

Silica-Alumina-Supported Molybdena Catalyst for Propene Metathesis

Hirofumi Aritani,* Osamu Fukuda, Takashi Yamamoto,† Tsunehiro Tanaka,† and Seiichiro Imamura
Faculty of Engineering and Design, Kyoto Institute of Technology, Sakyo-ku, Kyoto 606-0962

†*Department of Molecular Engineering, Graduate School of Engineering, Kyoto University, Sakyo-ku, Kyoto 606-8501*

(Received September 24, 1999; CL-990820)

Without reductive pretreatment, 10 wt% MoO₃/SiO₂-Al₂O₃ (JRC-SAH-1) exhibits high catalytic activity for propene metathesis. The Mo ions on SiO₂-Al₂O₃ may exist as dispersed polyanions, and they can be reduced easily in contact with propene even at room temperature. The reduced Mo ions formed in the initial step of the reaction are efficient for metathesis.

Molybdenum-containing heterogeneous catalysts for olefin metathesis have been of great interest¹ since Banks et al.² reported the first example. At the same time, the active Mo species for metathesis have been characterized. SiO₂-supported molybdenum is a typical catalyst exhibiting high metathesis reactivity as reported by Kazansky et al.^{3,4} They proposed that the active species for propene metathesis are tetrahedrally coordinated Mo⁴⁺-monoxo formed by prereluction with CO under photo-irradiation.^{5,6} For MoO₃/Al₂O₃, Grünert et al.^{7,8} also concluded that Mo⁴⁺ species formed by H₂ prereluction is active for metathesis. Whereas, Zhang et al.⁹ reported that Mo⁵⁺ dioxo-species on SiO₂, which is formed by photo-reduction with CO, is effective for metathesis. Many workers have concluded that Mo⁴⁺ acts as to the active species, however, several workers have shown that Mo⁵⁺ and/or its dimer species show the activity for metathesis. The detailed conclusion about the valence of Mo is still unclear, however, the reaction mechanism of metathesis has been provided. It is accepted generally that the reduced Mo ions can easily form Mo-alkylidene species by contact with olefins, and then, the metathesis reaction proceeds *via* metallacyclobutane intermediate.¹⁰⁻¹² The reduced Mo ions are thus necessary to form the alkylidene intermediates. In addition, it is also accepted that extent of reduction give a decrease of the activity. For instance, Tanaka et al.^{13,14} proposed that MoO₃/β-TiO₂ with *x*=2.3-2.9 is effective for propene metathesis. Segawa et al. reported that reduced MoO₃/TiO₂ in *x*=1.9 shows the maximum activity for propene metathesis.^{15,16} As described above, appropriate prereluction needs to give an active Mo species before the metathesis reaction. Nevertheless, we found that MoO₃/SiO₂-Al₂O₃ catalysts exhibit the catalytic activity for propene metathesis even at room temperature without reductive pretreatment. The detail is shown in this report.

Supported molybdenum catalysts were prepared by impregnation of each metal oxide support with an aqueous solution of (NH₄)₆Mo₇O₂₄·4H₂O (Nacalai Tesque). The oxide supports used in this study were SiO₂ (Aerosil), γ-Al₂O₃ (Nacalai Tesque; calcined at 873 K), TiO₂ (Wako; anatase-type) HY-zeolite (JRC-Z-Y5.6; containing 20.4 wt% of Al₂O₃, deionized to remove sodium ions by using HNO₃ solution and calcined at 873 K) and SiO₂-Al₂O₃ containing 28.6 wt% of Al₂O₃ (JRC-SAH-1; designated as SAH-1) and 13.8 wt% of Al₂O₃ (JRC-SAL-2, designated as SAL-2). The impregnating solution was stilled at room temperature and then evaporated at

343 K for 6 h to form a paste. The paste was then dried overnight and calcined at 773 K for 6 h. The metathesis reaction of propene was carried out in a conventional circulating reaction system. Each catalyst sample (0.5 g) was placed in the reaction vessel (total reaction volume of 871 cm³) and treated *in vacuo* at 773 K for 1 h before the reaction. In the case of prereluced sample, it was treated with hydrogen (80 Torr) at 773 K for 1 h, and then evacuated at 773 K for 1 h. After the pretreatment, reactant gas mixture consisting of propene (10 Torr) and helium (90 Torr) was introduced in the reaction vessel. The reaction gas was periodically analyzed by using on-line gas chromatograph (Shimadzu GC-8A) equipped with VZ-7 column (3 m). Since deuterated propene reactant was not used, only the products of 'productive metathesis'^{14,17,18} such as



could be analyzed, and 'degenerate-metathesis' reactivity could not be evaluated. Other products such as ethane, propane, or hexenes were not detected. In order to examine whether the reaction takes place catalytically or not, twice reaction was carried out successively. In this successive reaction, the catalyst was evacuated without any other treatment at the reaction temperature between the first and second reactions. UV-Vis spectra were recorded with a Perkin-Elmer Lambda19 spectrometer in a diffuse reflectance mode at room temperature.

