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H_2-reduced Pt/MoO_3 as a selective catalyst for heptane isomerization

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Abstract

H_2 reduction of Pt/MoO_3 was accompanied by an increase in the surface area. H_2-reduced Pt/MoO_3 exhibited the largest surface area of 250 m^2/g at reduction degrees of 60–70%. The surface area was enlarged only when Pt/MoO_3 was reduced after heating in a stream of H_2. The catalytic activity of H_2-reduced Pt/MoO_3 for heptane isomerization was also dependent on the extent of reduction. The highest isomerization activity appeared at a reduction degree of about 70%. Heptane was selectively isomerized on H_2-reduced Pt/MoO_3 with reduction degrees below 80%, and the high selectivity was preserved even at high conversion levels. The catalytic behaviors of H_2-reduced Pt/MoO_3 were strongly affected by heating atmosphere. Reduction after heating in H_2 provided a much more active and selective catalyst for heptane isomerization than reduction after heating in N_2. We suggest from the results of XRD measurements that reduction of Pt/MoO_3 through the formation of a H_xMoO_3 phase can be an important step to enlarge the surface area and to generate the active sites for heptane isomerization.

Keywords: H_2-reduced Pt/MoO_3; Heptane isomerization; Hydrocarbon upgrading

1. Introduction

Hydrocarbon upgrading processes such as reforming, hydrocracking, isomerization, and catalytic isodewaxing play an important role in the hydrocarbon processing industry. In these processes, hydrocarbon molecules are cracked, aromatized and/or isomerized. In particular, boosting the octane quality of a gasoline fraction by increasing the degree of branching of alkanes is an environmentally more acceptable alternative compared with other technologies such as blending with oxygenates and aromatics. Thus, skeletal isomerization of alkanes into the corresponding branched isomers has attracted much attention as a reaction to produce clean fuel with high octane quality. Bifunctional catalysts with acid functions balanced by metal functions have shown high efficiency in the isomerization of alkane. The isomerization of pentane and hexane has successfully been carried out using Pt/chlorinated Al_2O_3, Pt/H-mordenite, and Pt/SO_4^{2-}–ZrO_2 catalysts. However, difficulties are encountered with hydrocarbons larger than heptane because the cracking reaction becomes more significant over these isomerization catalysts as the chain length increases.

Pt/Hβ has been considered to be the best catalyst for the isomerization of heptane among Pt-loaded zeolites, owing to the faster diffusion of reactant and products through the tridirectional micropores [1–3]. Iglesia and co-workers [4–7] reported that WC modified by chemisorbed oxygen catalyzed heptane isomerization without excessive cracking. They have suggested that isomerization reaction on the oxygen-modified WC can proceed via the con-

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ventional bifunctional mechanism, with dehydrogenation–hydrogenation steps on sites with a metallic character (WC_x) and isomerization steps on acid sites (WO_x). Ledoux and co-workers [8–11] showed that oxygen-modified Mo_2C and carbon-modified MoO_3 were active and selective for heptane isomerization. Molybdenum oxycarbide, MoO_xC_y, which is formed by incorporating carbon atoms in the molybdenum oxide lattice, has been considered to be the active phase for heptane isomerization [12,13]. Since MoO_xC_y exhibited different catalytic behaviors in heptane isomerization from Pt/Hβ, Ledoux et al. have proposed a bond-shift mechanism via a metallocyclobutane intermediate on the MoO_xC_y phase.

We reported [14–17] that H_2 reduction of MoO_3 at 623 K gave an active and selective catalyst for heptane isomerization, and its activity was dependent on the extent of reduction. The dehydrogenation and the dehydration of 2-propanol proceeded simultaneously on H_2-reduced MoO_3 [16–18]. We have suggested on the basis of these experimental results that the isomerization of heptane on H_2-reduced MoO_3 can proceed via the conventional bifunctional mechanism. Loading of noble metal onto MoO_3 was reported to improve the catalytic activities for both heptane isomerization and 2-propanol dehydration [19,20]. The aim of the present work is to describe the effect of H_2 reduction on the catalytic behavior of Pt/MoO_3 for the isomerization of heptane. The catalytic activities of H_2-reduced Pt/MoO_3 for the dehydration and dehydrogenation of 2-propanol and for the hydrogenation of benzene are also studied to estimate the bifunctional properties.

2. Experimental

2.1. Materials

H_2, N_2 and He were purified by passage through a molecular sieve and a Mn/SiO_2 oxygen trap. H_2MoO_4 with a purity of 98% was purchased from Kanto Chemical Co. Inc. Commercially available platinum chloride was used without further purification. Heptane, 2-propanol and benzene were dried using a molecular sieve prior to use. The MoO_3 used in this study was obtained by calcination of H_2MoO_4 at 673 K for 3 h. Pt/MoO_3 of 0.01 mol% Pt was prepared by a conventional impregnation method using an aqueous solution of platinum chloride. The obtained sample was dried overnight at 393 K, and then was calcined at 673 K for 3 h. The catalyst powders were compressed into flakes, followed by crushing and sieving (30–60 mesh).

2.2. Reduction procedures

A prescribed amount of 0.01 mol% Pt/MoO_3 was packed at the central position of a cell, which was made of a Pyrex glass tube with an inner diameter of 8 mm. The sample was heated to a reduction temperature (373–773 K) at a rate of 5 K/min in a stream of H_2, and was kept at that temperature for a desired period. Our previous papers showed that the physical and catalytic properties of MoO_3 with and without Pt were influenced by the flow rate of H_2 in the reduction process [21–23]. Hence, the reduction was performed at a H_2 flow rate of 600 ml/min $g_{cat.}$ in this study. For comparison, Pt/MoO_3 was reduced after heating in a stream of N_2. Pt/MoO_3 reduced with H_2 after heating in H_2 and N_2 will be denoted as Pt/MoO_3(H_2) and Pt/MoO_3(N_2), respectively.

2.3. Characterization methods

The surface area was determined from an N_2 adsorption isotherm, which was obtained on the 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, adsorption of N_2 was measured at 77 K with a conventional high-vacuum static system.

