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Effect of the Flow Rate of H_2 in the Reduction Process on the Physical and Catalytic Properties of H_2-Reduced Pt/MoO_3

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The surface area of H_2-reduced Pt/MoO_3 decreased with increasing the flow rate of H_2 in the reduction process at 773 K, while the opposite tendency was observed at 523 and 623 K. The surface area was found to depend on the extent of reduction, which was raised by an increase in the H_2 flow rate. The largest surface area, about 300 m^2 g^{-1}, was obtained at a reduction degree of 64%. A study of reduction with a mixture of H_2 and H_2O showed that the extent of reduction declined in the presence of H_2O. We suggest from these results that the reduction of Pt/MoO_3 was prohibited by the action of H_2O produced by the reduction. The pentane isomerization activity of H_2-reduced Pt/MoO_3 was also dependent on the extent of reduction. The highest isomerization activity was obtained at a reduction degree of 76%. H_2-reduced Pt/MoO_3 exhibited a comparable catalytic activity for pentane isomerization to Pt/H-mordenite.

Molybdenum is an important catalytic component, and its physical and catalytic properties have been investigated in detail. In practice, molybdenum oxide and sulfide-based materials have been applied as catalysts for the selective oxidation of alkene and the hydrodesulfurization of petroleum feed stock. Unique physical and catalytic properties of Mo-based materials have been reported. Boudart and co-workers[1] have shown that a temperature-programmed reaction of MoO_3 with NH_3 provided a new way to prepare molybdenum nitride with a surface area as high as 220 m^2 g^{-1}. Temperature-programmed carburization of molybdenum nitride in a CH_4–H_2 mixture led to the formation of molybdenum carbide with a surface area of about 180 m^2 g^{-1}.[2,3] Molybdenum carbide prepared with the temperature-programmed carburization of MoO_3 in a CH_4–H_2 mixture also exhibited a high surface area.[4,5] Several reports have illustrated the abilities of molybdenum nitride and carbide to catalyze hydrogenolysis,[6] hydrogenation,[7] dehydrogenation,[8] and hydrodenitrogenation.[9] Ledoux and co-workers[10–12] have shown that the reaction of MoO_3 with a mixture of H_2 and heptane at 623 K yielded molybdenum oxycarbide, MoO_xC_y, with a surface area of about 150 m^2 g^{-1}, and that the MoO_xC_y catalyzed the skeletal isomerization of hexane and heptane without cyclization and excessive cracking.

We have reported in previous papers[13–15] that the H_2 reduction of MoO_3 at 623 K was accompanied by an increase in the surface area. The reduced MoO_3 exhibited a surface area of about 180 m^2 g^{-1} when the reduction degree was about 50%. Furthermore, the reduced MoO_3 was found to have micropores with diameters of 6 to 30 Å. We have also shown that MoO_3 reduced at 623 K was an active and selective catalyst for heptane isomerization. The dehydration and dehydrogenation of 2-propanol proceeded simultaneously on the reduced MoO_3, indicating that H_2-reduced MoO_3 was a porous transition metal oxide with bifunctional catalytic properties. The physical and catalytic properties of H_2-reduced MoO_3 were affected by the reduction temperature.[16,17] MoO_3 reduced at 673 K was less active for the conversions of heptane and 2-propanol than MoO_3 reduced at 623 K, and its surface area was about 50 m^2 g^{-1}, irrespective of the extent of reduction. XRD studies showed that the formation of hydrogen molybdenum bronze, H_xMoO_3, was observed at 623 K, while MoO_3 was directly converted to MoO_2 at 673 K. We have suggested from these results that the formation of the H_xMoO_3 phase can play an important role to enlarge the surface area and to create the bifunctional property.

It is generally known that MoO_3 absorbs a large amount of hydrogen without an equivalent amount of water being generated in the presence of a noble metal.[18,19] The process of hydrogen spillover leads to the insertion of hydrogen in the MoO_3 lattice and to the formation of H_xMoO_3. It has been reported in our previous papers[20,21] that the surface area and the heptane isomerization activity of MoO_3 with a noble metal were larger than those of MoO_3 after reduction at 623 K. Furthermore, the physical and catalytic properties of H_2-reduced Pt/MoO_3 were independent of the reduction temperature, and were related only by the reduction degree.[22] These results allow us to propose that the surface area and the catalytic activity can be improved when reduction of MoO_3 proceeds through the formation of H_xMoO_3, although a detailed reduction process is still under investigation. Our previous studies[23,24] indicated that the surface area and the catalytic behavior of H_2-reduced MoO_3 were influenced by the flow rate of H_2 in the reduction process as well as by the reduction temperature. The aim of the present work was to describe the effects of the flow rate of H_2 in the reduction process on the physical and the catalytic properties of H_2-reduced Pt/MoO_3.

