The Characterization of a Novel Metathesis Catalyst, β-Titanium Oxide-supported Molybdenum Oxide

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The results of the X-ray photoelectron spectroscopy of a novel metathesis catalyst, MoO_x/β-TiO_2, are discussed with reference to its catalytic behavior. It is concluded that the active center for the metathesis reaction of olefin is the molybdenum ion with an oxidation higher than +4 on the average, and that the hydrogen scrambling of olefin during the metathesis is caused by the OH group on the TiO_2 surface. During the preparation of this catalyst, the decomposition of titanic acid to TiO_2 is found to be accelerated by MoO_3; a similar thing can be seen of the reduction of MoO_3 to zero-valent molybdenum by TiO_2.

Many active catalysts, homogeneous and heterogeneous, have been developed[1] for the olefin-metathesis reaction, and its mechanism has been investigated since 1964;[2] the simultaneous hydrogen scrambling of olefin has been an intricate problem. We ourselves have reported a novel solid catalyst, MoO_x/β-TiO_2 (x=2.3—2.9), on which the metathesis reaction of olefin proceeds with a negligible extent of hydrogen scrambling of olefin.[3] When alumina and zirconia are used as catalyst supports, the hydrogen scrambling of olefin surpasses the metathesis.[4] In this paper, this novel catalyst was characterized, mainly by using X-ray photoelectron spectroscopy.

Experimental

The catalyst was prepared by impregnating a powder of β-titanic acid with an aqueous solution of ammonium molybdate and then dried at 120 °C. The sample (*ca.* 0.3 g) was oxidized with O_2 and evacuated at 500 °C in a conventional circulation apparatus with a volume of *ca.* 350 cm^3. Preceding the metathesis reaction, the following pretreatments of the catalyst were performed: it was reduced with hydrogen at 500 °C for 1 h and preconditioned by performing on it a reaction of N_2O (*ca.* 40 Pa) with H_2 (*ca.* 100 Pa) at 200 °C for 1 h.[4,5] By this pretreatment, the catalyst surface was controlled to give a characteristic activity for metathesis reaction; *i.e.*, it was active for metathesis, but had a negligible extent of hydrogen scrambling as well as of the isomerization of olefin.[4]

A mixture (1 : 1) of propene and [D_6]propene (CH_2=$CHCH_3$ and CD_2=$CDCD_3$) or *cis*-2-butene and [D_8]*cis*-2-butene was admitted at room temperature onto the catalyst at a total pressure of *ca.* 6×10^3 Pa, and its catalytic activities for the productive and degenerative metathesis, as well as for the hydrogen scrambling of olefin, were studied. The analysis of the products was carried out by GC, and the deuterated isomers separated by GC were analyzed by means of a mass spectrometer with low isonization voltages. The reagents used were of a chemically pure grade.

The X-ray photoelectron spectra of the catalyst were obtained by means of an ESCA-3 apparatus of the Vacuum Generator Co. The untreated samples prepared from ammonia molybdate and β-titanic acid were pressed on a sample hoder of the ESCA-3 apparatus and treated in a side chamber under conditions similar to those used in the catalyst pretreatments. The binding energies of Mo(3d) and Ti(2p) electrons were corrected using a reference of 530 eV for the ls electron from oxygen of oxide; this value is common for a variety of metal oxides.[6]

Results

The catalytic properties of 6.7 wt% MoO_3/TiO_2 change with the extent of reduction, as is shown in Fig. 1,[4] in which the extent of reduction (x in MoO_x) was estimated from the amount of hydrogen consumed in the reduction of an oxidized catalyst sample at 500 °C for 1 h. It was found that the molybdenum oxide supported on titanium oxide was finally reduced to the zero-valent state, although Ti^{3+} could not be detected by ESR during the reduction of the catalyst.[5]