The extent of reduction was calculated from the amounts of O_2 consumed in reoxidation, which was performed at 773 K by a pulse technique. Since H_2O was formed in the reoxidation, the concentration of O_2 was monitored with TCD gas chromatography using a Porapak N separation column.

Crystalline phases of H_2-reduced Pt/MoO_3 were determined by X-ray diffraction (XRD) using Ni-filtered Cu Kα radiation (Rigaku, Rint-1000). The sample for XRD measurements was obtained as follows: Pt/MoO_3 was subjected to H_2 reduction at temperature in the range 373–773 K for a desired period, 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 bulk oxidation.

Temperature-programmed reduction (TPR) study was carried out to investigate the reducibility of Pt/MoO_3. Pt/MoO_3 of 0.4 g was calcined at 673 K for 1 h, and then was cooled to room temperature in a stream of Ar. Pt/MoO_3 was kept for 30 min at room temperature in a stream of 20% H_2–80% Ar (100 ml/min), followed by heating to 1073 K at a rate of 5 K/min. The concentrations of H_2 and H_2O were monitored with TCD gas chromatography using a Porapak N separation column at 373 K.

2.4. Catalytic tests

Reaction of heptane was carried out at 498–623 K, typically at 523 K under atmospheric pressure in a conventional fixed bed flow reactor equipped with a sampling valve for gas chromatographic analysis. After H_2 reduction and cooling to reaction temperature in a stream of H_2, heptane was introduced onto the catalyst bed at partial pressure of 9211 Pa with H_2 as a complement to atmospheric pressure. Reaction of 2-propanol was carried out at 398 K and at a molar He/2-propanol ratio of 20. Reaction conditions of benzene hydrogenation were as follows: temperature, 423 K; H_2/benzene, 10. The composition of effluent gases was analyzed by FID gas chromatography using a TC-1 glass capillary separation column, and using a Porapak Q separation column.

3. Results and discussion

3.1. Surface area

Fig. 1 shows the surface area of H_2-reduced $Pt/MoO_3(H_2)$ as a function of reduction temperature. Here, Pt/MoO_3 was heated in a stream of H_2, and then was reduced for 12 h at each temperature. The parent Pt/MoO_3 had a surface area of about 5 m^2/g. H_2 reduction enlarged the surface area, depending on reduction temperature. $Pt/MoO_3(H_2)$ reduced at 373 and 473 K exhibited almost the same surface areas as the parent Pt/MoO_3. The surface area was markedly enlarged by reduction at temperatures above 523 K. $Pt/MoO_3(H_2)$ reduced at 673 K exhibited the largest surface area among the reduced samples. Reduction at 773 K lowered the surface area markedly.

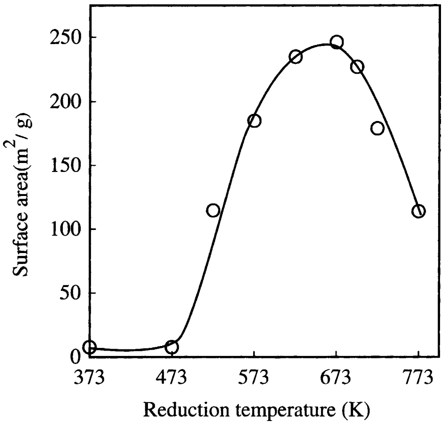

Fig. 1. Surface area of H_2-reduced $Pt/MoO_3(H_2)$ as a function of reduction temperature. Reduction period, 12 h.

The surface area of H_2-reduced $Pt/MoO_3(H_2)$ was dependent on reduction period as well as on reduction temperature. Fig. 2 shows the effect of reduction period on the surface area of H_2-reduced $Pt/MoO_3(H_2)$. $Pt/MoO_3(H_2)$ exhibited a surface area of about 180 m^2/g after reduction at 623 K for 1 h. The surface area increased slowly in proportion to the reduction period at 623 K, and reached a constant value of 240 m^2/g after reduction for 12 h. H_2 reduction at 723 K for 1–4 h changed the surface area little, while

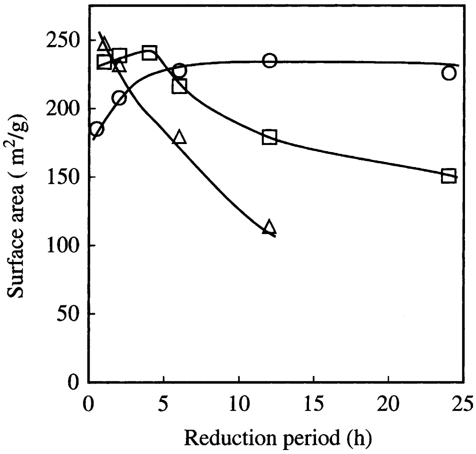

Fig. 2. Surface area of H_2-reduced $Pt/MoO_3(H_2)$ as a function of reduction period. Reduction temperature: 623 K (○), 723 K (□), 773 K (△).

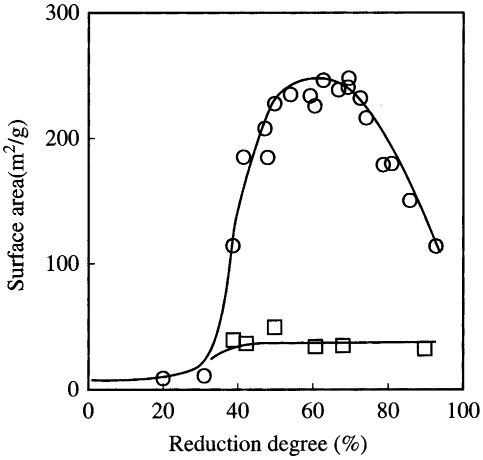

Fig. 3. Dependency of the surface area of H_2-reduced Pt/MoO_3 on the reduction degree. $Pt/MoO_3(H_2)$ (○), $Pt/MoO_3(N_2)$ (☐).