Experimental

H_2 and N_2 were purified by passing through a molecular sieve and a Mn/SiO_2 oxygen trap. Commercially available $PtCl_4$·$5H_2O$ and $[Pt(NH_3)_4]Cl_2$·H_2O were used without further purification. The MoO_3 used in this study was obtained by the calcination of

H_2MoO_4 with a purity of 98% (Kanto Chemical Co., Inc) at 673 K for 3 h. MoO_3 with 0.01 mol% Pt (Pt/MoO_3) was prepared by a conventional impregnation method using an aqueous solution of $PtCl_4$. Pt/MoO_3 was dried overnight at 393 K, followed by calcination at 673 K for 3 h. Hβ (SiO_2/Al_2O_3 = 25), HM (SiO_2/Al_2O_3 = 18), and HY (SiO_2/Al_2O_3 = 12) were purchased from Nikki Universal Co., Inc. Pt/zeolites with 0.5 wt% Pt were prepared by an impregnation method using an aqueous solution of $[Pt(NH_3)_4]Cl_2$. After drying at 393 K, Pt/zeolites were calcined at 573 K for 3 h. The powders were made into pellets, crushed, and then sieved (30–60 mesh) for charging into a reactor.

Pt/MoO_3 (0.2 g) was packed at the central position of a reactor, which was made of a pyrex glass tube with an inner diameter of 6 mm. Pt/MoO_3 was heated to a desired temperature (523, 623, or 773 K) at a rate of 5 K min^{-1} in a stream of H_2, and was kept at that temperature for 12 h. The flow rate of H_2 was varied from 7.5 to 120 mL min^{-1}. H_2-reduced Pt/MoO_3 will be denoted as Pt/MoO_3 (523), Pt/MoO_3 (623), and Pt/MoO_3 (773). The value in parentheses represents the reduction temperature. Pt/zeolites were reduced at 773 K for 3 h prior to a reaction.

The surface area was determined from an N_2 adsorption isotherm, which was obtained on a sample without exposure to air. The reduced sample was cooled to room temperature under H_2 flow. After evacuation for 0.5 h at room temperature, the adsorption of N_2 was measured at 77 K using a conventional high-vacuum static system. To determine the pore-size distribution, the adsorption-desorption isotherms of N_2 were measured with an automatic gas-adsorption apparatus (Sorptomatic 1990, Carlo Erba). Pore-size distribution curves were obtained by analyzing the adsorption data using the Horvath–Kawazoe method.

The extent of reduction was calculated from the amounts of O_2 consumed in the complete reoxidation to MoO_3. A pulse technique was employed in the reoxidation. Since H_2O was formed in the reoxidation, the concentration of O_2 was monitored by TCD gas chromatography using a Porapak N separation column. The detailed procedures were described previously.[21]

Crystalline phases of H_2-reduced Pt/MoO_3 were determined by X-ray diffraction using Ni-filtered Cu-$K\alpha$ radiation (Rigaku, Rint-1200). Pt/MoO_3 was subjected to H_2 reduction at a desired temperature, followed by flowing N_2 for 0.5 h at the same temperature. After cooling to room temperature under N_2 flow, the reduced sample was transferred to a glove box without exposure to air, and was dispersed in a solution of heptane to avoid any strong bulk oxidation.

The reaction of pentane was carried out at 523 K under atmospheric pressure in a conventional fixed-bed flow reactor with a sampling valve for gas chromatographic analysis. After reduction and cooling to the reaction temperature in a stream of H_2, pentane was introduced onto the catalyst bed at a partial pressure of 9211 Pa with H_2 as a complement to the atmospheric pressure. The composition of effluent gases was analyzed by means of FID gas chromatography using a TC-1 glass capillary column.

Results and Discussion

Figure 1 shows the surface area of H_2-reduced Pt/MoO_3 as a function of the flow rate of H_2 in the reduction process. Here, reduction was performed for 12 h at each temperature. Pt/MoO_3 exhibited a surface area of about 5 m^2 g^{-1} before reduction. The reduction of Pt/MoO_3 induced an increase in the surface area, irrespective of the reduction temperature. The surface area of H_2-reduced Pt/MoO_3, however, changed by the flow rate of H_2 in the reduction process as well as by the reduction temperature. The surface area of Pt/MoO_3 (523) was enlarged from 56 m^2 g^{-1} to 115 m^2 g^{-1} by an increase in the H_2 flow rate from 15 mL min^{-1} to 120 mL min^{-1}. A same tendency was observed at 623 K, although Pt/MoO_3 (623) had a large surface area compared with Pt/MoO_3 (523). In contrast, the surface area of Pt/MoO_3 (773) declined markedly with an increase in the flow rate of H_2. Pt/MoO_3 (773) reduced at a H_2 flow rate of 7.5 mL min^{-1} had a surface area of 312 m^2 g^{-1}, while a surface area of 152 m^2 g^{-1} was obtained at a H_2 flow rate of 120 mL min^{-1}.

