Pentane Isomerization over Molybdenum Oxide Prepared by H_2 Reduction of a Hydrogen Molybdenum Bronze

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Physical and catalytic properties of hydrogen molybdenum bronze, $H_{1.55}MoO_3$ varied markedly with H_2 reduction. The surface area was enlarged from 10 m^2/g to 250 m^2/g by H_2 reduction at 673–723 K. $H_{1.55}MoO_3$ became an active and selective catalyst for pentane isomerization after reduction. H_2-reduced $H_{1.55}MoO_3$ exhibited a comparable isomerization activity to H_2-reduced Pt/MoO_3.

The isomerization of straight chain alkanes into the corresponding branched isomers has attracted much attention as a reaction to boost the octane quality of a gasoline fraction. Bifunctional catalysts consisting of acidic oxide and noble metal show high efficiency in the isomerization of alkanes. In practice, the isomerization reaction has been carried out on an industrial scale using Pt/chlorinated Al_2O_3, Pt/mordenite, and Pt/SO_4^{2-}-ZrO_2 catalysts. Oxygen modified tungsten carbide and molybdenum oxycarbide have been reported to catalyze alkane isomerization with high selectivity.[1,2]

We showed in previous papers[3–5] that H_2 reduction of Pt/MoO_3 was accompanied by an increase in the surface area, and Pt/MoO_3 became an active and selective catalyst for the isomerization of pentane and heptane after reduction. The physical and catalytic properties of H_2-reduced Pt/MoO_3 were improved only when its reduction proceeded through the formation of hydrogen molybdenum bronze, H_xMoO_3. Since the surface area and the isomerization activity of the H_xMoO_3 formed in reduction of Pt/MoO_3 were comparable to those of the parent Pt/MoO_3, we have suggested that reduction of H_xMoO_3 can be an important step to improve the surface area and the isomerization activity. The roles of Pt in reduction of H_xMoO_3, however, are still under investigation. The main purpose of the present work is to describe the effect of H_2 reduction on the physical and catalytic properties of hydrogen molybdenum bronze prepared in the absence of Pt.

MoO_3 was obtained by calcination of molybdic acid at 673 K for 3 h. Hydrogen molybdenum bronze, H_xMoO_3 was prepared at room temperature using Zn metal and an aqueous solution of HCl. MoO_3 20 g was mixed with Zn 18 g, and then 140 mL of 4 M HCl solution was added. The slurry was washed many times in water to eliminate $ZnCl_2$ and HCl. The final product was dried in vacuo, and was stored under Ar atmosphere. 0.01 mol%Pt/MoO_3 was prepared by a conventional impregnation method using an aqueous solution of $[Pt(NH_3)_4]Cl_2$. The sample (0.2 g) was heated to 573, 623, 673, 723, or 773 K at a rate of 5 K/min in a stream of H_2 (120 mL/min), and was kept for 12 h. After reduction and evacuation at room temperature, the adsorption isotherm of N_2 was measured at 77 K to determine the surface area. Average valence of Mo in the reduced sample was calculated from the amounts of O_2 consumed in the reoxidation that was performed at 773 K. The samples for XRD measurement were obtained as follows: H_2-reduced samples were transferred to a glove box without exposure to air, followed by dispersion in heptane to avoid any strong bulk oxidation. Reaction of pentane was isothermally carried out at 523 K under atmospheric pressure in a conventional fixed bed flow reactor. After reduction and cooling to reaction temperature, a gas mixture of H_2/pentane $= 10$ was introduced onto the catalyst bed. Concentration of the products in the effluent gas stream was analyzed by means of gas chromatography. The catalytic activity was evaluated using data after a 1 h run.

