CHEMISTRY LETTERS, pp. 1101-1104, 1982. © The Chemical Society of Japan 1982

# EXAFS STUDY OF HIGHLY ACTIVE $Mo_2$ CATALYST

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Mo K absorption spectrum was measured on the fixed $Mo_2$ catalyst which has been supposed to have a well-defined "paired" structure according to its preparation procedures and from the results by UV diffuse reflectance, IR, ESR, XPS and chemical analysis. The analysis of EXAFS data provides a direct structural information that strongly supports the proposed paired structure of this catalyst.

The $Mo_2$ catalyst fixed on alumina support is prepared from the selective chemical reaction between $Mo_2(\pi\text{-}C_3H_5)_4$ and surface OH groups of γ-alumina. The subsequent reductions and oxidations produce different chemical states of this catalyst which shows higher activities for propene metathesis than conventional Mo catalysts prepared by an ordinary impregnation method.[1,2] As the structures of these catalysts give profound effect on the catalytic activities, it is of great importance to elucidate the structures of these catalysts. A well-defined "paired" structure (Fig. 1) has been proposed for one of the states of the $Mo_2$ catalyst on the basis of the results by UV diffuse reflectance, IR, ESR, XPS and chemical analysis. However, there has been no direct structural evidence for the paired structure. Since EXAFS data can provide structural information around an X-ray absorbing atom (here, Mo), we have investigated the surface structure of this catalyst by means of EXAFS spectroscopy.

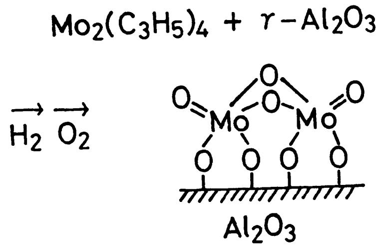

Fig. 1. Proposed structure for the $Mo_2$ catalyst.

The fixed $Mo_2$ catalyst of the above-mentioned state (Fig. 1) which is stable in the air, was prepared by the method already described.$^{1)}$ The surface area of the alumina support was 385 $m^2/g$, the number of surface OH groups having been controlled to be 4.5 $OH/nm^2$. The prepared catalyst contained 0.56 wt.% Mo. Potassium molybdate, $K_2MoO_4$, and Mo powder were chosen as the model compounds for obtaining the parameters required in the analysis of Mo K EXAFS data of the catalyst.

X-Ray absorption measurements were carried out with a laboratory EXAFS system, which utilized a high power rotating-anode X-ray generator (Rigaku model RU-1000) as an X-ray source.$^{3)}$ With a Cu target, the generator was operated at 45 kV with 950 mA. We obtained EXAFS data with a flat crystal monochromator which used Ge(111) as the reflecting plane, the fourth-order harmonics being used for the Mo K EXAFS measurements. The energy resolution at the Mo K-edge was about 20 eV. The data collection time was about 24 hours, accumulating 140,000 counts both for incident and transmitted beams at each measurement point. To prevent a sample from absorbing water in the air, it was placed in a cell in which dry $N_2$ gas was flowing.

The Mo K absorption spectrum of the catalyst is shown in Fig. 2. Though the Mo content was rather small, we could obtain a spectrum with sufficient edge jump, because alumina has a small absorption coefficient in the concerned X-ray energy region. The Fourier transform of the observed EXAFS data is shown in Fig. 3. We carried out curve-fitting analysis over the k-range of 4-12 $Å^{-1}$ with the $k^3$-weighting scheme by use of the empirical and theoretical methods.$^{3)}$ Experimentally determined Mo K absorption edge energies were 20020.2, 20011.8, and 20020.2 eV for $K_2MoO_4$, Mo powder, and the $Mo_2$ catalyst, respectively. In the empirical method the phase and amplitude parameters were determined from the analysis of the EXAFS data of the model compounds by use of the known crystallographic data.$^{4,5)}$ The theoretical method means that we used the amplitude and phase functions which have been theoretically given.$^{6,7)}$

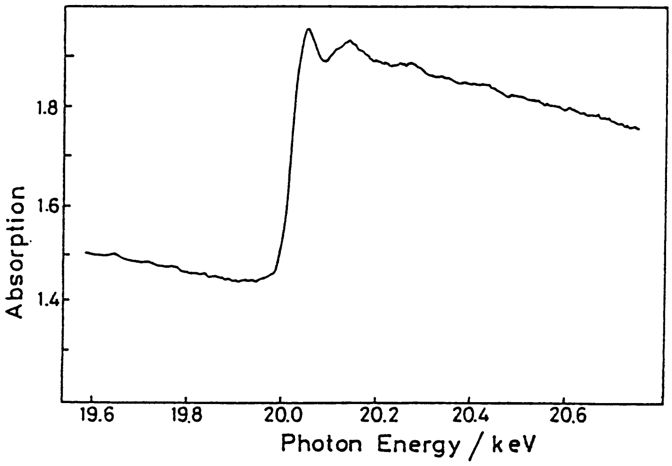

Fig. 2. X-ray absorption spectrum of the $Mo_2$ catalyst.

