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Isomerization of heptane on molybdenum oxides treated with hydrogen

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Isomerization of heptane was carried out at 573 K under atmospheric pressure using molybdenum oxides as catalysts. MoO_3 was inactive for this reaction. H_2 reduction of MoO_3 at 623 K, however, enhanced the isomerization activity and selectivity, which became almost constant after the reduction for 24 h. The reduced MoO_3 exhibited a higher isomerization activity than a typical bifunctional catalyst, 0.5 wt% Pt/USY zeolite, while there was no appreciable difference in product distribution between these two catalysts. These results indicate that the reduced MoO_3 catalyzed the isomerization of heptane via a conventional bifunctional mechanism.

Keywords: molybdenum oxide, H_2 reduction, isomerization, heptane

1. Introduction

Since the early work of Boudart and Levy [1], several publications have illustrated the ability of metallic carbides to catalyze many chemical reactions, including hydrogenolysis, hydrogenation, dehydrogenation, isomerization, and hydrodenitrogenation. A large number of papers have emphasized an analogy between the catalytic behaviors of transition metal carbides and those of group VIII metals.

Mo_2C and WC with clean surface are active for the hydrogenolysis of alkane, and those activities are comparable to that of noble metals. The introduction of a controlled amount of oxygen on the surface of carbides, however, has deeply modified the selectivity for the isomerization of saturated hydrocarbons at the expense of the hydrogenolysis reaction. Iglesia and co-workers [2–5] have reported that WC modified by chemisorbed oxygen catalyzed heptane isomerization without cyclization and excessive hydrogenolysis. Similar results were shown by Ledoux et al. [6–8] over a high surface area Mo_2C oxidized at 623 K. Iglesia and co-workers proposed that isomerization reaction on the oxygen-modified WC proceeded via a conventional bifunctional mechanism, with dehydrogenation–hydrogenation steps on sites with a metallic character (WC_x) and isomerization steps on sites of acidic type (WO_x), whereas Ledoux groups suggested the formation of a new catalytically active phase, molybdenum oxicarbide (MoO_xC_y), and a bond-shift mechanism via a metallocyclobutane intermediate. Ledoux and co-workers also reported [9,10] that the treatment of MoO_3 with a mixture of H_2 and hydrocarbon at 623 K gave molybdenum oxicarbide phase, and this carbon-modified MoO_3 was active and selective for the isomerization of hexane and heptane. On the other hand, Katrib et al. [11] showed recently that the isomerization of 2-methylpentane was catalyzed by MoO_2.

The aim of the present work is to investigate the effect of H_2 reduction on the catalytic properties of molybdenum oxides for the conversion of heptane, and to compare the activity and selectivity with those of a typical bifunctional catalyst, Pt/USY zeolite.

2. Experimental

Heptane (Kanto Chemical Inc.) with a purity of 99.4% was dried using molecular sieve prior to use. The main organic impurities are methylcyclohexane, 3-methylhexane, and 3,3-dimethylpentane, which are subtracted from the effluent gas analysis before calculation. H_2 was purified at room temperature by passage through an oxygen trap.

MoO_3 used in this study was obtained by calcination of $H_2MoO_4 \cdot H_2O$ (Kanto Chemical Inc.) at 673 K for 3 h. Pt/USY with a 0.5 wt% Pt loading was prepared by conventional ion-exchange of ultra-stable Y zeolite (Tosoh Corp. $SiO_2/Al_2O_3 = 14.6$) in an aqueous solution of $[Pt(NH_3)_4]Cl_2$ at 333 K for 6 h. After filtration and washing with deionized water, the sample was dried at 383 K overnight, followed by calcination in flowing oxygen at 573 K for 3 h. The catalyst powder was made into pellets, crushed, and then sieved (250–500 μm) for charging into a reactor. The crystalline phases of the catalyst were determined by X-ray diffraction using Ni-filtered Cu Kα radiation.