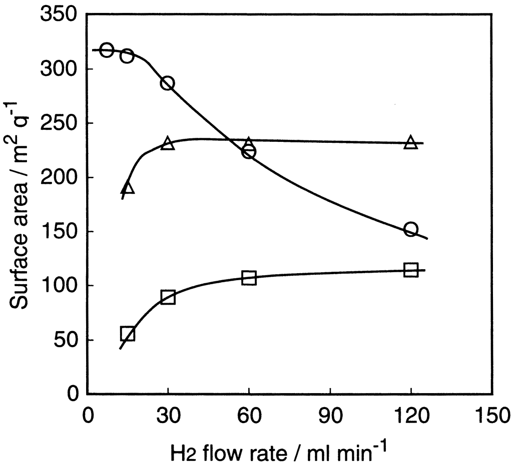

Fig. 1. Effect of the flow rate of H_2 in the reduction process on the surface area of H_2-reduced Pt/MoO_3. Pt/MoO_3 (0.2 g) was reduced at 523 K (□), 623 K (△), and 773 K (○) for 12 h.

Changes in the XRD patterns of Pt/MoO_3 (773) on H_2 reduction are illustrated in Fig. 2. Pt/MoO_3 (773) reduced at a H_2 flow rate of 15 mL min^{-1} provided the diffraction lines at 2θ = 38.1°, 40.5°, and 44.3°. The line at 2θ = 40.5° is assigned to the *d*(001) diffraction of the Mo metal phase. Ledoux and co-workers[25] have reported that molybdenum oxycarbide, MoO_xC_y, gave diffraction lines at 2θ = 38.2° and 43.5°. Delporte and co-workers[11] have stated that hydrogen atom was able to act like carbon atom to form MoO_xH_y, and a diffraction line of this phase appeared at 2θ = 44.5°. Thus, the lines appearing at 2θ = 38.1° and 44.3° seem to reflect the formation of the MoO_xH_y phase. The intensity of the lines due to the MoO_xH_y phase decreased, and the diffraction lines corresponding to the Mo metal phase were markedly strengthened by an increase in the flow rate of H_2. These results indicate that the extent of reduction was affected by the flow rate of H_2 in the reduction process. In the case of Pt/MoO_3 (623), the formation of Mo metal was not detected, and the diffraction lines appeared only at 2θ = 38.1° and 44.3°. Pt/MoO_3 (523) gave no diffraction lines, and was almost amorphous with respect to XRD.

The extent of reduction was determined by measuring the amounts of O_2 consumed in the complete reoxidation to MoO_3. Here, the complete reduction of MoO_3 to Mo metal is defined to be a reduction degree of 100%. The reduction degrees of Pt/MoO_3 (773) reduced at H_2 flow rates of 15, 60, and 120 mL min^{-1} were calculated to be 64, 83, and 93%, respectively. A

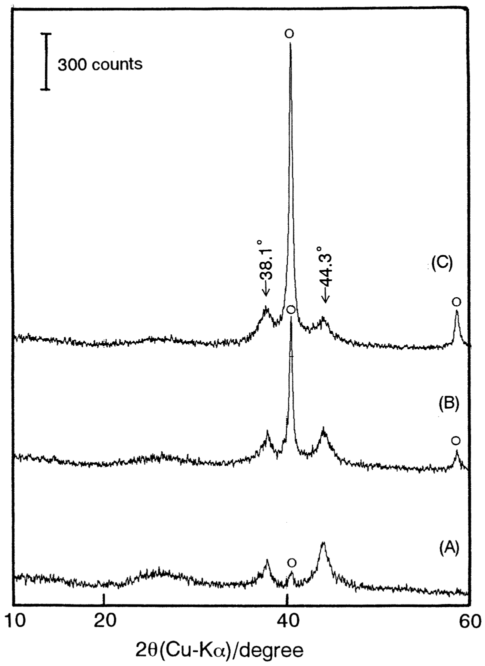

Fig. 2. XRD patterns of Pt/MoO_3 (773) reduced for 12 h at the H_2 flow rates of 15 mL min^{-1} (A), 60 mL min^{-1} (B), and 120 mL min^{-1} (C). ○, Mo metal.

similar tendency was observed at 523 and 623 K, although the changes in the reduction degree at these temperatures were small compared with that at 773 K. The reduction degrees of Pt/MoO_3 were varied from 29 to 32% at 523 K, and from 41 to 52% at 623 K when the flow rate of H_2 increased from 15 to 120 mL min^{-1}. It was shown in our previous paper[22] that the surface area of H_2-reduced Pt/MoO_3 was related to the reduction degree. Hence, the surface areas shown in Fig. 1 were plotted against the reduction degree. As shown in Fig. 3, the surface area of H_2-reduced Pt/MoO_3 was raised in proportion to the reduction degree, and reached the maximum value at a reduction degree of about 64%. It is obvious from these results that the surface area of Pt/MoO_3 was dependent on the reduction degree, which changed by the flow rate of H_2 in the reduction process as well as by the reduction temperature.

