XAFTS Study of the Photo-Active Site of Mo/MCM-41

Daisuke Miyamoto, Nobuyuki Ichikuni, Shogo Shimazu

Department of Applied Chemistry and Biotechnology, Chiba University, Chiba 263-8522, Japan

Abstract. An Mo/MCM-41 catalyst was prepared and used for study of propene and 1-butene photo-metathesis reactions. XAFS analysis revealed that hydrogen reduction leads to a decreased role for the Mo=O site. The Mo-O site plays an important role for the olefin photo-metathesis reaction on the H2 reduced Mo/MCM-41. From EXAFS analysis, the active site of photo-metathesis reaction is the Mo=O part for oxidized Mo/MCM-41, whereas it is the Mo-O site for reduced Mo/MCM-41.

Keywords: Photo-metathesis, XAFS, Mo oxide, MCM-41

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INTRODUCTION

Molybdenum oxide is widely used as catalyst for various reactions in industry such as metathesis of hydrocarbons [1]. Recently attention has been given to its use as a photo-catalyst [2]. Anchoring metal oxides on support enables the design of local structures around active sites and to increase the number of active sites [3,4].

In our previous work, we prepared Mo/MCM-41 catalysts with different pore size and used them in applications including the 1-butene photo-metathesis reaction. The cross-metathesis activity was enhanced by reducing a pore diameter. On the other hand, low cross-metathesis activity was observed on Mo/SiO2 (without pore). The photo-catalysis seems to depend on the local structure around Mo atoms and the oxidation state of Mo species.

In this study we found that the Mo oxidation state and the morphology of the Mo cluster on MCM-41 was changed by H2 pretreatment. The local structure and the oxidation state of Mo were investigated by the XAFS technique. Structural difference caused by H2 treatment is discussed.

EXPERIMENTAL

MCM-41 was synthesized using sodium silicate as the starting material and alkylammonium bromide (CnH2n+1N(CH3)3Br: n = 10-16) as the template. The molar composition of the reaction mixture was 1.0 SiO2: 0.5 CnH2n+1N(CH3)3Br: 50, 70, 82.5, 82.5 (n=10, 12, 14, 16) H2O. The reaction mixture was stirred for 0.5 h, and the pH was adjusted to 11.0 with H2SO4. The crystallization was performed at 373 K for 6 days in Teflon lined stainless-steel autoclaves. The solid was recovered by filtration and washing with distilled water, followed by dried in vacuo. Thereafter the product was dried under N2 flow at 823 K for 1 h and calcined under flow of dry air at 823 K for 5 h.

5 wt% Mo/MCM-41 catalyst was prepared by impregnating a solution of molybdenum(V) chloride dissolved in cyclohexane into MCM-41. It was dried at 393 K for 1 h, followed by calcination at 673 K for 1 h.

The structures of the catalysts were characterized by X-ray diffraction (XRD) and X-ray absorption fine structure (XAFS). XRD measurements were performed with a MXP3 diffractometer (Bruker axis) using Cu-Kα radiation (λ=0.15418 nm). The hexagonal unit cell parameter (a0) was calculated from 2d/√3 and a diffraction peak of (100), obtained from 2θ of the first peak in the XRD patterns by the Bragg equation (2d sin θ=A). The value of a0 is equal to the internal pore diameter plus one pore wall thickness. The pore sizes of the MCM-41 samples were calculated by subtracting the size of the wall thickness of about 1 nm from the value of a0.

Mo K-edge XAFS measurements were carried out at BL-10B at the IMSS-PF, Tsukuba, Japan (Proposal No. 2003G079). The spectra were collected at room temperature in transmission mode with a Si(311) channel cut monochromator by using two ion-chambers filled with 50 % Ar + 50 % N2 and 100% Ar for I0 and I, respectively. The pretreated samples were sealed in an Al cell with Kapton windows in order to protect from contact with air. Coordination number (CN) and atomic
distance \( (r) \) were evaluated by curve-fitting analysis in \( k \)-
space using the REX2000 program (Rigaku Co.). Standard reference
materials, Mo foil, MoO\(_3\) and K\(_2\)MoO\(_4\) were used to extract back
scattering amplitude and phase shift functions for terminal Mo=O,
bridging Mo-O and Mo-(O)-Mo bonding, respectively.