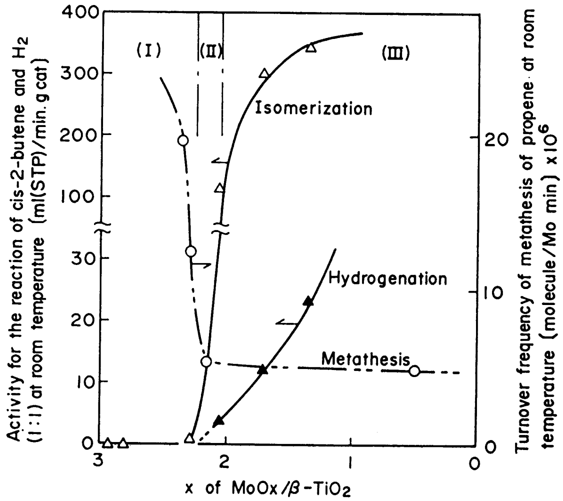

Fig. 1. Characteristic profile of the catalytic activity of MoO_x/β-TiO_2 for reactions of olefins at room temperature.

Only oxidation of olefin was caused by a catalyst, MoO_x/β-TiO_2, with an x value larger than 2.9. However, the catalyst of x=2.3—2.9, State I, gave preferentially olefin metathesis with little hydrogen scrambling of the olefins. As a result, a mixture of propene and [D_6]propene yielded mainly [D_2] and [D_4]propene by degenerative metathesis, and [D_0], [D_2], and [D_4]ethylene by productive metathesis, respectively. In contrast to the State I surface, the catalyst of x=2.0—2.3, State II, is active for the isomerization of olefin in the presence of hydrogen. The more reduced surface, described by State III, of a catalyst with x value less than 2.0 can catalyze the isomerization in the absence of hydrogen. Such an isomerization caused by a process other than metathesis can be followed by interconversion between 1-butene and 2-butene.[7] The hydrogenation of olefin is also brought about over the catalyst surfaces of States II and III. A more reduced surface has a higher activity for hydrogenation. We found that a State I or II surface can be prepared from a reduced catalyst by carrying out on it the reaction of N_2O with H_2 at 200 °C or with CO at room temperature for 1 h.

Figure 2 shows the amount of hydrogen consumption in the reduction of oxidized catalyst samples at 500 °C for 1 h, in which the stoichiometric reduction of MoO_3 is brought about if the catalyst samples are loaded with less than *ca.* 10 wt% of MoO_3.

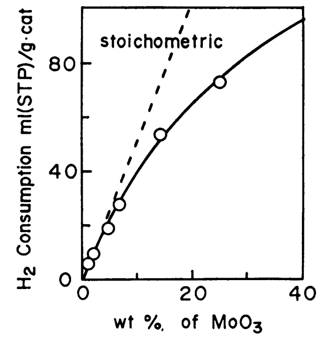

Fig. 2. Amounts of H_2 consumed in reduction of MoO_3/β-TiO_2 catalysts loaded with different amounts of MoO_3 at 500 °C for 1 h.

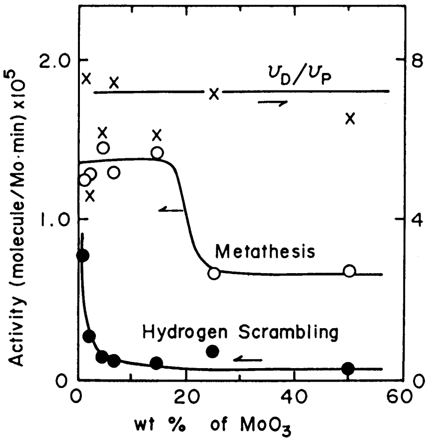

Fig. 3. Catalytic activity changes of MoO_x/β-TiO_2 (x= 2.3—2.9) depending on the amount of loaded MoO_3.