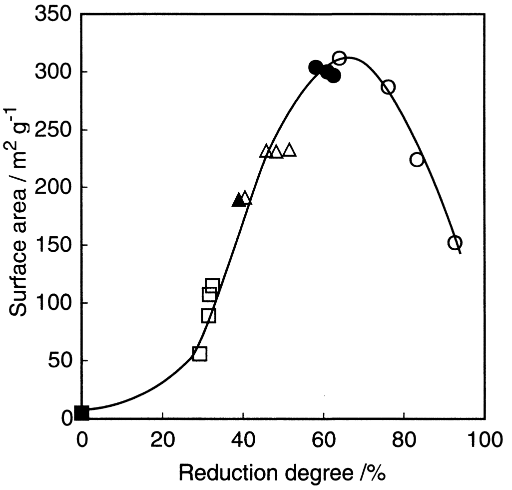

Fig. 3. Variation in the surface area of H_2-reduced Pt/MoO_3 with the reduction degree. Before reduction (■). Pt/MoO_3 reduced with H_2 at 523 K (□), 623 K (△), and 773 K (○). Pt/MoO_3 reduced with H_2 + H_2O at 623 K (▲), and 773 K (●).

We have proposed that the reduction of MoO_3 through the formation of hydrogen molybdenum bronze, H_xMoO_3, can be accompanied by an increase in the surface area.[16,22,26] In order to confirm the formation of H_xMoO_3, the change in the crystalline phase of Pt/MoO_3 during heating to 773 K was studied. Here, Pt/MoO_3 was heated to a desired temperature in a stream of H_2, and then quenched to room temperature. The XRD diagrams of Pt/MoO_3 heated in the different flow rates of H_2 are illustrated in Fig. 4. Pt/MoO_3 was converted to H_xMoO_3 at room temperature, due to the effect of hydrogen spillover. The lines appearing at $2\theta = 12.6$, 24.4, and 38.7 were assigned to the $d(200)$, $d(110)$, and $d(600)$ diffraction of the $H_{1.64}MoO_3$ phase, respectively. The $H_{1.64}MoO_3$ phase disappeared, and the diffraction lines corresponding to the MoO_xH_y phase were detected at 573 K. As shown in Fig. 4, the formations of $H_{1.64}MoO_3$ and MoO_xH_y were not affected by the flow rate of H_2. We suggest from these results that the flow rate of H_2 in the reduction process had an effect mainly on the formation of Mo metal. This can be helpful to explain the strong dependency of the reduction degree on the flow rate of H_2 at 773 K.

The Langmuir isotherm gave a better fit of the N_2 adsorption data on H_2-reduced Pt/MoO_3 than the BET isotherm. Figure 5 demonstrates the adsorption-desorption isotherms of N_2 on H_2-reduced Pt/MoO_3 with reduction degrees of 32%, 64%, and 93%. These Pt/MoO_3 exhibited surface areas of 107 m^2 g^{-1}, 312 m^2 g^{-1}, and 152 m^2 g^{-1}, respectively. The adsorption and desorption isotherms of N_2 on H_2-reduced Pt/MoO_3 were shaped as type I, irrespective of the reduction degree. No hysteresis appeared, and the amounts of N_2 adsorption increased sharply at very low pressures, and changed little at intermediate pressures. These phenomena are characteristics of microporous materials.

Pore-size distribution curves were obtained using the Horvath–Kawazoe method to confirm the formation of pores. Figure 6 shows the pore-size distributions for H_2-reduced Pt/MoO_3. Pt/MoO_3 with a reduction degree of 32% was found to have pores with the radii of 3 to 50 Å. No appreciable difference appeared in the pore-size distribution among the samples tested. However, the Dv/Dr value was dependent on the reduction degree. The Dv/Dr value increased in proportion to the reduction degree, and reached the maximum value at a reduction degree of 64%. The porous structure is likely to progress up to a reduction degree of about 60–65%. Further reduction lowered the Dv/Dr value, indicating a rupture of the pores. The relationship between the pore volume at $P/P_0 = 0.973$ and the reduction degree is depicted in Fig. 7. Pt/MoO_3 exhibited a pore volume of 0.58×10^{-1} cm^3 g^{-1} when the extent of reduction was 32%. The pore volume was raised by an increase in the reduction degree, and the largest pore volume of 1.54×10^{-1} cm^3 g^{-1} was obtained at a reduction degree of 64%. This relationship is almost identical with that observed in the surface area. We conclude from these results that the H_2 reduction of Pt/MoO_3 was accompanied by the formation of pores, resulting in an increase in the surface area.