There are two peaks in the Fourier transform shown in Fig. 3. The first peak can be attributed to Mo-O distance. The second peak might be due to oxygen, aluminium or molybdenum atom. To determine the main atomic species responsible for the second-shell, we took out the region of the second peak and carried out curve-fitting analysis for three possibilities. The best fit was obtained when the second peak was assumed to be due to molybdenum atom.

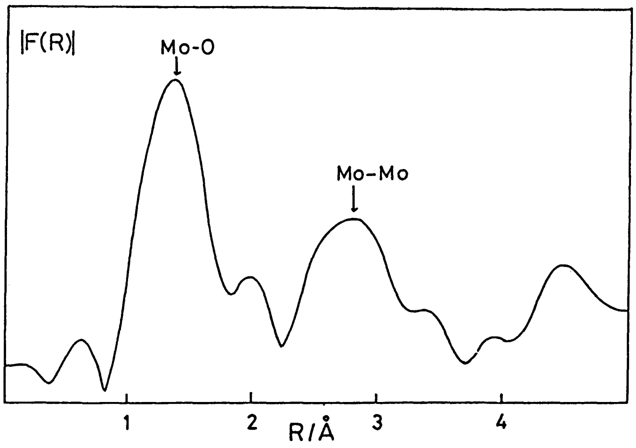

Fig. 3. Fourier transform of the $Mo_2$ catalyst.

Assuming that the first-shell is composed of oxygen atoms and the second-shell is composed of molybdenum atoms, we performed curve-fitting analysis over the entire region including the two peaks both by the empirical and theoretical methods. The obtained results are summarized in Table 1. The curve-fitting result by the theoretical method is shown in Fig. 4, where the main structure of the $k^3\chi(k)$ curve is determined by the first nearest atoms, oxygen, and the contribution from the second nearest ones, molybdenum, gives the structure in the range of 9-12 $Å^{-1}$. The empirical method provided a similar result except a slight difference in the range of 6-8 $Å^{-1}$.

As regards the first-shell, both methods gave the same conclusion that there are 4-5 oxygen atoms at the distance of 1.76-1.78 Å from the X-ray absorbing Mo atom. The two methods gave somewhat different distances and coordination numbers for

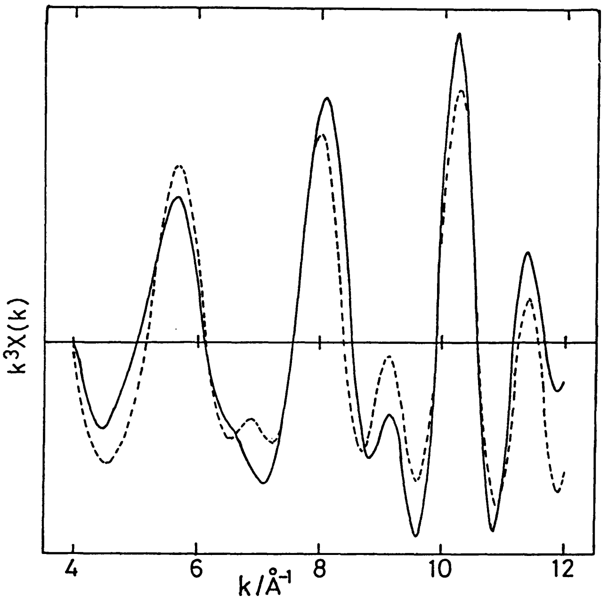

Fig. 4. Curve-fitting of EXAFS signal $k^3\chi(k)$ for the $Mo_2$ catalyst. ——: exptl, - - -: calcd

TABLE 1. EMPIRICAL AND THEORETICAL CURVE-FITTING RESULTS

| Shell | Empirical |  | Theoretical |  |
|---|---|---|---|---|
|  | Distance/Å | No. | Distance/Å | No. |
| First(Mo-O) | 1.76(1) | 4.4(2) | 1.78(1) | 4.8(5) |
| Second(Mo-Mo) | 3.25(2) | 0.6(1) | 3.12(2) | 1.7(3) |

the second-shell, but it can be safely said that about one Mo atom exists at the distance of 3.12-3.25 Å from the absorbing Mo atom. These results are in good agreement with the previously proposed structural model shown in Fig. 1. Although the results of the analyses of the EXAFS data described above can not completely exclude the possibility that more than one Mo atoms exist around the absorbing Mo atom, such a possibility can be regarded to be quite small when we take into account the population of surface OH group of the used alumina and the amount of fixed Mo atoms.

Thus we consider that the results of the present EXAFS study can be a good proof of the paired structure of the catalyst. The success in the analyses of the EXAFS data may be due to the existence of a well-defined structure of this catalyst, since the result of analyses will become more ambiguous if there is a significant disorder as regards the local structure around Mo atom. The Mo-Mo distance has been reported to be 3.23(1) Å in $K_2Mo_3O_{13}$, a compound with five coordinate oxygen atoms around a molybdenum (VI) atom.[8] The Mo-Mo distance obtained for the present $Mo_2$ catalyst, 3.12-3.25 Å, is fairly close to this value.

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(Received May 14, 1982)