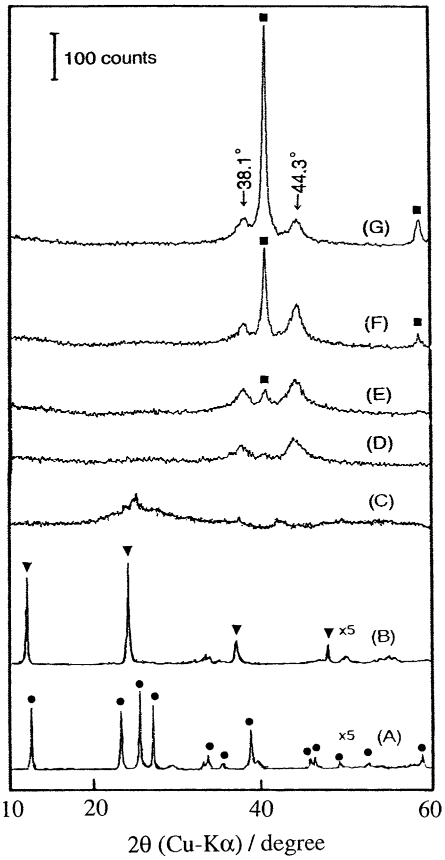

Fig. 4. XRD patterns of H_2-reduced $Pt/MoO_3(H_2)$. Reduction degree: (A) 0%; (B) 20%; (C) 32%; (D) 54%; (E) 70%; (F) 81%; (G) 93%. (●) MoO_3; (▼) $H_{1.64}MoO_3$; (■) Mo metal.

longer periods of reduction lowered the surface area. In contrast, the surface area of $Pt/MoO_3(H_2)$ reduced at 773 K decreased with increasing reduction period.

The extent of reduction depends on reduction conditions. Hence, the surface areas shown in Figs. 1 and 2 were represented as a function of the reduction degree. Typical results are displayed in Fig. 3, where reduction of MoO_3 to Mo metal is defined to be a reduction degree of 100%. A good relationship was obtained between the surface area and the reduction degree, suggesting that the variation in the surface area shown in Figs. 1 and 2 resulted from the change in the reduction degree. H_2 reduction did not induce an increase in the surface area up to reduction degrees of 20–30%. The surface area of $Pt/MoO_3(H_2)$ was drastically enlarged by further reduction. The surface area of $Pt/MoO_3(H_2)$ increased in proportion to the reduction degree, and reached a maximum value of 250 m^2/g at reduction degrees of 60–70%. Further reduction lowered the surface area.

Changes in the XRD patterns of $Pt/MoO_3(H_2)$ on H_2 reduction are illustrated in Fig. 4. $Pt/MoO_3(H_2)$ with a reduction degree of 20% gave diffraction lines at $2\theta = 12.6°$, 24.4°, 38.7° and 48.2°. These lines were assigned to the diffraction of the hydrogen molybdenum bronze phase, $H_{1.64}MoO_3$. $Pt/MoO_3(H_2)$ with a reduction degree of 32% gave no peak corresponding to the $H_{1.64}MoO_3$ phase, and was almost amorphous with respect to XRD. The surface areas of these $Pt/MoO_3(H_2)$ were 9 and 11 m^2/g, respectively, indicating that the formation of $H_{1.64}MoO_3$ and the amorphisation were not accompanied by an increase in the surface area. The XRD diagram of $Pt/MoO_3(H_2)$ with a reduction degree of 54% indicated the appearance of a new phase apart from the MoO_2 and Mo metal phases. Two peaks were observed at $2\theta = 38.1°$ and 44.3°. Further reduction promoted the formation of Mo metal, although the peaks at $2\theta = 38.1°$ and 44.3° were observed even at a reduction degree of 93%. In the reduction of $Pt/MoO_3(H_2)$, the formation of the MoO_2 phase was not detected by XRD at all.

Delporte et al. [12] reported that a treatment of MoO_3 with a mixture of H_2 and hydrocarbon (hexane or heptane) at 623 K yielded a mixture of MoO_2 and molybdenum oxycarbide, MoO_xC_y, where carbon atoms were substituted for some of oxygen atoms. This material had a surface area of about 150 m^2/g. They stated that hydrogen was able to act like carbon atom to form molybdenum oxyhydride, MoO_xH_y. Ledoux and co-workers [24] have recently showed that the pure MoO_xC_y phase was obtained by treating hydrogen molybdenum bronze, $H_{0.34}MoO_3$, which was prepared by introducing MoO_3 into an aqueous solution of HCl containing chips of Zn metal, with a flow of H_2/hydrocarbon. The pure MoO_xC_y was reported to provide the diffraction lines at $2\theta = 38.2°$ and 43.5°. We deduce on the basis of these reported results that the diffraction lines at $2\theta = 38.1°$ and 44.3° reflected the formation of a MoO_xH_y phase.

To study the reduction process of Pt/MoO_3, TPR was performed. Fig. 5 illustrates the profiles of H_2 consumption and of H_2O formation during TPR in a 20% H_2–80% Ar gas mixture. Pt/MoO_3 reacted with H_2 without an equivalent amount of water being generated at room temperature, indicating the formation of the H_xMoO_3 phase. This phenomenon can be understood by hydrogen spillover. H_2O was formed with consuming H_2 in temperatures of 448–598 K. Since the amounts of H_2O formed is greater than those of H_2 consumed, the H_xMoO_3 phase is likely to decompose in this temperature region. No appreciable difference appeared between the amounts of H_2O formed and those of H_2 consumed at temperatures above 598 K. These results are consistent with the results of XRD (Fig. 4): Pt/MoO_3(H_2) was reduced through the formation of the H_xMoO_3 phase.

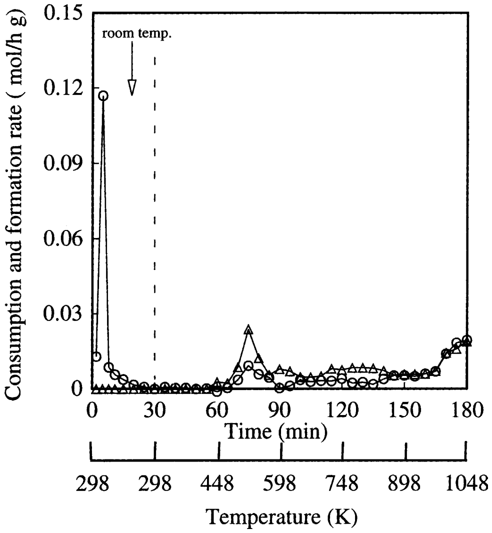

Fig. 5. TPR spectra of Pt/MoO_3. Pt/MoO_3, 0.4 g; 20% H_2–80% Ar, 100 ml/min; H_2 (○), H_2O (△).

