

Pentane Isomerization over Molybdenum Oxide Prepared by H₂ Reduction of a Hydrogen Molybdenum Bronze

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Physical and catalytic properties of hydrogen molybdenum bronze, H_{1.55}MoO₃ varied markedly with H₂ reduction. The surface area was enlarged from 10 m²/g to 250 m²/g by H₂ reduction at 673–723 K. H_{1.55}MoO₃ became an active and selective catalyst for pentane isomerization after reduction. H₂-reduced H_{1.55}MoO₃ exhibited a comparable isomerization activity to H₂-reduced Pt/MoO₃.

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 Al₂O₃, Pt/mordenite, and Pt/SO₄²⁻-ZrO₂ 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 H₂ reduction of Pt/MoO₃ was accompanied by an increase in the surface area, and Pt/MoO₃ became an active and selective catalyst for the isomerization of pentane and heptane after reduction. The physical and catalytic properties of H₂-reduced Pt/MoO₃ were improved only when its reduction proceeded through the formation of hydrogen molybdenum bronze, H_xMoO₃. Since the surface area and the isomerization activity of the H_xMoO₃ formed in reduction of Pt/MoO₃ were comparable to those of the parent Pt/MoO₃, we have suggested that reduction of H_xMoO₃ can be an important step to improve the surface area and the isomerization activity. The roles of Pt in reduction of H_xMoO₃, however, are still under investigation. The main purpose of the present work is to describe the effect of H₂ reduction on the physical and catalytic properties of hydrogen molybdenum bronze prepared in the absence of Pt.

MoO₃ was obtained by calcination of molybdic acid at 673 K for 3 h. Hydrogen molybdenum bronze, H_xMoO₃ was prepared at room temperature using Zn metal and an aqueous solution of HCl. MoO₃ 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 ZnCl₂ and HCl. The final product was dried in vacuo, and was stored under Ar atmosphere. 0.01 mol%Pt/MoO₃ was prepared by a conventional impregnation method using an aqueous solution of [Pt(NH₃)₄]Cl₂. 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 H₂ (120 mL/min), and was kept for 12 h. After reduction and evacuation at room temperature, the adsorption isotherm of N₂ was measured at 77 K to determine the surface area. Average valence of Mo in the reduced sample was calculated from the amounts of O₂ consumed in

the reoxidation that was performed at 773 K. The samples for XRD measurement were obtained as follows: H₂-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 H₂/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 MoO₃ and H_xMoO₃. The H_xMoO₃ prepared using Zn metal and an aqueous solution of HCl provided no diffraction lines due to a MoO₃ phase, and the lines were observed at 2θ = 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}MoO₃ phase. The H_xMoO₃ was heated to 773 K in vacuo, and then was reoxidized to MoO₃ by introducing the prescribed amounts of O₂. The value of *x* in H_xMoO₃ was determined to be 1.55 from the amounts of O₂ consumed in the reoxidation. The H_xMoO₃ used in this study will be denoted to H_{1.55}MoO₃ in the following sections.

Figure 2 shows the surface areas of H_{1.55}MoO₃, MoO₃, and 0.01 mol%Pt/MoO₃ as a function of reduction temperature. These materials had surface areas of 5–10 m²/g before reduction. The surface areas varied markedly, depending on reduction temperature. MoO₃ reduced at 623 K exhibited a surface area of 180 m²/g, but reduction at higher temperatures enlarged the sur-

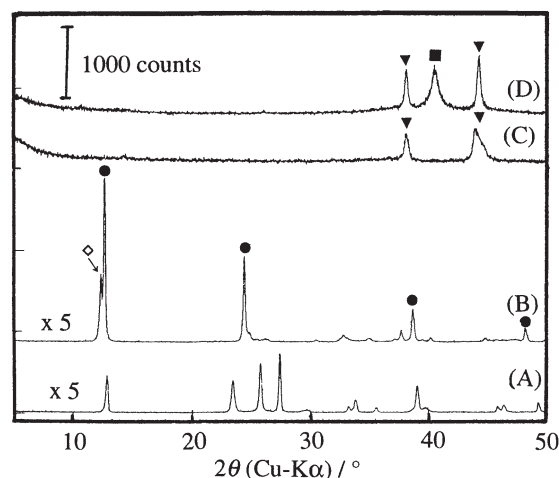


Figure 1. XRD patterns of MoO₃ and H_xMoO₃. (A), MoO₃; (B), H_xMoO₃; (C), (B) reduced at 573 K for 12 h; (D), (B) reduced at 773 K for 12 h. (●), H_{1.68}MoO₃; (▼), MoO_xH_y; (■), Mo metal; (◇), unknown.