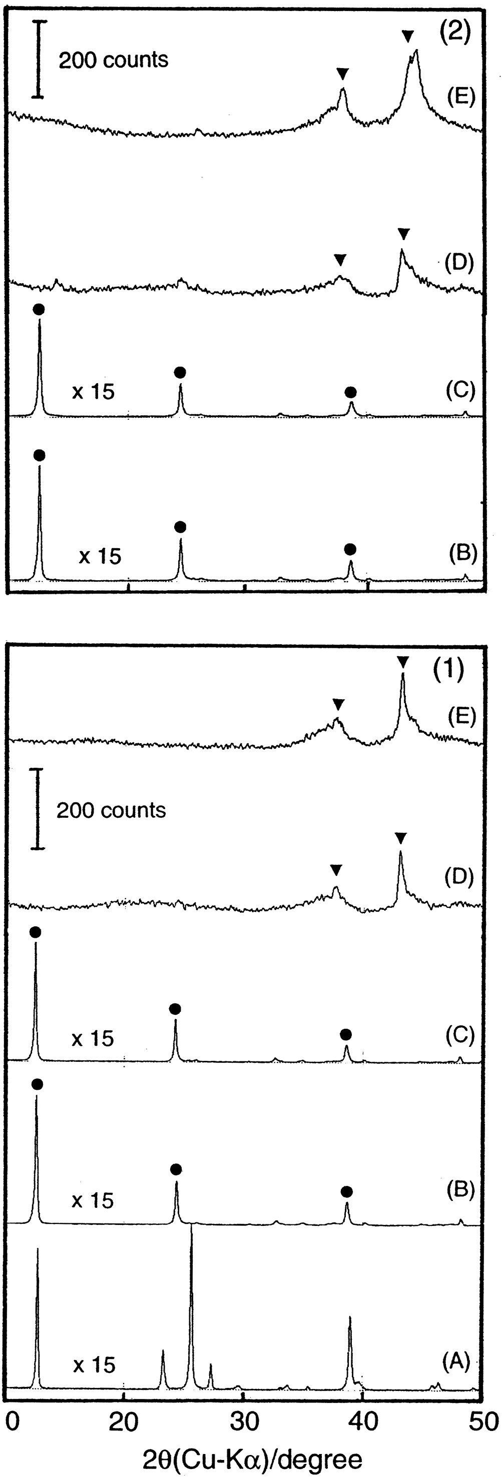

Fig. 4. Change in the XRD patterns of Pt/MoO_3 during heating in a stream of H_2. The flow rate of H_2: 15 mL min^{-1} (1), 120 mL min^{-1} (2). The parent Pt/MoO_3 (A), room temperature (B), heated to 473 K (C), 573 K (D), 773 K (E). ●, $H_{1.64}MoO_3$, ▼; MoO_xH_y.

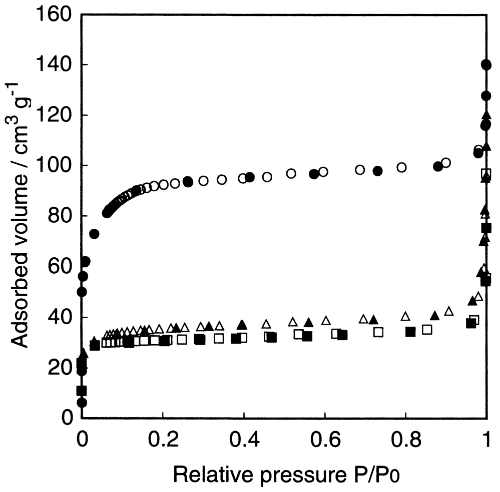

Fig. 5. Adsorption-desorption isotherms of N_2 on H_2-reduced Pt/MoO_3 with the reduction degrees of 32% (■□), 64% (●○), and 93% (▲△). Isotherm: solid symbols, adsorption; open symbols, desorption.