**RESULTS AND DISCUSSION**

The XRD patterns of MCM-41 and Mo/MCM-41 exhibited well-defined (100) diffraction originating from the hexagonal structure. Table 1 summarizes the \( d_{100} \), hexagonal unit cell parameters \( (a_0) \), and specific BET surface area for the Mo/MCM-41 series. No major difference was seen in both the hexagonal unit cell parameter and the BET surface area after Mo fixation into MCM-41. It can be said that the pore structure is maintained and that the Mo is highly dispersed.

Crucial information about bonding properties of Mo/MCM-41 was provided by Mo K-edge EXAFS spectroscopy. Figure 1 shows the \( k^3 \)-weighted oscillations and Fourier transforms of Mo K-edge EXAFS spectra for Mo/MCM-41 obtained over the 36-144 \( \text{nm}^{-1} \) \( k \)-range. The peak at 0.16-0.20 nm was attributed to Mo=O and Mo-O pairs. The results of curve-fitting analysis are summarized in Table 2. The CN of Mo=O increases as the pore size broadens. The data suggest that having large pore size leads to highly dispersed states. In propylene photo-metathesis reactions, catalysts with large pore size showed high activity. Since it is reported that Mo=O is the active site for photo-metathesis reaction [2], there is a correlation between the EXAFS result and photo-metathesis reactivity.

The normalized Mo K-edge XANES spectra for Mo/MCM-41, K\(_2\)MoO\(_4\) (tetra-coordinated molybdate), and MoO\(_3\) (hexa-coordinated molybdate) are shown in Fig. 2. In the XANES spectra, a characteristic feature of the pre-edge peak for Mo/MCM-41 due to the so-called “1s-4d transition” of the Mo ions was observed [5]. For the oxidized Mo/MCM-41, the shape of the spectra has similarity to both K\(_2\)MoO\(_4\) and MoO\(_3\). Mo species on the oxidized Mo/MCM-41, exist in Mo\(^{VI}\)-oxide form, not only tetra-coordinated but also hexa-coordinated molybdate. The intensity of the pre-edge peak decreases as the H\(_2\) treatment temperature increases, indicating that Mo oxidation state is controlled by the temperature.
TABLE 2. Curve fitting results for Mo/MCM-41.

<table>
<thead>
<tr>
<th>compound coordination</th>
<th>CN</th>
<th>( r / \text{nm} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mo/MCM-41(10) Mo=O</td>
<td>1.28</td>
<td>0.162</td>
</tr>
<tr>
<td>Mo/MCM-41(10) Mo-O</td>
<td>0.53</td>
<td>0.198</td>
</tr>
<tr>
<td>Mo/MCM-41(12) Mo=O</td>
<td>1.35</td>
<td>0.161</td>
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<tr>
<td>Mo/MCM-41(12) Mo-O</td>
<td>0.50</td>
<td>0.197</td>
</tr>
<tr>
<td>Mo/MCM-41(14) Mo=O</td>
<td>1.40</td>
<td>0.162</td>
</tr>
<tr>
<td>Mo/MCM-41(14) Mo-O</td>
<td>0.38</td>
<td>0.199</td>
</tr>
<tr>
<td>Mo/MCM-41(16) Mo=O</td>
<td>1.44</td>
<td>0.162</td>
</tr>
<tr>
<td>Mo/MCM-41(16) Mo-O</td>
<td>0.25</td>
<td>0.200</td>
</tr>
</tbody>
</table>

Figure 3 shows the Fourier transforms of the \( k^3 \)-weighted Mo K-edge EXAFS spectra for Mo/MCM-41(10). To estimate the Mo cluster size and the oxidation state, the ratio of coordination number (\( R_{\text{CN}} \): Mo=O / Mo-O) was determined based on CF result (Table 3). The \( R_{\text{CN}} \) for reduced Mo/MCM-41(10) was smaller than that for the oxidized one. The \( R_{\text{CN}} \) became smaller as the \( H_2 \) pretreatment temperature was raised. The 773 K \( H_2 \) pretreated catalyst showed an activity increase in the propylene photo-metathesis reaction. This result does not agree with our assumption that only the Mo=O is responsible for activity. On the other hand, the \( H_2 \) treated catalyst was active under short-wavelength filtered conditions.

EXAFS data reveals that Mo=O is changed to Mo-O by \( H_2 \) pretreatment. For the \( H_2 \) treated Mo catalysts, the bridged Mo-O site also acts as active center for photo-metathesis reaction.

FIGURE 3. Fourier transforms of EXAFS spectra for Mo/MCM-41(10) with different treatment; (a) 573 K \( O_2 \), (b) 573 K \( H_2 \), (c) 673 K \( H_2 \), (d) 773 K \( H_2 \).

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REFERENCES