Figure 1 demonstrates the XRD patterns of MoO_3 and H_xMoO_3. The H_xMoO_3 prepared using Zn metal and an aqueous solution of HCl provided no diffraction lines due to a MoO_3 phase, and the lines were observed at $2\theta = 12.7°$, 24.4°, and 38.7°, and 48.3°. These diffraction lines are assigned to *d*(200), *d*(110), *d*(600), and *d*(020) diffraction of the $H_{1.68}MoO_3$ phase. The H_xMoO_3 was heated to 773 K in vacuo, and then was reoxidized to MoO_3 by introducing the prescribed amounts of O_2. The value of x in H_xMoO_3 was determined to be 1.55 from the amounts of O_2 consumed in the reoxidation. The H_xMoO_3 used in this study will be denoted to $H_{1.55}MoO_3$ in the following sections.

Figure 2 shows the surface areas of $H_{1.55}MoO_3$, MoO_3, and 0.01 mol%Pt/MoO_3 as a function of reduction temperature. These materials had surface areas of 5–10 m^2/g before reduction. The surface areas varied markedly, depending on reduction temperature. MoO_3 reduced at 623 K exhibited a surface area of 180 m^2/g, but reduction at higher temperatures enlarged the sur-

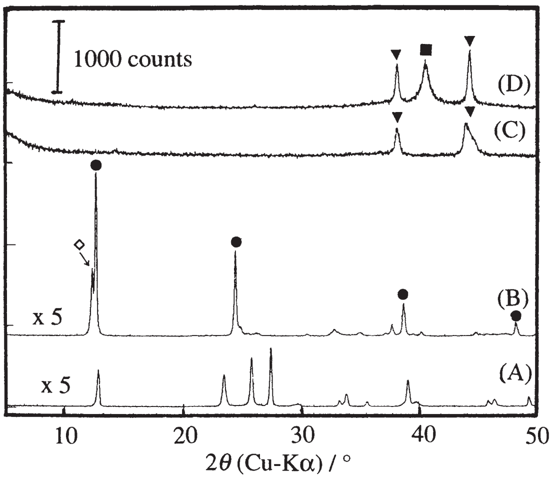

Figure 1. XRD patterns of MoO_3 and H_xMoO_3. (A), MoO_3; (B), H_xMoO_3; (C), (B) reduced at 573 K for 12 h; (D), (B) reduced at 773 K for 12 h. (●), $H_{1.68}MoO_3$; (▼), MoO_xH_y; (■), Mo metal; (◇), unknown.

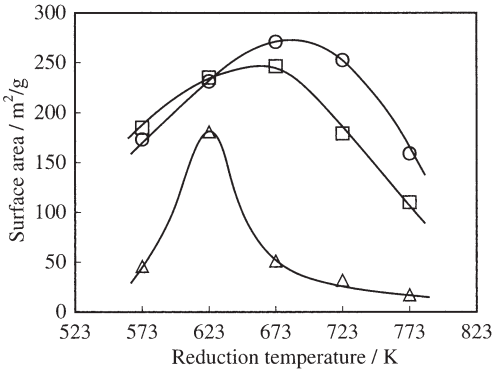

Figure 2. Effect of reduction temperature on the surface areas of $H_{1.55}MoO_3$ (○), MoO_3 (△), and Pt/MoO_3 (□). Reduction period: 12 h.

face area very little. In the cases of $H_{1.55}MoO_3$ and Pt/MoO_3, the surface area increased in proportion to reduction temperature, and the largest surface area was obtained after reduction at 673 K. H_2-reduced Pt/MoO_3 with large surface area was reported to possess pores with the diameter of 0.6–3.0 nm.[3,5] H_2 reduction of $H_{1.55}MoO_3$ was also accompanied by the formation of micropores. If one compares the surface area at reduction temperatures above 673 K, $H_{1.55}MoO_3$ and Pt/MoO_3 exhibited much larger surface areas than MoO_3. The average valence of Mo in $H_{1.55}MoO_3$, Pt/MoO_3, and MoO_3 which were reduced at 673 K for 12 h were 2.64, 2.04, and 2.65, respectively. So, the extent of reduction can not account for the difference in the surface area among these materials.