Reaction was isothermally carried out at 573 K under atmospheric pressure in a conventional fixed-bed flow reactor equipped with a gas sampling valve for gas chromatographic analysis. A prescribed amount of catalyst (0.05–0.25 g) was packed at the central position of a reac-

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Table 1
Catalytic activity and selectivity of molybdenum oxides for the conversion of heptane [a]

Catalyst	MoO_3(0)	MoO_3(2)	MoO_3(6)	MoO_3(12)	MoO_3(24)	MoO_3(48)	MoO_3(2)	MoO_3(12)	Pt/USY
reduction temperature (K)	–	623	623	623	623	623	673	673	–
surface area ($m^2 g^{-1}$)	3.7	5.1	20.0	35.0	47.9	49.9	4.5	4.8	–
%conversion	0.1	3.4	29.2	40.1	46.1	44.4	0.9	1.6	27.6
selectivity (C-mol%)									
isomerization	–	89.0	91.6	94.3	94.5	95.4	88.4	90.1	94.2
cracking	–	10.5	7.4	4.5	4.1	3.6	11.1	9.3	3.4
cyclization	–	0.5	1.0	1.2	1.4	1.0	0.5	0.6	2.0
distribution (C-mol%)									
isomerization products									
2-MH	–	43.1	43.4	41.4	40.4	40.2	46.1	41.2	39.8
3-MH	–	39.0	40.2	41.6	42.1	42.5	39.8	47.6	46.0
DMP	–	16.3	14.7	15.0	15.3	15.0	12.5	10.6	12.2
others	–	1.1	1.7	2.0	2.2	2.3	1.6	0.6	2.0
cracking products									
C_1	–	4.3	1.9	1.8	2.0	2.3	0	6.4	2.2
C_2	–	4.8	3.0	2.6	2.7	2.8	0	8.9	4.9
C_3	–	35.6	34.6	34.5	33.5	33.0	44.4	15.6	29.0
C_4	–	44.0	46.5	49.0	49.4	47.7	55.6	30.2	45.3
C_5	–	6.4	7.0	5.8	5.8	7.4	0	17.6	10.8
C_6	–	5.0	6.1	6.3	6.5	7.2	0	21.3	8.1

[a] Reaction conditions: temperature, 573 K; H_2/heptane, 40; W/F, 12.5 g-cat h mol-C_7^{-1}. Data were taken after 1 h of run.

tor, and then was heated to 623 K, or 673 K at a rate of 5 K min^{-1} in a stream of H_2 and kept for several hours. The treated MoO_3 samples will be denoted by MoO_3(2), MoO_3(12), etc.. The values in parentheses represent the period of H_2 reduction. After cooling to reaction temperature in H_2 atmosphere, heptane was introduced onto the catalyst at the pressure of 2471 Pa with H_2 as complement to the atmospheric pressure. 0.5 wt% Pt/USY was reduced with H_2 at 773 K for 3 h prior to reaction. The composition of effluent gases was analyzed by means of FID gas chromatography using a TC-1 glass capillary separation column with temperature-programmed heating from 303 to 393 K, and a TCD gas chromatography using unibead 1S separation column at 373 K.

3. Results and discussion

The conversion of heptane was carried out at 573 K under atmospheric pressure using molybdenum oxides as catalysts. Typical results are demonstrated in table 1, where data taken after 1 h of run are shown. The parent MoO_3 was completely inactive both for isomerization and for cracking of heptane. H_2 reduction of MoO_3 at 623 K, however, enhanced the catalytic activity, which became almost constant after the reduction for 24 h. The selectivity for isomerization increased slightly with increasing period of H_2 reduction. Usually isomerization of alkane proceeds on a bifunctional catalyst consisting of a highly dispersed Pt metal supported on an acidic oxide. It has been shown [12] that isomerization of heptane was selectively catalyzed by large-pore bifunctional zeolites with high SiO_2/Al_2O_3 ratios such as Pt/β and Pt/USY zeolites. Hence, the catalytic properties of molybdenum oxides are compared with that of 0.5 wt% Pt/USY. As shown in table 1, MoO_3 reduced for 12 h and longer were active for this reaction compared with 0.5 wt% Pt/USY, while there was no appreciable difference in the isomerization selectivity among these catalysts.

Figure 1 shows the variation in activity and isomerization selectivity of MoO_3(24) catalyst with time on stream. The catalytic activity of MoO_3(24) decreased with time on stream, while the selectivity did not change at all. There was no appreciable difference in the degree of catalyst deactivation when MoO_3 was reduced for 6 h and longer. On the other hand, the catalytic activity and