We reported that the surface area of MoO_3 reduced at 623 K were much greater than that of MoO_3 reduced at 673 K even when the reduction degree was comparable [15]. XRD studies showed that reduction of MoO_3 at 623 K proceeded via the formation of the H_xMoO_3 phase, while MoO_3 was directly reduced to MoO_2 at 673 K. We have suggested from these results that the surface area can be enlarged when MoO_3 is reduced through the formation of the H_xMoO_3 phase. It is considered from the result of TPR that Pt/MoO_3 can be reduced without the formation of the H_xMoO_3 phase when Pt/MoO_3 is heated in a stream of N_2, and then is reduced at temperature above 598 K. Hence, H_2 reduction of Pt/MoO_3 was carried out at 673–773 K after heating in a stream of N_2. These samples are denoted as Pt/MoO_3(N_2). As shown in Fig. 3, the surface area of Pt/MoO_3(N_2) changed little by H_2 reduction, and was independent of the reduction degree. H_2-reduced Pt/MoO_3(N_2) exhibited a much smaller surface area than H_2-reduced Pt/MoO_3(H_2). XRD studies showed that Pt/MoO_3(N_2) was reduced to MoO_2 and to Mo metal without the formation of the H_xMoO_3 phase. Furthermore, the formation of the MoO_xH_y phase was not detected in H_2-reduced Pt/MoO_3(N_2). We conclude from these results that the H_xMoO_3 phase can play an important role to enlarge the surface area. The formation of MoO_xH_y phase, which can be derived presumably from the H_xMoO_3 phase, seems to cause the enlargement of surface area.

3.2. Reaction of heptane

Conversion of heptane was carried out at 523 K under atmospheric pressure using H_2-reduced Pt/MoO_3 as a catalyst. The isomerization activity was determined using data at the heptane conversion level below 10%. The conversion level was adjusted by changing the flow rate of reactant gas and/or the weight of catalyst. The catalytic activity of H_2-reduced Pt/MoO_3 for the conversion of heptane declined with time on stream. No appreciable difference appeared in catalyst deactivation when the reduction degree was below 70%. Further reduction promoted catalyst deactivation. Hence, the isomerization activity and selectivity

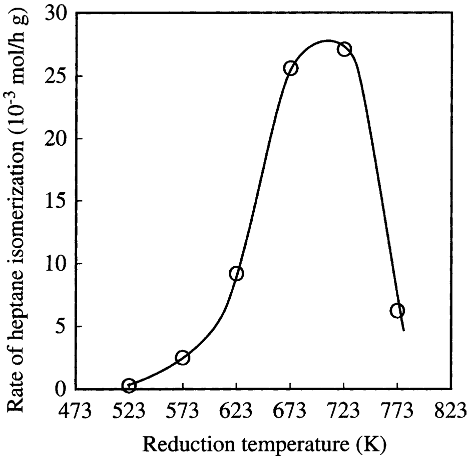

Fig. 6. Catalytic activity of H_2-reduced Pt/MoO_3(H_2) for heptane isomerization as a function of reduction temperature. Reduction period, 12 h. Reaction conditions: temperature, 523 K; H_2/heptane, 10.

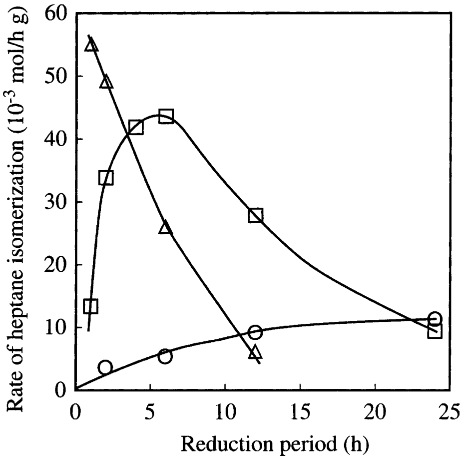

Fig. 7. Catalytic activity of H_2-reduced Pt/MoO_3(H_2) for heptane isomerization as a function of reduction period. Reaction conditions: see Fig. 6. Reduction temperature: 623 K (○), 723 K (□), 773 K (△).

were estimated using data after a 1 h run to minimize the effect of catalyst deactivation. Fig. 6 shows the isomerization activity of H_2-reduced Pt/MoO_3(H_2) as a function of reduction temperature. Here, Pt/MoO_3 was heated in a stream of H_2, and then was reduced for 12 h at each temperature. Pt/MoO_3(H_2) reduced at 523 K was almost inactive for the isomerization of heptane. Pt/MoO_3(H_2) became an active catalyst after reduction at 573 K. The isomerization activity was raised with reduction temperature, and reached a maximum value at 723 K. Reduction at 773 K lowered the isomerization activity markedly.

The isomerization activity of H_2-reduced Pt/MoO_3 (H_2) was affected not only by reduction temperature but also by reduction period. Fig. 7 shows the effect of reduction period on the isomerization activity of Pt/MoO_3(H_2), which was reduced after heating in H_2. The isomerization activity increased slowly in keeping with the reduction period at 623 K. When reduced at 723 K, the isomerization activity passed through a maximum with the reduction period. In contrast, the isomerization activity of Pt/MoO_3 reduced at 773 K decreased markedly with increasing reduction period.