Figure 3 shows the specific activities for a metathesis reaction and for a simultaneous hydrogen scrambling of olefin over catalysts with various wt% MoO_3, where the catalysts were prepared by oxidation, and the reduction at 500 °C, followed by the reaction of N_2O with H_2 at 200 °C for 1 h and its evacuation at 500 °C. The ratio of a productive metathesis to a degenerative one is plotted in Fig. 3. The turnover frequency in this figure is evaluated by assuming that all the molybdenum loaded on TiO_2 is active for the reactions. Up to *ca.* 15 wt% MoO_3, the turnover frequency of metathesis is nearly constant, while that of hydrogen scrambling decreases steeply.

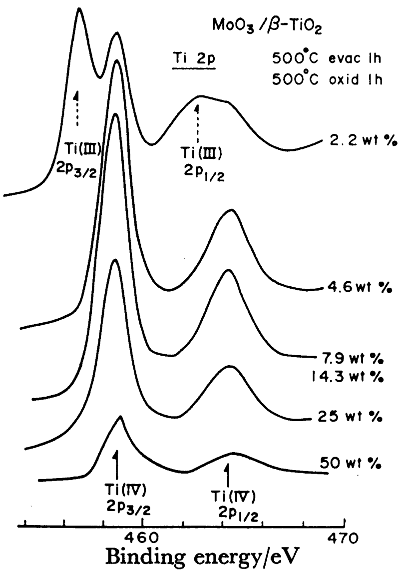

Fig. 4. XPS spectra of Ti(2p) electrons from surfaces of MoO_3/β-TiO_2 with different amounts of loaded MoO_3.

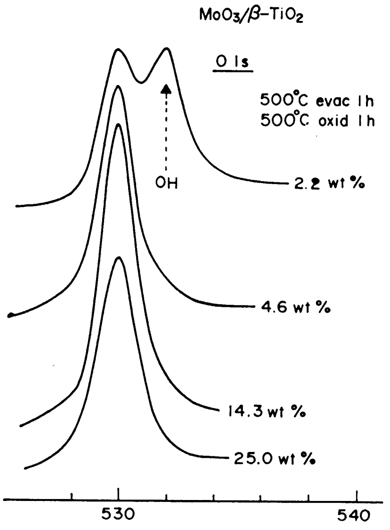

Fig. 5. XPS spectra of O(1s) electrons from surfaces of MoO_3/β-TiO_2 with different amounts of loaded MoO_3.

Figures 4 and 5 show the XPS spectra of Ti(2p) and O(1s) of oxidized samples with various wt% MoO_3. The XPS peak areas of Mo(3d), Ti(2p), and O(1s), observed as measures of the surface concentrations of these components, are plotted in Fig. 6 against the loaded amounts of MoO_3.

Discussion

The activity for metathesis reaction increases proportionally to the amount of loaded MoO_3 up to *ca.* 15 wt%, as can be seen from the constant turnover frequency for metathesis shown in Fig. 3. This result implies that molybdenum is dispersed rather homogeneously on the

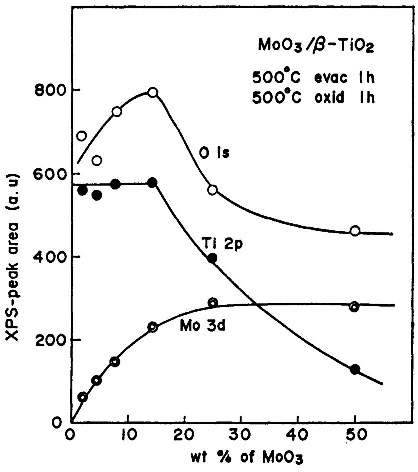

Fig. 6. Changes of XPS-peak areas of Mo(3d), Ti(2p), and O(1s) electrons from the surfaces of $MoO_3/\beta\text{-}TiO_2$ catalysts with different amounts of loaded MoO_3.

catalyst surface when the loaded MoO_3 is less than *ca.* 15 wt%. The valence state of the molybdenum ion is quite sensitive to a metathesis reaction, as is shown in Fig. 1, and a characteristic activity for metathesis reaction appears only in the range of x=2.3—2.9 of MoO_x/TiO_2. In contrast to the result of Iwasawa *et al.*,⁸⁾ the activity for metathesis reaction became higher when the average oxidation state was slightly higher than Mo^{4+}.