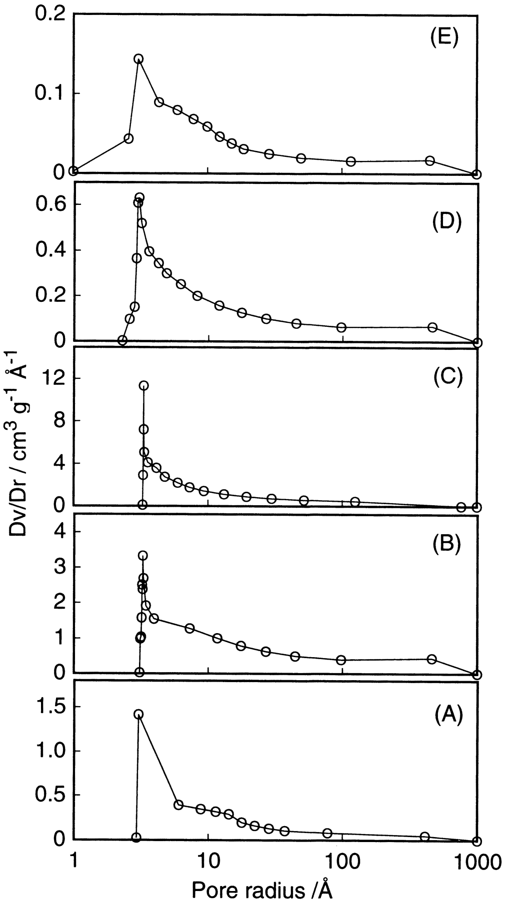

Fig. 6. Pore-size distribution curves for H_2-reduced Pt/MoO_3 with the reduction degree of 32% (A), 52% (B), 64% (C), 76% (D), and 93% (E).

It has been reported that molybdenum nitride with a lager surface area was produced at a greater flow rate of NH_3 in temperature-programmed reaction of MoO_3 with NH_3.[27,28] The resultant high surface area was achieved only when the reaction took place at a slow, controlled rate, so that oxygen could be removed and replaced with nitrogen without a substantial reorganization of the metal lattice. The concentration gradient of

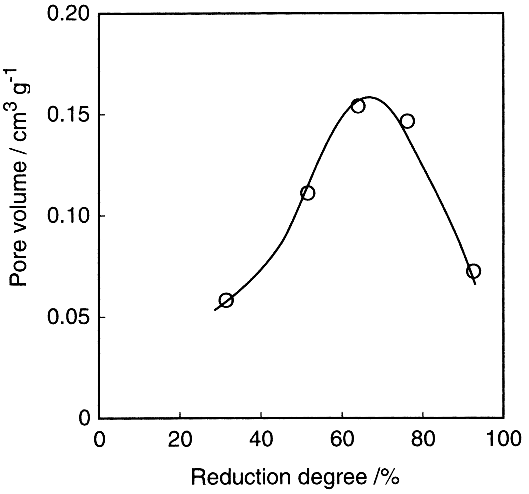

Fig. 7. Dependency of the pore volume in H_2-reduced Pt/MoO_3 on the extent of reduction.

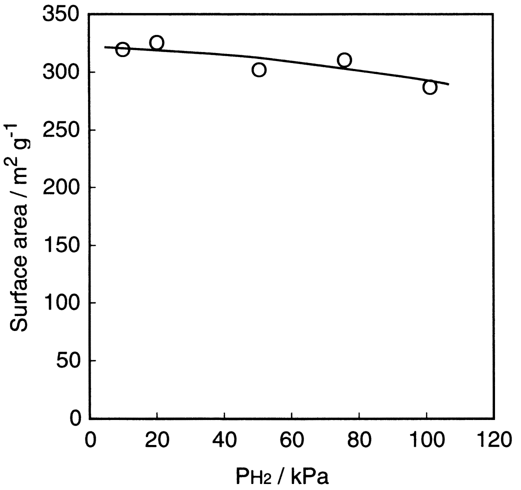

Fig. 8. Effect of partial pressure of H_2 on the surface area of Pt/MoO_3 (773). Pt/MoO_3 was reduced for 12 h at a H_2 flow rate of 30 mL min^{-1}.

NH_3 in a MoO_3 bed was thus suggested to affect the surface area of the resultant molybdenum nitride. The importance of the space velocity has also been stated concerning the synthesis of molybdenum carbide in the temperature-programmed reduction of MoO_3 with a gas mixture of H_2 and CH_4.[28] Figure 8 shows the effect of the partial pressure of H_2 (P_{H_2}) on the surface area of Pt/MoO_3 (773). Here, the flow rate of H_2 was fixed to be 30 mL min^{-1}. The surface area was slightly enlarged by a decrease in P_{H_2}. The reduction at P_{H_2} of 10.1 and 101.3 kPa yielded products with surface areas of 320 and 287 m^2 g^{-1}, respectively. These results indicate that the surface area was hardly affected by the concentration gradient of H_2.

