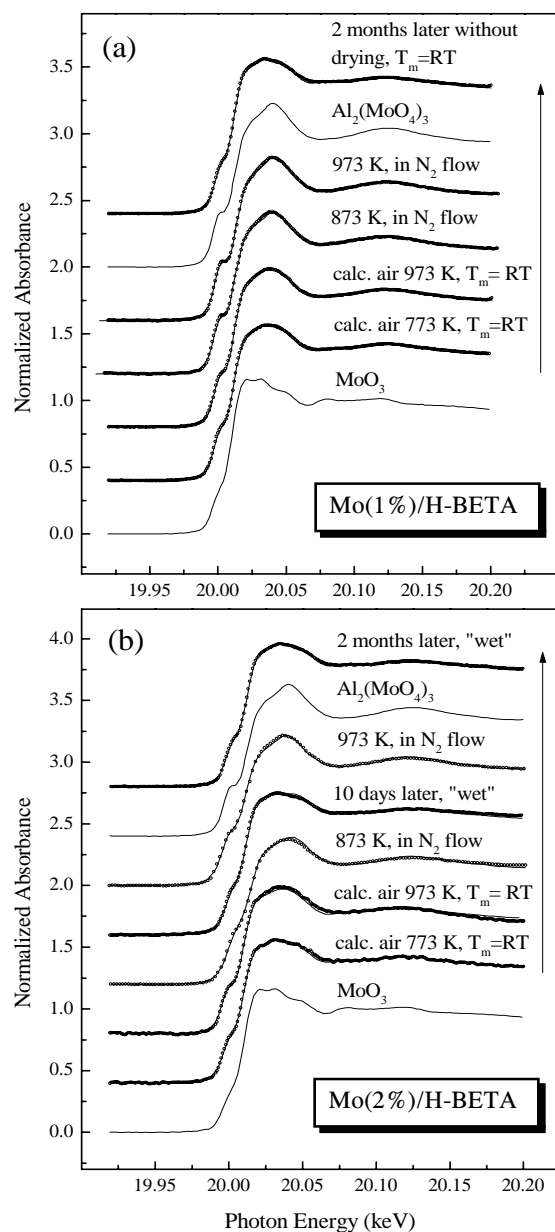


Figure 3
Ex situ and *in situ* Mo K-edge XANES spectra of (a) 1% and (b) 2% Mo/H-BETA samples. XANES of standard Mo compounds are also shown for comparison. In (b), “wet” means absence of drying treatment ($T_m = RT$).

evolve to a dominant Mo coordination very close to that of Mo in $Al_2(MoO_4)_3$. This general behaviour was observed in all the catalysts. Hence, we choose the Mo/H-BETA catalysts to describe the processes involved. Figure 3 displays the complete series of XANES for the 1 and 2 wt% Mo loading. In Fig. 3(a) it can be seen that already from the first spectrum (773 K) the catalyst is not as similar to MoO_3 as the spectra below 873 K presented by Liu *et al.* (1999) and Li *et al.* (2000). In the 2% loaded sample (Fig. 3(b)), this effect is less pronounced. The spectra in both samples clearly evolve to an $Al_2(MoO_4)_3$ -like species as function of annealing temperature. The reversibility of this evolution is apparent in the *ex situ* spectra taken, after the soak in flowing N_2 at 973 K (Fig. 3(a)) and 873 and 973 K (Fig. 3(b)), some time later without drying the samples prior to the measurement. In Fig. 3, solid lines are best least-squares fits to