Table 1 shows the metathesis reactivity of the supported molybdena catalysts at 473 K. Prereluced MoO₃/Al₂O₃ and MoO₃/SiO₂ show higher conversion than unreduced ones. On the other hand, prereluced MoO₃/SiO₂-Al₂O₃ catalysts such as HY, SAH-1, and SAL-2 show lower activity than unreduced ones. It is noted that MoO₃/SAH-1 and MoO₃/SAL-2 exhibit a much higher activity for propene metathesis than other catalysts. These results suggest that the silica-alumina support give a different effect on the formation of active molybdena species from other supports. The reactivity of MoO₃/SAH-1 with various molybdena contents at 293 and 473 K is examined. The result is summarized in Table 2. In the both reaction temperatures, 10 wt% MoO₃/SAH-1 possesses the maximum activity. The result of the 2nd reaction is also shown in the table. For

Table 1 Reactivity of supported molybdena catalysts for propene metathesis (at 473 K)

| Catalyst ^a | Conversion of propene / % | |
|--|---------------------------|----------------------|
| | unreduced ^b | reduced ^c |
| MoO ₃ /SiO ₂ | 1.6 | 3.3 |
| MoO ₃ /Al ₂ O ₃ | 5.7 | 8.0 |
| MoO ₃ /TiO ₂ | trace | trace |
| MoO ₃ /HY-zeolite | 5.9 | 0.4 |
| MoO ₃ /SAH-1 | 50.2 | 31.5 |
| MoO ₃ /SAL-2 | 46.3 | 21.8 |

^a MoO₃ loading : 10 wt%.

^b evacuated at 773 K as the pretreatment

^c pre treated with H₂ at 773 K for 1h and then evacuated at 773 K.

Table 2 Reactivity of MoO₃/SAH-1 catalysts (evacuated at 773 K) for propene metathesis

| MoO ₃ content / wt% | Reaction temp. / K | Conversion of propene / % | |
|--------------------------------|--------------------|---------------------------|--------------------|
| | | 1st ^{a,b} | 2nd ^{a,c} |
| 2.5 | 473 | 42.3 | 38.9 |
| 5.0 | | 48.2 | 36.0 |
| 10.0 | | 50.2 | 40.0 |
| 15.0 | | 44.3 | 30.6 |
| <hr/> | | | |
| 2.5 | 293 | 32.9 | 33.1 |
| 5.0 | | 34.9 | 34.8 |
| 10.0 | | 37.1 | 36.0 |
| 15.0 | | 36.3 | 35.5 |

^a Between the 1st and 2nd reaction, the gas phase was evacuated (without any other treatment) at the reaction temperature.

^b reacted for 120 min.

^c reacted for 80 min.

all MoO₃/SAH-1 samples at 473 K, the conversion of propene in the 2nd reaction becomes lower than that in the 1st run. However, it is scarcely seen at 293 K. For 10 wt% MoO₃/SAH-1 containing 695 μmol/g of MoO₃, 806 μmol/g of propene was converted through the 'productive metathesis' mechanism in the twice reaction at 473 K. It is evident that the reaction proceeds catalytically. It is concluded that 10 wt% MoO₃/SAH-1 exhibits a high catalytic activity for the productive metathesis of propene without reductive pretreatment.

The active molybdena species on SAH-1 are characterized by means of UV-Vis spectroscopy. Figure 1 shows the spectra of MoO₃/SAH-1 before and after the reaction. In the case of the sample calcined at 873 K, the absorption due to LMCT (O²⁻ → Mo⁶⁺) band is seen below 400 nm. It can be attributed to the coexistence of distorted Mo-O₆ octahedra and Mo-O₄ tetrahedra,^{19,20} suggesting that the Mo ions are stabilized as polyanion-like species. This absorption is slightly changed after evacuation at 773 K (as the non-reductive pretreatment) but low-valence Mo ions can not be seen. Thus, Mo⁶⁺ only exists and reduced ions are absent prior to contact with propene. On the other hand, the broad band at the wavelengths longer than 380 nm appears after the metathesis reaction. In the samples reacted at 473 K, the intensity of the band shows more intense than that at 293 K. This absorption can be assigned to the *d-d* transition in low-valence molybdenum ions such as Mo⁵⁺ and/or Mo⁴⁺.^{20,21} It indicates that the reduction Mo ions are brought about during the reaction. It is reasonable that the Mo species

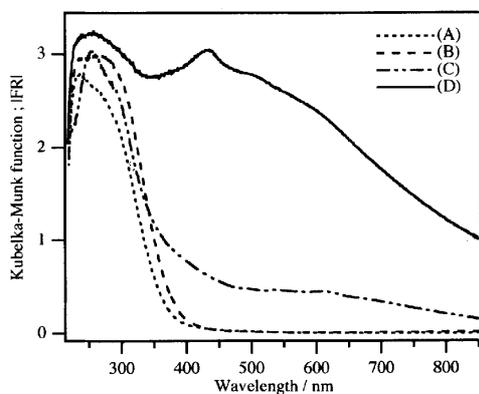


Figure 1 UV-Vis spectra of MoO₃/SAH-1 (A) calcined at 873K; (B) evacuated at 773 K prior to the reaction; (C) after the metathesis reaction (once) at 293 K for 2 h; (D) after the metathesis reaction (once) at 473 K for 2 h.