The extent of reduction depends on reduction conditions. Hence, the isomerization activities shown in Figs. 6 and 7 were represented as a function of the reduction degree. Fig. 8 displays the relationship between the isomerization activity and the reduction degree. The isomerization activity was evaluated by taking the surface area into consideration, because the surface area was markedly varied with the extent of reduction. There was a good relationship between the isomerization activity and the reduction degree. This implies that the variation in the isomerization activity shown in Figs. 6 and 7 was caused by the change in the reduction degree. H_2-reduced Pt/MoO_3(H_2) with

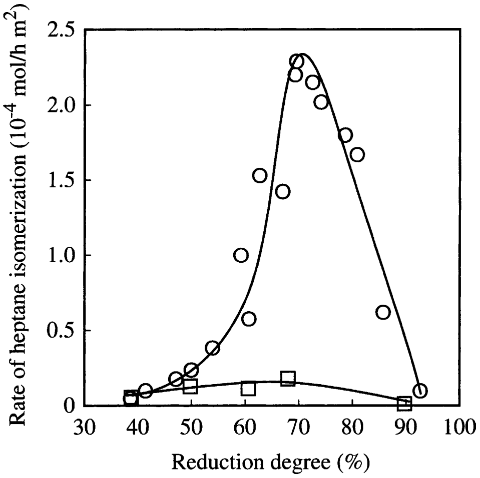

Fig. 8. Dependency of the heptane isomerization activity of H_2-reduced Pt/MoO_3 on the reduction degree: Pt/MoO_3(H_2) (○), Pt/MoO_3(N_2) (□).

a reduction degree of 40% was almost inactive for heptane isomerization. The isomerization activity was improved by an increase in the extent of reduction, and the highest isomerization activity appeared at a reduction degree of about 70%. The dependency of the isomerization activity on the reduction degree was analogous to that of the surface area, although the isomerization activity was estimated by taking the surface area into consideration. H_2-reduced $Pt/MoO_3(H_2)$ with a reduction degree of 40% had a surface area of 130 m^2/g, but its isomerization activity was markedly low. These results indicate that the enlargement of the surface area gave little effect on the isomerization activity. The improved isomerization activity is likely to result from change in the chemical nature of surface.

Product distributions in the conversion of heptane are demonstrated in Table 1, where the conversion level was adjusted to be about 40%. Under the reaction conditions employed, heptane was selectively isomerized with a minor contribution of cracking. The isomerization selectivity changed little when the reduction degree was below about 80%. $Pt/MoO_3(H_2)$ with a reduction degree of 92% exhibited a slightly low isomerization selectivity compared with other catalysts. The extent of reduction had no effect on the distribution of isomerization products. Heptane was mainly isomerized to 2- and 3-methylhexanes (MHs) in equal amounts. By contrast, the distribution of cracking products varied with the reduction degree. On $Pt/MoO_3(H_2)$ with a reduction degree of 54%, heptane was cracked to C_1–C_6 hydrocarbons. At a reduction degree of 70%, C_3 and C_4 hydrocarbons were mainly formed as the cracking products. The selectivity for C_3 and C_4 hydrocarbons was lowered by further reduction. $Pt/MoO_3(H_2)$ with a reduction degree of 93% provided similar cracking products to $Pt/MoO_3(H_2)$ with a reduction degree of 54%.

Variations in the isomerization products and in the isomerization selectivity with the conversion levels are shown in Fig. 9. Here, H_2-reduced $Pt/MoO_3(H_2)$ with a reduction degree of 70% was used because this catalyst was most active for heptane isomerization. The yield of MHs increased in proportion to the conversion level, and reached a maximum value of about 50% at a conversion level of 80%. The formation of dimethylpentanes (DMPs) was enhanced at the conversion level above 50%. Trimethylbutane (TMB) was formed at the high conversion levels. H_2-reduced $Pt/MoO_3(H_2)$ exhibited an isomerization selectivity of 95% when the conversion level was below 60%. The isomerization selectivity decreased to 82% with an

Table 1
Product distributions in the conversion of heptane on H_2-reduced $Pt/MoO_3(H_2)$

	Reduction degree/%			
	54	70	81	93
% Conversion	42.5	50.1	46.2	39.5
Selectivity/mol%				
Isomerization	96.8	95.2	95.2	91.6
Cracking	2.2	3.8	4.3	7.2
Distribution/mol%				
Isomerization products				
2-Methylhexane	39.4	37.1	37.5	34.1
3-Methylhexane	44.0	38.2	39.5	38.2
DMPs	14.8	20.0	18.3	21.3
Others	1.9	4.8	4.7	6.4
Cracking products				
C_1	15.5	2.7	8.6	15.2
C_2	11.7	1.2	3.7	8.0
C_3	28.0	46.1	39.1	29.3
C_4	29.9	46.6	40.3	30.9
C_5	8.4	1.6	3.4	6.4
C_6	6.6	1.8	4.9	10.3

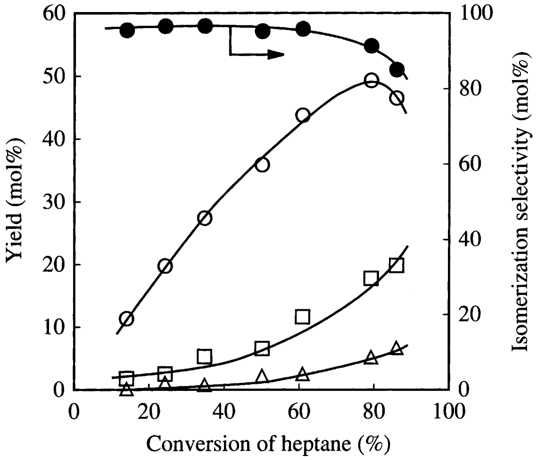

Fig. 9. Variation in the distribution of isomerization products and the isomerization selectivity with the conversion level. Selectivity (●) MHs (○), DMPs (□), TMB (△). Catalyst: H_2-reduced $Pt/MoO_3(H_2)$ with a reduction degree of 70%. Reaction conditions: see in Fig. 6.