Arnoldy and co-workers[29] have shown that the reducibility of MoO_3 depended on the content of H_2O in a reducing gas, because the formation of low valence Mo atoms, which could catalyze the dissociation of H_2, was suppressed in the presence of H_2O. We also reported in a previous paper[24] that the reduction of MoO_3 was prohibited by the action of H_2O produced by the reduction. In order to study the effect of H_2O on the reduction of Pt/MoO_3, reduction was performed at 773 K for 12 h using a gas mixture of H_2O and H_2. The surface area and the reduction degree of Pt/MoO_3 (773) as a function of P_{H_2O} are shown in Fig. 9, where the flow rate of H_2 was fixed to be 120 mL min^{-1}. The reduction degree of Pt/MoO_3 (773) decreased from 93% to 63% with an increase in P_{H_2O} from zero to 863 Pa. A further increase in P_{H_2O} slightly lowered the reduction degree. It is obvious from these results that the reduction of MoO_3 was prohibited by H_2O even in the presence of Pt. We suggest based on these results that the partial pressure of H_2O produced by the reduction of Pt/MoO_3 can be enlarged at a small flow rate of H_2, leading to a suppression of reduction.

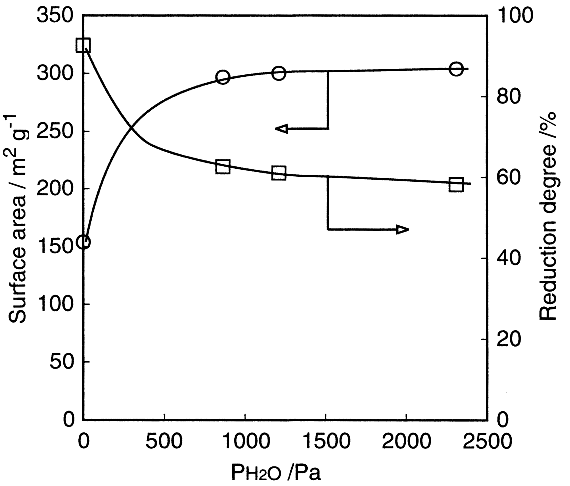

Fig. 9. Effect of partial pressure of H_2O on the surface area (○) and the reduction degree (□) of Pt/MoO_3 (773). Pt/MoO_3 was reduced at 12 h at a H_2 flow rate of 120 mL min^{-1}.

The surface area of Pt/MoO_3 (773) increased from 154 m^2 g^{-1} to 304 m^2 g^{-1} with increasing P_{H_2O} from zero to 2310 Pa. As mentioned above, the surface area of Pt/MoO_3 is dependent on the reduction degree. Hence, the results shown in Fig. 9 are plotted in Fig. 2. The surface area of Pt/MoO_3 was highly related to the extent of reduction, independently of P_{H_2O}.

The conversion of pentane was carried out at 523 K under atmospheric pressure using H_2-reduced Pt/MoO_3 as a catalyst. Pentane was isomerized to 2-methylbutane on all of the catalysts tested, of which the isomerization selectivity was 96–99%. The isomerization activity was estimated using the formation rate of 2-methylbutane at a conversion level below 10%. The isomerization activity of Pt/MoO_3 (773) as a function of the H_2 flow rate in the reduction process is shown in Fig. 10, where the catalytic activity was compared using data after a 0.5 h run to minimize the effect of catalyst deactivation. As described above, the surface area was markedly varied with the flow rate of H_2. Hence, the isomerization activity was evaluated by taking the surface area into consideration. The isomerization activity of Pt/MoO_3 (773) was improved by an increase in the flow rate of H_2, and the highest isomerization activity appeared at a H_2 flow rate of 30 mL min^{-1}. These results indicate that the flow rate of H_2 in the reduction process affected not only the surface area, but also the chemical nature

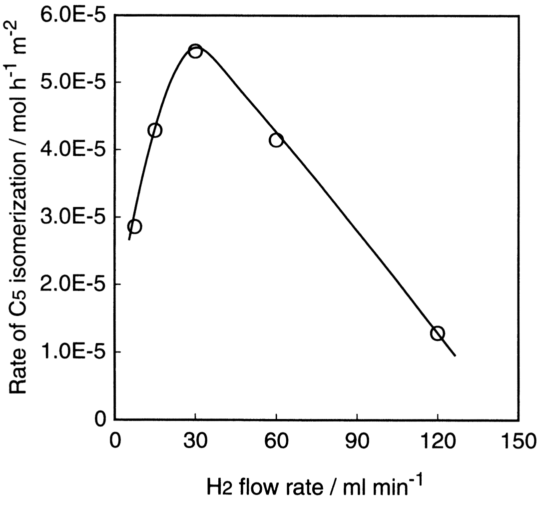

Fig. 10. Effect of the flow rate of H_2 in the reduction process on the pentane isomerization activity of Pt/MoO$_3$ (773). Pt/MoO$_3$ (0.2 g) was reduced at 773 K for 12 h.