containing reduced ions act as the active center for metathesis. It was reported that the extent of the reduction of loaded molybdena on SiO₂-Al₂O₃ shows a maximum when Al₂O₃ content is 25 wt%.²² Thereby, the molybdena on SAH-1 can be reduced easier than that on other supports. It is concluded that MoO₃/SAH-1 can be reduced easily to form active species for metathesis even by contacting with propene. The reductive pretreatment is unnecessary to form Mo-alkylidene species as an intermediate of metathesis.

This work is supported by a Grant-in-Aid (No. 11750675) from the Ministry of Education, Science, Sports, and Culture.

References and Notes

- J. C. Mol and J. A. Moulijn, *Catal. Sci. Technol.*, **8**, 69 (1988).
- R. L. Banks and G. C. Bailey, *Ind. Eng. Chem., Prod. Res. Develop.*, **3**, 170 (1964).
- V. B. Kazansky, B. N. Shelimov, and K. A. Vikulov, "Proc. 10th Int. Congr. Catal." ed by L. Guzzi, F. Solymosi, and P. Tétényis, Elsevier, Budapest (1992) p. 515.
- K. A. Vikulov, B. N. Shelimov, V. B. Kazansky, and J. C. Mol, *J. Mol. Catal.*, **90**, 61 (1994).
- B. N. Shelimov, I. V. Elev, and V. B. Kazansky, *J. Catal.*, **98**, 70 (1986).
- I. V. Elev, B. N. Shelimov, and V. A. Kazansky, *J. Catal.*, **113**, 256 (1988).
- W. Grünert, A. Y. Stakheev, R. Feldhaus, K. Anders, E. S. Shpiro, and K. M. Minachev, *J. Catal.*, **135**, 287 (1992).
- W. Grünert, A. Y. Stakheev, W. Mörke, R. Feldhaus, K. Anders, E. S. Shpiro, and K. M. Minachev, *J. Catal.*, **135**, 269 (1992).
- Y. Zhang, K. M. Leo, A. F. Sarofim, Z. Hu, and M. Flytzani-Stephanopoulos, *Catal. Lett.*, **31**, 75 (1995).
- NATO ASI Series, C326 "Olefin Metathesis and Polymerization Catalysts" ed by Y. Imamoglu, B. Zumreoglu-Karan, and A. J. Amass, Kluwer, Kemer, (1990) p. 271.
- K. Tanaka, K. Tanaka, H. Takeo, and C. Matsumura, *J. Am. Chem. Soc.*, **109**, 2422 (1987).
- E. K. Borgarello, M. Gratzel, E. Pelizzetti, and M. Visca, *J. Am. Chem. Soc.*, **104**, 2996 (1982).
- K. Tanaka, K. Miyahara, and K. Tanaka, "Proc. 7th Int. Congr. Catal." ed by T. Seiyama and K. Tanabe, Kodansha-Elsevier, Tokyo (1980) p. 1318.
- K. Tanaka, K. Miyahara, and K. Tanaka, *J. Mol. Catal.*, **15**, 133 (1982).
- K. Segawa, D. S. Kim, Y. Kurusu, and I. E. Wachs, "Proc. 9th Int. Congr. Catal." ed by M. J. Phillips and M. Ternan, Chemical Institute of Canada, Calgary (1988) p. 1960.
- K. Segawa, T. Soeya, and D. S. Kim, "Catalytic Science and Technology" ed by S. Yoshida, N. Takezawa and Y. Ono, Kodansha, Tokyo (1991) p. 153.
- J. Goldwasser, J. Engelhardt, and W. K. Hall, *J. Catal.*, **71**, 381 (1981).
- J. Engelhardt, J. Goldwasser, and W. K. Hall, *J. Catal.*, **70**, 364 (1981).
- M. Che, F. Figueras, M. Forisser, J. McAtter, M. Perrin, J. L. Portefaix, and H. Praliaud, "Proc. 6th Int. Congr. Catal." ed by G. C. Bond, P. B. Wells and F. C. Tompkins, The Chemical Society, London (1976) p. 261.
- H. Aritani, T. Tanaka, T. Funabiki, S. Yoshida, K. Eda, N. Sotani, M. Kudo, and S. Hasegawa, *J. Phys. Chem.*, **100**, 19495 (1996).
- H. Praliaud, "Proc. Climax 3rd Int. Conf. Chemistry and Uses of Molybdenum" ed by P. C. H. Mitchell and A. Seamans, Climax Molybdenum Co., Ann Arbor (1976) p. 195.
- S. Rajagopal, H. J. Marini, J. A. Marzari, and R. Miranda, *J. Catal.*, **147**, 417 (1994).