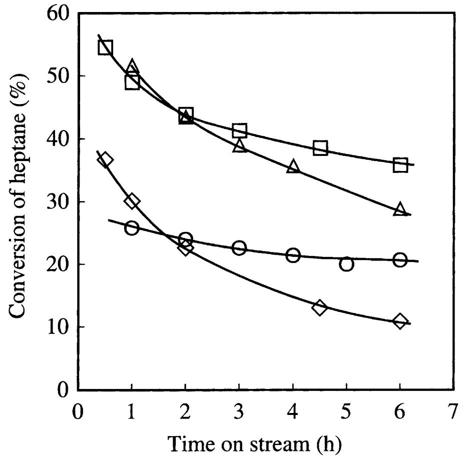

Fig. 10. Effect of reaction temperature on the catalytic activity of H_2-reduced Pt/MoO_3(H_2) for the conversion of heptane. Catalyst: H_2-reduced Pt/MoO_3(H_2) with a reduction degree of 70%. Reaction temperature: 523 K (○), 548 K (□), 573 K (△), 623 K (◇). Conditions: W/F, 5 g_{cat}/h mol; H_2/heptane, 10.

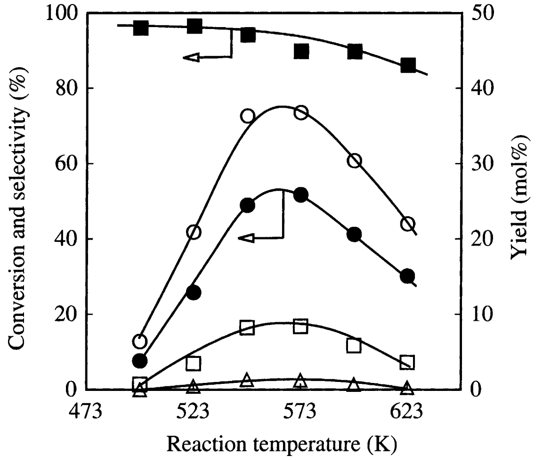

Fig. 11. Effect of reaction temperature on the isomerization selectivity of H_2-reduced Pt/MoO_3(H_2) for the conversion of heptane. Catalyst: H_2-reduced Pt/MoO_3(H_2) with a reduction degree of 70%. Conditions: W/F, 5 g_{cat}/h mol; H_2/heptane, 10. Conversion (●), isomerization selectivity (■), MHs (○), DMPs (□), TMB (△). Data taken after a 1 h run.

increase in the conversion level to 85%. H_2-reduced Pt/MoO_3(H_2) retained high isomerization selectivity even at high conversion levels.

Fig. 10 shows the effect of reaction temperature on the catalytic activity of H_2-reduced Pt/MoO_3(H_2) with a reduction degree of 70% for the conversion of heptane. The catalytic activity declined slightly with time on stream at 523 K. Catalyst deactivation was promoted by an increase in reaction temperature, although the conversion level in the initial stage of run was raised. The catalytic activity of H_2-reduced Pt/MoO_3(H_2) at 623 K was low compared with that at 573 K, probably due to promotion of catalyst deactivation. As shown in Fig. 11, the yields of the isomerization products increased in proportion to reaction temperature, and the maximum yields were obtained at 573 K. At temperatures above 573 K, the yields of the isomerization products were lowered. The isomerization selectivity decreased with increasing reaction temperature. H_2-reduced Pt/MoO_3(H_2), however, exhibited an isomerization selectivity of about 85% at 623 K. These results indicate that H_2-reduced Pt/MoO_3(H_2) catalyzed the cracking reactions of heptane and the corresponding branched isomers very little even at high reaction temperatures. H_2-reduced Pt/MoO_3(H_2) was a selective catalyst for heptane isomerization.

3.3. Reactions of 2-propanol and benzene

Isomerization reaction of alkane is usually catalyzed by bifunctional catalyst with acid functions balanced by metal functions. To study the bifunctional property of H_2-reduced Pt/MoO_3(H_2), reaction of 2-propanol was carried out at 398 K. In this study, the conversion level of 2-propanol was adjusted to be below 10% by varying the flow rate of reactant gas and/or the weight of catalyst. We reported in the previous papers [16,17] that the catalytic activity of H_2-reduced MoO_3 in the conversion of 2-propanol was not stable against deactivation. Hence, the catalytic activities were compared using data after a 0.5 h run to minimize the effect of catalyst deactivation.

Under the reaction conditions employed, 2-propanol was converted to propylene and diisopropylether (DIPE) by dehydration and to acetone by dehydrogenation. The catalytic activities of H_2-reduced Pt/MoO_3(H_2) as a function of the reduction degree are shown in Fig. 12, where the catalytic activities were evaluated by taking the surface area into consideration. H_2-reduced Pt/MoO_3(H_2) with a reduction degree of 40% was almost inactive for the dehydration. The formations of propylene and DIPE were promoted by an increase in the reduction degree. The highest

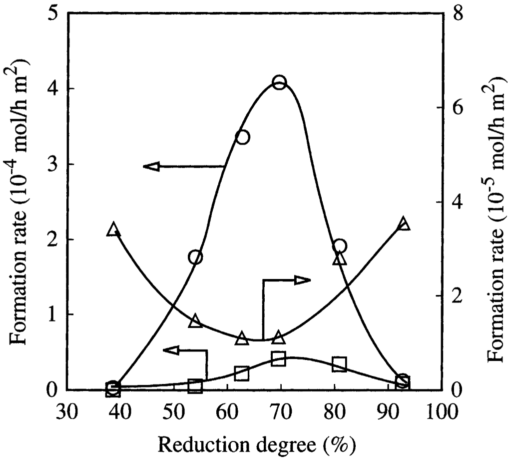

Fig. 12. Catalytic activity of H_2-reduced Pt/MoO_3(H_2) for the conversion of 2-propanol as a function of the reduction degree. Propylene (○), DIPE (□), acetone (△). Reaction conditions: temperature, 398 K; He/2-propanol, 20.