As shown in Figure 1, $H_{1.55}MoO_3$ reduced at 573 K for 12 h, of which the average valence of Mo was 3.97, gave no diffraction lines due to a MoO_2 phase, and the diffraction lines appeared at $2\theta = 38.1°$ and $44.1°$. These lines seem to reflect the formation of the MoO_xH_y phase, which is analogous to the molybdenum oxycarbide, MoO_xC_y phase.[6] Reduction at 673 K strengthened the intensity of the diffraction lines at $2\theta = 38.1°$ and $44.1°$. The diffraction line due to the Mo metal phase was detected at $2\theta = 40.6°$ after reduction at 773 K. These phenomena are almost the same as those observed in Pt/MoO_3:Pt/MoO_3 was reduced to MoO_xH_y and Mo metal without the formation of MoO_2.[3] We reported in previous papers[7,8] that reduction of MoO_3 at 623 K involved the formation of H_xMoO_3, while MoO_3 was directly reduced to MoO_2 at 673 K. Pt/MoO_3 was converted to H_xMoO_3 during heating to reduction temperature so that reduction proceeded through the formation of H_xMoO_3, irrespective of reduction temperature. This phenomenon can easily be understood by taking hydrogen spillover into consideration. $H_{1.55}MoO_3$ exhibited a large surface area even after reduction at temperatures above 673 K. Furthermore, there was no appreciable difference in the surface area between H_2-reduced $H_{1.55}MoO_3$ and H_2-reduced Pt/MoO_3. We conclude from these results that molybdenum oxide with a large surface area can be formed by reduction of hydrogen molybdenum bronze, and this reduction process cannot be affected by the presence of Pt.

Conversion of pentane was carried out at 523 K. Pentane was selectively isomerized to 2-methylbutane on all of the catalysts tested. Hence, the isomerization activity was estimated using the formation rate of 2-methylbutane. Figure 3 displays the relationship between the isomerization activity and the average valence of Mo. Here, the isomerization activity was evaluated by taking the surface area into consideration, because the surface area differed markedly for the different catalysts. No appreciable difference appeared in the isomerization activity among the catalysts tested when their average valences of Mo were in the range of 5–3. The isomerization activity of H_2-reduced MoO_3 was lowered by further reduction. In contrast, the isomerization activity of 0.01 mol%Pt/MoO_3 was enlarged by a decrease in the average valence of Mo, and the highest activity appeared at a Mo average valence of 1.4. The isomerization activity of H_2-reduced $H_{1.55}MoO_3$ depended on the average valence of Mo similarly to that of H_2-reduced Pt/MoO_3. $H_{1.55}MoO_3$ reduced at 773 K for 6 h, of which the Mo average valence was 1.5 exhibited a lower isomerization activity than H_2-reduced Pt/MoO_3 with a Mo average valence of 1.4. However, difference in the activity between $H_{1.55}MoO_3$ and Pt/MoO_3 was very small except for these two catalysts. These results clearly show that reduction of H_xMoO_3 can generate the active sites for pentane isomerization. In the case of Pt/MoO_3, the major role of Pt will be to promote the formation of H_xMoO_3.

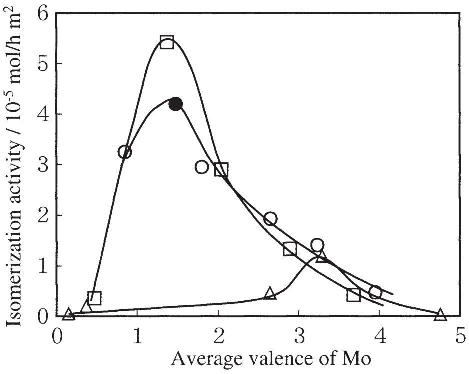

Figure 3. Relationship between the pantane isomerization activity and the average valence of Mo. $H_{1.55}MoO_3$ (○), MoO_3 (△), and Pt/MoO_3 (□) were reduced at 573–773 K for 12 h. $H_{1.55}MoO_3$ (●) was reduced at 773 K for 6 h. Reaction conditions: temperature, 523 K; H_2/C_5, 10; W/F, 10 g-cat./h mol.

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