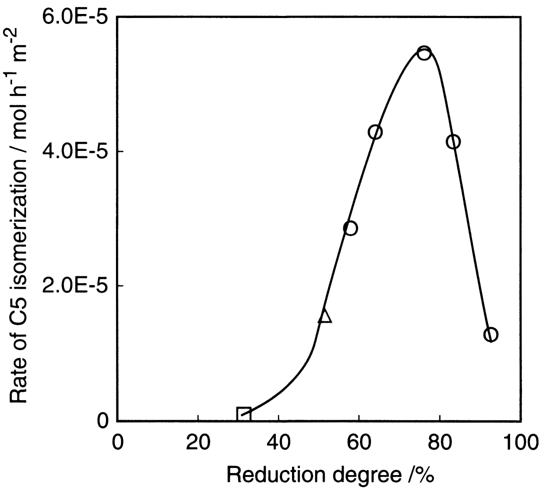

Fig. 11. Variation in the pentane isomerization activity of H_2-reduced Pt/MoO$_3$ with the reduction degree. Pt/MoO$_3$ was reduced at 523 K (□), 623 K (△), and 773 K (○) for 12 h.

of the surface.

Figure 11 shows the relationship between the extent of reduction and the catalytic activity of Pt/MoO$_3$ for pentane isomerization. Pt/MoO$_3$ was almost inactive for the isomerization of pentane when its reduction degree was 32%. The isomerization activity increased in proportion to the reduction degree, and the highest isomerization activity was obtained at a reduction degree of 76%. This tendency is almost similar to that observed in the surface area. These results suggest that the H_2 reduction of Pt/MoO$_3$ was accompanied by the generation of active sites for pentane isomerization in addition to the enlargement of the surface area, although the isomerization activity was maximized at a large reduction degree compared with the surface area.

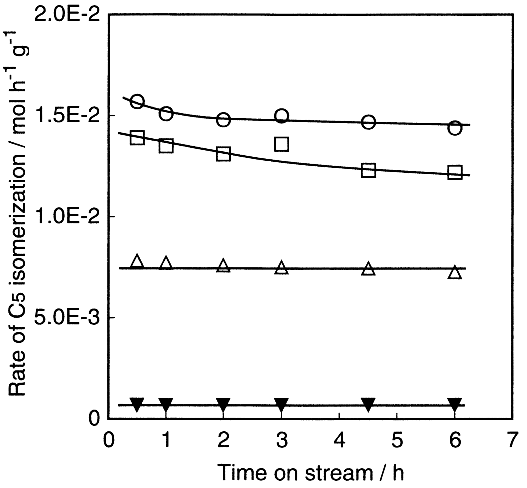

Fig. 12. Variation in the pentane isomerization activities of Pt/MoO$_3$ (○), Pt/HM (□), Pt/Hβ (△), and Pt/HY (▼) with time on stream.

The isomerization of alkane is generally catalyzed by bifunctional catalysts consisting of highly dispersed Pt metals on acidic oxide supports. The catalytic properties of Pt/zeolite for the skeletal isomerization of alkane have been investigated in detail. In practice, Pt/H-mordenite has been applied as a catalyst for the isomerization of C_5–C_6 hydrocarbons. Hence, the pentane isomerization activity of Pt/MoO$_3$ (773) with a reduction degree of 76% was compared with those of Pt/zeolite catalysts. Typical results are shown in Fig. 12. All of the catalysts exhibited almost stable isomerization activities against deactivation under the reaction conditions tested. Pt/MoO$_3$ (773) exhibited a comparable isomerization activity to Pt/HM, which was the most active catalyst among Pt/zeolites. These results allow us to suggest that Pt/MoO$_3$ can be an effective catalyst for pentane isomerization, although the abilities of Pt/MoO$_3$ (773) to act as an acid catalyst and a hydrogenation-dehydrogenation catalyst are still under investigation. The bifunctional property of Pt/MoO$_3$ and its dependency on the reduction degree will be described in a further study.

Conclusion

The surface area of H_2-reduced Pt/MoO$_3$ was influenced by the flow rate of H_2 in the reduction process. The reduction of Pt/MoO$_3$ was promoted by an increase in the H_2 flow rate. There was a good relationship between the reduction degree and the surface area of H_2-reduced Pt/MoO$_3$. H_2-reduced Pt/MoO$_3$ exhibited the largest surface area at a reduction degree of 64%. The formation of pores with radii of 3–50 Å was found to be a reason for the enlargement of the surface area. A study of reduction with a mixture of H_2 and H_2O showed that the extent of reduction was lowered by an increase in the partial pressure of H_2O. We suggest from these results that the partial pressure of H_2O produced by the reduction of Pt/MoO$_3$ can be enlarged at a small flow rate of H_2, leading to a suppression of reduction. The pentane isomerization activity of Pt/MoO$_3$ was also related to the extent of reduction, and was maximized at a reduction degree of 76%. Pt/MoO$_3$ exhibited a comparable pentane isomerization activity to Pt/HM, which was the most active catalyst among Pt/zeolites.

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