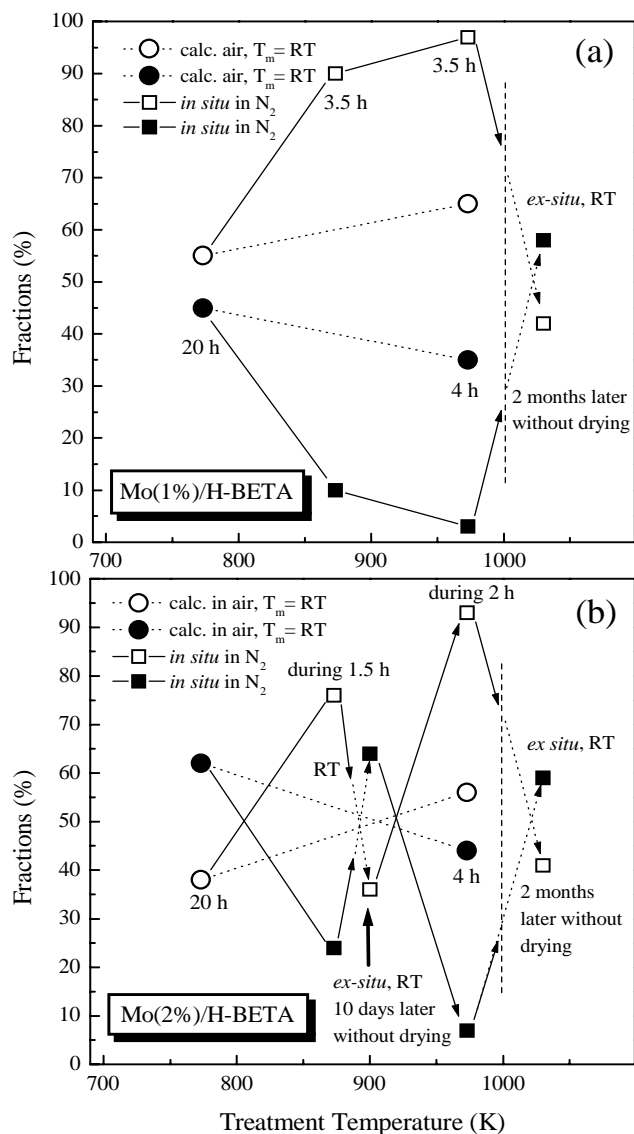


Figure 4

Fitted relative fractions of MoO_3 (NN=6, black symbols) and $\text{Al}_2(\text{MoO}_4)_3$ (NN=4, hollow symbols) to the Mo K-edge XANES spectra of Fig. 3, as function of treatment temperature: (a) 1% and (b) 2% wt. Mo loading.

the data using a linear combination of only two standards: MoO_3 (NN=6) and $\text{Al}_2(\text{MoO}_4)_3$ (NN=4). All other possible combinations were rejected by the fit. In Fig. 4 the relative fractions NN=4 and NN=6 coming from the fits of each XANES series are displayed as function of treatment temperature. The 1% loaded Mo/H-BETA catalyst begins with a high concentration of NN=4 (see Fig. 4(a)). The calcination in air rises this concentration, but not as high as the 100% reached during N_2 treatments. The same rules for the 2% samples (see Fig. 4(b)). One can suppose that the different atmospheres produce different concentration effects in our samples. But if one considers the apparent reversibility of the process each time the samples return to RT and are measured without a drying treatment, this suggests that the sample state in the air calcination series is an “image” of the state he really reaches during treatment, which depends on the calcination temperature and its drying degree. This interpretation is in agreement with water elimination (occurring between 773-973 K, with a maximum rate at 873 K) measured by mass spectroscopy by Li *et al.* (2000) during exchange treatments in air in their samples. Moreover, Mo $L_{2,3}$ -edge XANES experiments

(Lede *et al.*, 2000) performed under high vacuum (10^{-7} mbar) at RT on the same samples show the same abrupt increase of the NN=4 fraction in respect to the sample state at RT in air, suggesting a similar effect of dehydration. At 973 K in N_2 , our samples almost reach 100% of NN=4 fraction, provided they stay enough time in this state. This species must be the exchanged Mo species in the zeolite. This fraction cannot be extra-framework $\text{Al}_2(\text{MoO}_4)_3$ since, in such a case, the reversibility should imply that this compound decompose with decreasing temperature in air. Moreover, the samples were subjected to a dealumination process before exchange. As the NN=4 fraction drops to values even lower than the initial ones, this evidences that the NN=6 species should be only the Mo exchanged species but hydrated (with two more oxygen atoms in its NN coordination). This also shows that a “ MoO_3 -like” species (NN=6), which is not present, does not develop in air at higher calcination temperatures as could have been expected, due to the efficiency of the preparation method for Mo incorporation as counter-ion. These results are in agreement with EXAFS measurements, not shown here (Rentería *et al.*, 2000). Indeed, *in situ* EXAFS allows us to detect the structural coordination with NN of the exchanged and activated (dehydrated) Mo species; the *ex situ* EXAFS (at 80K) is the one that enables to detect, in addition, about 2-4 second Al neighbours belonging to the zeolite framework and about 0.1-1 Mo second neighbour. Combination of these results with measurements of EDX/XPS of Si and Al leading to an $\text{Al}_{\text{surface}}/\text{Al}_{\text{channels}}$ ratio of approximately 1:100, could show also that the NN=4 species is almost completely exchanged in the Brønsted acid sites inside the zeolite channels. New EXAFS under suitable conditions are necessary to distinguish between a monomer or a dimer form for the exchanged Mo species.

Conclusions

Ex situ and *in situ* XANES experiments on low (1 and 2 wt%) loaded Mo/ H-ZSM-5, H-ZSM-11 and H-BETA zeolites have shown the high exchange efficiency of our sample preparation method. They also enlightened on the suitable conditions to correctly characterize with EXAFS the Mo exchanged active species, which are XANES characterized with a 4-fold oxygen coordination in its dehydrated (activated) state and a 6-fold one in its hydrated state. The combination of these results with EXAFS and EDX/XPS measurements is in agreement with a total Mo exchange inside the channels of the zeolites. Calcinations in air at temperatures higher than that of the exchange procedure do not modify the nature of the exchanged Mo species.

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