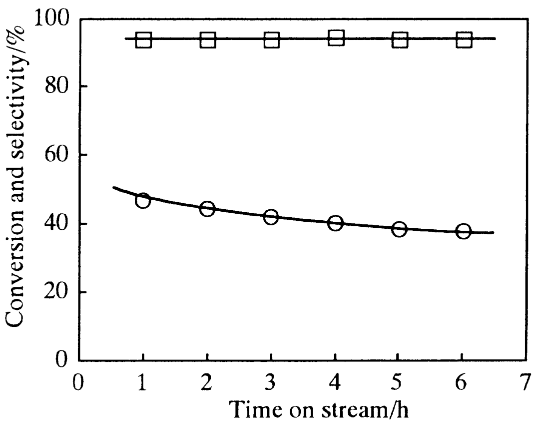

Figure 1. Variation in %conversion of heptane (○) and isomerization selectivity (□) on MoO_3(24) reduced at 623 K with time on stream. Reaction conditions: temperature, 573 K; W/F, 12.5 g-cat h mol^{-1}; H_2/C_7, 40.

isomerization selectivity of the parent MoO_3 and $MoO_3(2)$ increased slowly with time on stream, probably due to the reduction of MoO_3 during reaction. As shown in figure 2, 0.5 wt% Pt/USY catalyst exhibited a stable isomerization activity against deactivation. The reduced MoO_3 had a disadvantage of catalyst deactivation over Pt/USY. Ledoux and co-workers [6–9] reported that the oxygen-modified Mo_2C and MoO_3 showed a long induction period in the isomerization of heptane at 623 K and they suggested the formation of a new catalytically active phase, molybdenum oxicarbide where carbon atoms fill oxygen vacancies, in the course of the reaction. The formation of this active phase was reported to be accompanied by an increase in the isomerization selectivity and a shift of major cracking products from $C_3 + C_4$ to $C_1 + C_6$. As shown in table 1, the reduced MoO_3 provided similar cracking products to 0.5 wt% Pt/USY. The major cracking products are $C_3 + C_4$. It is obvious from these results that the reduced MoO_3 exhibited different catalytic behaviors in the isomerization of heptane from the catalysts reported by Ledoux et al.

Figure 3 shows the XRD patterns of molybdenum oxides. H_2 reduction of MoO_3 at 623 K led to the formation of MoO_2. However, it took a long time to achieve the complete transformation of MoO_3 to MoO_2. $MoO_3(24)$ consisted of both MoO_2 and MoO_3 phases, although the amount of MoO_3 phase was small. $MoO_3(48)$ provided only MoO_2 phase. Katrib and co-workers [11] showed that the isomerization of 2-methylpentane proceeded both on MoO_3 reduced with H_2 and on MoO_2. Since the formation of molybdenum oxicarbide such as MoO_xC_y was not detected by the XPS measurements, they suggested that the active species for isomerization of alkanes is the MoO_2 phase. The results obtained in this study support their suggestion because the reduced MoO_3 is active and selective for the isomerization of heptane.

As shown in table 1, the reduction of MoO_3 to MoO_2 by H_2 at 623 K was accompanied by an increase in specific surface area. A similar trend was already reported by Volpe and Boudart in temperature-programmed reaction of MoO_3 with a mixture of H_2 and NH_3 [13], by Yamada et al. in carburization under a H_2 and CH_4 mixture [14], and by Delporte et al. in reduction by H_2 [10]. This phenomenon has been explained as follows [15]: the reduction of MoO_3 begins preferentially at the shared plains, which are crystallographic defects created by the aggregation of oxygen vacancies to form planes of

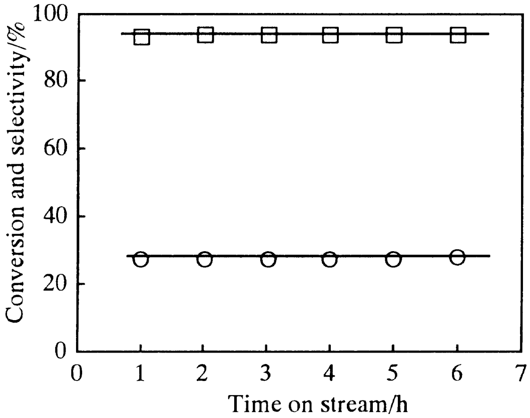

Figure 2. Variation in %conversion of heptane (○) and isomerization selectivity (□) on 0.5 wt% Pt/USY catalyst with time on stream. Reaction conditions: see figure 1.