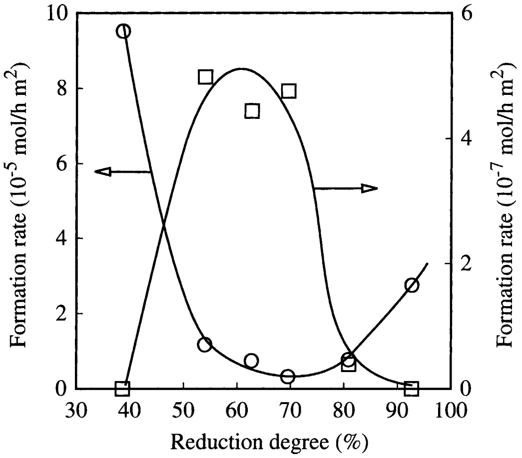

Fig. 13. Catalytic activity of H_2-reduced Pt/MoO_3(H_2) for the conversion of benzene as a function of the reduction degree. Cyclohexane (○), methylcyclopentane (□). Reaction conditions: temperature, 423 K; H_2/benzene, 10.

dehydration activity was obtained at a reduction degree of 70%. H_2-reduced Pt/MoO_3(H_2) yielded propylene much more selectively from 2-propanol than it yielded DIPE. The catalytic activity of H_2-reduced Pt/MoO_3(H_2) for the dehydrogenation of 2-propanol was lowered by H_2 reduction up to reduction degrees of 60–70%, and then was improved by further reduction. The dehydration activity of H_2-reduced Pt/MoO_3(H_2) was much higher than the dehydrogenation activity.

There is a possibility that the catalytic activity of H_2-reduced Pt/MoO_3(H_2) for 2-propanol dehydrogenation is affected by H_2O formed by the dehydration of 2-propanol. Indeed, Hall and co-workers [25] pointed out that the hydrogenation reaction of propylene on H_2-reduced MoO_3/Al_2O_3 was poisoned with H_2O. Hence, reaction of benzene hydrogenation was performed at 423 K to study the metal function of H_2-reduced Pt/MoO_3(H_2). Typical results are shown in Fig. 13, where data after a 0.5 h run were employed. The dependency of the rate of cyclohexane formation on the reduction degree was almost identical with that of the 2-propanol dehydrogenation activity. Hercules and co-workers [26,27] investigated the benzene hydrogenation activities of H_2-reduced MoO_3/TiO_2 and MoO_3/Al_2O_3 catalysts. They suggested from the results of systematic studies using the catalytic reaction in association with spectroscopic techniques that Mo metal and Mo^{2+} were the only active centers for benzene hydrogenation. In the case of H_2-reduced Pt/MoO_3(H_2) with low reduction degrees, Pt will be responsible for the dehydrogenation and the hydrogenation reactions. Reduction at high temperature, which leads to an increase in the extent of reduction, is likely to promote sintering of Pt, resulting in the low dehydrogenation and hydrogenation activities. On deeply reduced Pt/MoO_3(H_2), the dehydrogenation and the hydrogenation reactions may proceed mainly on Mo with low valence, such as Mo metal.

Ledoux and co-workers [12,13] have reported that the skeletal isomerization of alkane can proceed on molybdenum oxycarbide, MoO_xC_y via a metallocyclobutane bond-shift mechanism. In the conversion of heptane, C_1 and C_6 hydrocarbons are mainly formed as the cracking products on MoO_xC_y catalyst. The catalytic behavior of H_2-reduced Pt/MoO_3(H_2) observed in this study is different from that of MoO_xC_y. As shown in Table 1, H_2-reduced Pt/MoO_3(H_2), of which the reduction degree is 70%, provided C_3 and C_4 hydrocarbons as the major cracking products, and this catalyst was most active for heptane isomerization. The formation of C_1 and C_6 hydrocarbons was promoted on H_2-reduced Pt/MoO_3(H_2) with a lower isomerization activity. H_2-reduced Pt/MoO_3(H_2) catalyzed the dehydration and dehydrogenation of 2-propanol simultaneously. As shown in Fig. 13, benzene was hydroisomerized into methylcyclopentane on H_2-reduced $Pt/MoO_3(H_2)$ with reduction degrees of 50–80%. Both the metal function and the acid function are required to convert benzene into methylcyclopentane. The results obtained in the conversions of 2-propanol and benzene allow us to suggest that H_2-reduced $Pt/MoO_3(H_2)$ can catalyze the isomerization of heptane through the bifunctional mechanism, with dehydrogenation–hydrogenation steps on metallic sites and C–C bond rearrangement steps on acid sites. Since the dependency of the isomerization activity on the reduction degree is very similar to that of the dehydration activity, the ability of H_2-reduced $Pt/MoO_3(H_2)$ to act as an acid catalyst seems to control the isomerization activity. Keller et al. [28,29] have proposed the presence of dual sites on H_2-reduced $MoO_3/\alpha\text{-}Al_2O_3$. Coordinatively unsaturated sites, such as Mo^{4+} and Mo^{2+} will be responsible for dehydrogenation and hydrogenation reactions, and Brönsted acidity can originate from hydroxyl groups coordinated to Mo^{5+}. The results obtained in this study are somewhat different from the results of Keller et al. In the case of H_2-reduced $Pt/MoO_3(H_2)$, the highest dehydration activity appeared at a reduction degree of 70%. This implies that Mo species, of which the valence is smaller than 5, can contribute to generate the acid sites.

3.4. *Catalytic properties of H_2-reduced $Pt/MoO_3(N_2)$*

The catalytic properties of $Pt/MoO_3(N_2)$, which was reduced at temperatures above 673 K after heating in a stream of N_2, were compared with those of H_2-reduced $Pt/MoO_3(H_2)$. The catalytic activity was estimated by taking the surface area into consideration because the surface area of H_2-reduced Pt/MoO_3 was strongly affected by the heating atmosphere (Fig. 3). As shown in Fig. 8, the heptane isomerization activity of $Pt/MoO_3(N_2)$ changed little by H_2 reduction, and was independent of the reduction degree. Furthermore, H_2-reduced $Pt/MoO_3(N_2)$ was less active for heptane isomerization than H_2-reduced $Pt/MoO_3(H_2)$ even when their surface areas were taken into consideration. The isomerization selectivity of H_2-reduced $Pt/MoO_3(N_2)$ was low compared with that of H_2-reduced $Pt/MoO_3(H_2)$: H_2-reduced $Pt/MoO_3(N_2)$ with a reduction degree of 68% exhibited an isomerization selectivity of 87% at a conversion level of 5%. Since H_2 reduction after heating in H_2 provided a much more active and selective catalyst for heptane isomerization than that after heating in N_2, we deduce that reduction of the H_xMoO_3 phase can generate the active sites for heptane isomerization.