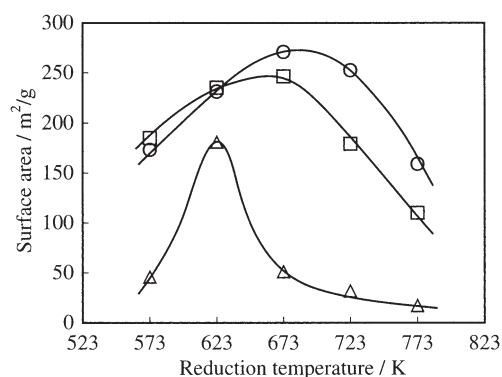


Figure 2. Effect of reduction temperature on the surface areas of H_{1.55}MoO₃ (○), MoO₃ (△), and Pt/MoO₃ (□). Reduction period: 12 h.

face area very little. In the cases of H_{1.55}MoO₃ and Pt/MoO₃, the surface area increased in proportion to reduction temperature, and the largest surface area was obtained after reduction at 673 K. H₂-reduced Pt/MoO₃ with large surface area was reported to possess pores with the diameter of 0.6–3.0 nm.^{3,5} H₂ reduction of H_{1.55}MoO₃ was also accompanied by the formation of micropores. If one compares the surface area at reduction temperatures above 673 K, H_{1.55}MoO₃ and Pt/MoO₃ exhibited much larger surface areas than MoO₃. The average valence of Mo in H_{1.55}MoO₃, Pt/MoO₃, and MoO₃ 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}MoO₃ reduced at 573 K for 12 h, of which the average valence of Mo was 3.97, gave no diffraction lines due to a MoO₂ phase, and the diffraction lines appeared at $2\theta = 38.1^\circ$ 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 $2\theta = 38.1^\circ$ and 44.1° . The diffraction line due to the Mo metal phase was detected at $2\theta = 40.6^\circ$ after reduction at 773 K. These phenomena are almost the same as those observed in Pt/MoO₃:Pt/MoO₃ was reduced to MoO_xH_y and Mo metal without the formation of MoO₂.³ We reported in previous papers^{7,8} that reduction of MoO₃ at 623 K involved the formation of H_xMoO₃, while MoO₃ was directly reduced to MoO₂ at 673 K. Pt/MoO₃ was converted to H_xMoO₃ during heating to reduction temperature so that reduction proceeded through the formation of H_xMoO₃, irrespective of reduction temperature. This phenomenon can easily be understood by taking hydrogen spillover into consideration. H_{1.55}MoO₃ exhibited a large surface area even after reduction at temperatures above 673 K. Furthermore, there was no appreciable difference in the surface area between H₂-reduced H_{1.55}MoO₃ and H₂-reduced Pt/MoO₃. 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

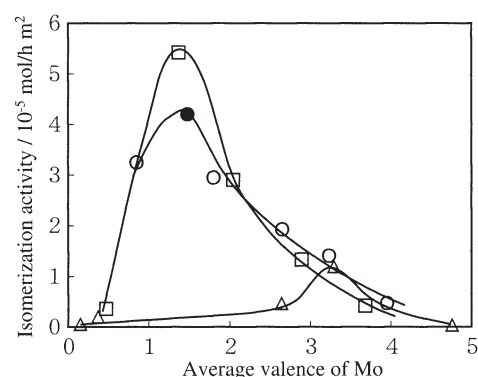


Figure 3. Relationship between the pentane isomerization activity and the average valence of Mo. H_{1.55}MoO₃ (○), MoO₃ (△), and Pt/MoO₃ (□) were reduced at 573–773 K for 12 h. H_{1.55}MoO₃ (●) was reduced at 773 K for 6 h. Reaction conditions: temperature, 523 K; H₂/C₅, 10; W/F, 10 g-cat./h mol.

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 H₂-reduced MoO₃ was lowered by further reduction. In contrast, the isomerization activity of 0.01 mol%Pt/MoO₃ 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 H₂-reduced H_{1.55}MoO₃ depended on the average valence of Mo similarly to that of H₂-reduced Pt/MoO₃. H_{1.55}MoO₃ reduced at 773 K for 6 h, of which the Mo average valence was 1.5 exhibited a lower isomerization activity than H₂-reduced Pt/MoO₃ with a Mo average valence of 1.4. However, difference in the activity between H_{1.55}MoO₃ and Pt/MoO₃ was very small except for these two catalysts. These results clearly show that reduction of H_xMoO₃ can generate the active sites for pentane isomerization. In the case of Pt/MoO₃, the major role of Pt will be to promote the formation of H_xMoO₃.

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