It was confirmed⁷⁾ that, in the hydrogen scrambling of olefin, the relative contribution of *n*- and *s*-alkyl species to the catalyst of State II is quite similar to that of the MoS_2 catalyst.⁹⁾ With the MoS_2 catalyst, the selectivity for isomerization and hydrogenation of olefin has been found to be sensitive to the degree of the coordinative unsaturation of the central Mo ion.⁹⁾

The turnover frequency for a metathesis reaction decreases with an increase in the loaded amount of MoO_3 above *ca.* 20 wt%, as can be seen in Fig. 3, while the ratio of the degenerative metathesis to the productive one, v_D/v_P, is constant, irrespective of the loaded amount of MoO_3. These results imply that the active sites on MoO_x/TiO_2 are not influenced by the loaded amount of MoO_3. In contrast to this, the turnover frequency for the simultaneous hydrogen scrambling of olefin is quite sensitive to the amount of MoO_3 loaded on TiO_2. It was found that the O(1s) peak at 531.5 eV in the XPS spectra, which may be attributed to the OH group,¹⁰⁾ was observed in the present experiments only on a catalyst with 2.2 wt% MoO_3 (Fig. 5), and the hydrogen scrambling might be caused by this OH group on the TiO_2 surface.

As is shown in Fig. 6, the XPS peak area of Ti(2p) decreases steeply, while that of Mo(3d) increases to a plateau, with an increase in the loaded amount of MoO_3 above *ca.* 20 wt%. The samples subjected to XPS measurements were completely oxidized, so that this catalyst may be different from the catalyst used for the metathesis reaction. Titanium oxide is not influenced by the pretreatment of the catalysts, and the reproducible results shown in Fig. 2 were obtained. This fact may indicate that the distribution of the molybdenum ion on the catalyst surface is not changed by this pretreatment. The results given in Fig. 6 suggest that MoO_3 loaded with more than *ca.* 20 wt% causes its aggregation on the TiO_2 surface and is more difficult to be reduced by hydrogen, as is shown in Fig. 2. As a result, the specific activity for the metathesis reaction decreases with an increase in the loaded amount of MoO_3, as is shown in Fig. 3.

Figures 4 and 5 show the XPS spectra of a sample of 2.2 wt% MoO_3. It is interesting that the sample loaded with MoO_3 less than 4.6 wt% gives the exceptional peaks of the Ti^{3+} ion and the O(1s) peak of the OH group. This fact indicates that the decomposition of titanic acid to TiO_2 is accelerated by MoO_3 loaded more than 4.6 wt%. Furthermore, it has been reported¹¹⁾ that the reduction of MoO_3/TiO_2 was far faster than those of MoO_3 supported on SiO_2, MgO, ThO_2, *etc.* It was found in this work that MoO_3 loaded on TiO_2 with *ca.* 10 wt% or less could be reduced to nearly the zero-valent state of molybdenum with hydrogen at 500 °C for 1 h, while MoO_3 loaded by an amount of more than 10 wt% was hard to be reduced to zero valence. This result is in contrast to the MoO_3 loaded on alumina, which is difficult to be reduced to a state lower than Mo^{4+}.¹²⁾ It may be concluded that a special interaction between molybdenum oxide and titanium oxide can keep the valence state of the molybdenum ion suitable for metatheses, while the coordinative unsaturation of oxygen on the molybdenum ion may be more important in hydrogenation and/or isomerization reactions, such as in the case of the MoS_2 catalyst.⁷,⁹⁾

By referring to the results shown in Figs. 2, 3, and 6, we see that the catalyst of 6.7 wt% MoO_3, used by chance,³,⁴,⁷⁾ is one of the most effective catalysts for the selective metathesis of olefin, causing a negligible simultaneous hydrogen scrambling of olefin.

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