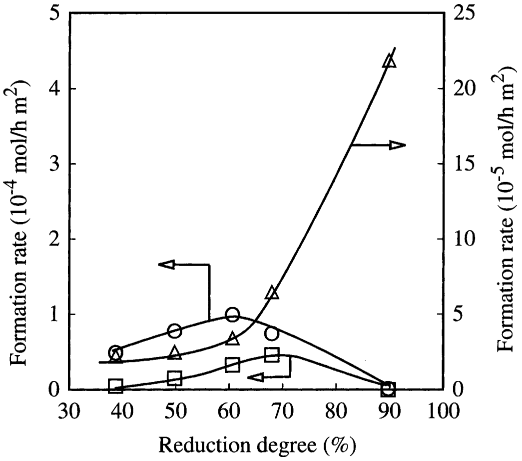

Fig. 14. Catalytic activity of H_2-reduced $Pt/MoO_3(N_2)$ for the conversion of 2-propanol as a function of the reduction degree. Propylene (○), DIPE (□), acetone (△). Reaction conditions: temperature, 398 K; He/2-propanol, 20.

Fig. 14 shows the results of the 2-propanol conversion on $Pt/MoO_3(N_2)$, which was reduced at temperatures above 673 K after heating in a stream of N_2. Here, the catalytic activities were evaluated by taking the surface area into consideration. The formations of propylene and DIPE on H_2-reduced $Pt/MoO_3(N_2)$ were slightly improved by an increase in the extent of reduction. The highest dehydration activity appeared at a reduction degree of 60–70%. This tendency is same as that observed in $Pt/MoO_3(H_2)$ which was reduced after heating in H_2. The formation rate of propylene on H_2-reduced $Pt/MoO_3(N_2)$, however, was markedly small compared with that on H_2-reduced $Pt/MoO_3(H_2)$. The dehydrogenation activity of H_2-reduced $Pt/MoO_3(N_2)$ depended on the reduction degree differently from that of H_2-reduced $Pt/MoO_3(H_2)$. The dehydrogenation activity of H_2-reduced $Pt/MoO_3(N_2)$ changed little in the reduction degrees of 40–60%, and a sharp upturn in the dehydrogenation activity appeared at a reduction degree above 60%. H_2-reduced $Pt/MoO_3(N_2)$ was more active for the dehydrogenation than H_2-reduced

$Pt/MoO_3(H_2)$. It is obvious from these results that the surface property of H_2-reduced Pt/MoO_3 was strongly affected by heating atmosphere, and that the low heptane isomerization of H_2-reduced $Pt/MoO_3(N_2)$ resulted from its low acidic property.

As mentioned above, $Pt/MoO_3(H_2)$ which was heated to reduction temperature under H_2 flow was reduced through the formation of the H_xMoO_3 phase. In contrast, the H_xMoO_3 phase was not formed when Pt/MoO_3 was reduced after heating under N_2 flow. H_2-reduced $Pt/MoO_3(H_2)$ with a reduction degree of 70% exhibited the highest dehydration activity, and this catalyst contained the MoO_xH_y phase. In contrast, $Pt/MoO_3(N_2)$ which was reduced after heating in N_2 consisted of MoO_2 and Mo metal. Thus, the acid sites seem to originate from the MoO_xH_y phase, which may be formed by reduction of the H_xMoO_3 phase. In general, the ability of OH groups to release protons is improved by an increase in the electronegativity of the surrounding atoms, due to inductive effect. Acidity of MoO_3/Al_2O_3 has been explained by the inductive effect [30]. Since the average Sanderson electronegativity of Al_2O_3 is 3.72, while that of MoO_3 is 3.89, hydroxyl groups on Al_2O_3 which near MoO_3 can be made more acidic by the inductive effect. When MoO_3 is reduced to MoO_2, of which the electronegativity is 3.53, MoO_2/Al_2O_3 becomes less acidic. Interaction of Mo^{n+}–OH and $Mo^{(n+1)+}$ in the MoO_xH_y phase is likely to generate the acid sites, which are responsible for both heptane isomerization and 2-propanol dehydration. We suggest that heptane isomerization on H_2-reduced $Pt/MoO_3(H_2)$ can proceed through the bifunctional mechanism, with dehydrogenation–hydrogenation steps on Pt and/or Mo metal sites and C–C bond rearrangement steps on the MoO_xH_y phase.

4. Conclusions

H_2 reduction of Pt/MoO_3 through the formation of hydrogen molybdenum bronze, H_xMoO_3 induced an increase in the surface area. The largest surface area of 250 m^2/g was obtained at reduction degrees of 60–70%. H_2-reduced Pt/MoO_3 with large surface areas was found to contain the molybdenum oxyhydride phase, MoO_xH_y. In contrast, the surface area changed little when Pt/MoO_3 was reduced to MoO_2 and Mo metal without the formation of H_xMoO_3. The catalytic activity of H_2-reduced Pt/MoO_3 for heptane isomerization increased in proportion to the extent of reduction, and reached a maximum at a reduction degree of about 70%. H_2-reduced Pt/MoO_3 was a highly selective catalyst for heptane isomerization when its reduction degree was below 80%. The dependency of the 2-propanol dehydration activity on the reduction degree was very similar to that of the isomerization activity. On the other hand, the opposite tendency was observed in the 2-propanol dehydrogenation and in the benzene hydrogenation. We suggest from these results that the isomerization activity of H_2-reduced Pt/MoO_3 can be controlled by the ability to act as an acid catalyst. H_2-reduced Pt/MoO_3 was almost inactive for heptane isomerization and for 2-propanol dehydration when Pt/MoO_3 was reduced without the formation of H_xMoO_3, suggesting that the acid sites can be generated by reduction of the H_xMoO_3 phase. The MoO_xH_y phase, which may be derived from the H_xMoO_3 phase, seems to play an important role to create the acid sites.

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