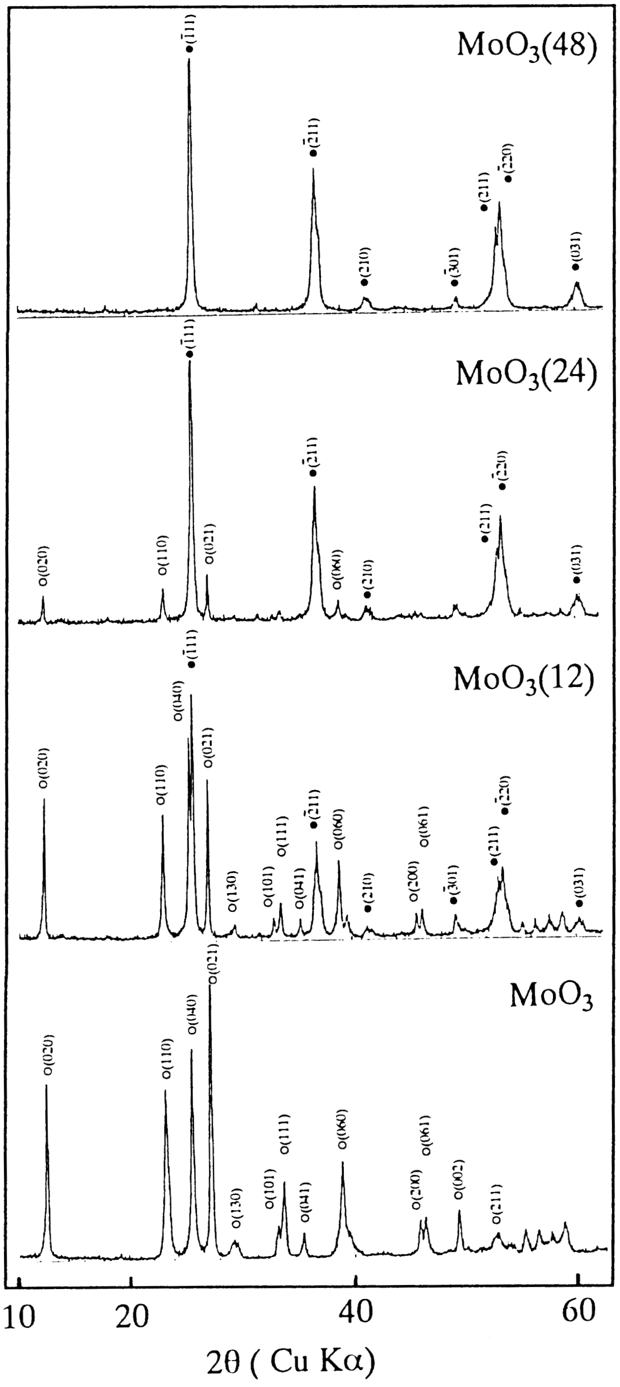

Figure 3. XRD patterns of MoO_3 reduced by H_2 at 623 K. (○) MoO_3 phase; (●) MoO_2 phase.

molybdenum bound to a tetrahedron of oxygen atoms instead of the octahedrally bound molybdenum of bulk MoO_3. As reduction proceeds in these planes, the metal lattice contracts and fractures the crystal to generate a large surface area.

To study the effect of surface area, the catalytic activity was compared by taking surface area into consideration. Results are demonstrated in figure 4, where data taken after 1 h run are shown. Here, the rate of isomerization (denoted by r_{iso}) was determined using data at the conversion level below 10%. The value in the units of mol h^{-1} m^{-2} account for sample surface area. The r_{iso} per surface area increased with increasing reduction time, and reached maximum after reduction for 6 h. This result suggests that the partially reduced MoO_3, namely MoO_x ($2 < x < 3$), was more active than MoO_2.

MoO_3 was more easily reduced to MoO_2 at 673 K. The XRD measurements indicated that MoO_3 was completely converted to MoO_2 by H_2 reduction for 12 h at this temperature. As shown in table 1, however, the catalytic activity of MoO_3 reduced at 673 K was markedly low, irrespectively of the reduction time. No appreciable change was observed in its surface area. The r_{iso} on $MoO_3(2)$ and $MoO_3(12)$ reduced at 673 K were determined to be 1.41×10^{-4} and 2.39×10^{-4} mol h^{-1} m^{-2}, respectively. These values are significantly low compared with those on MoO_3 reduced at 623 K. Distribution of cracking products on $MoO_3(12)$ reduced at 673 K was different from those on MoO_3 reduced at 623 K. It is obvious from these results that the catalytic activity of MoO_3 was strongly affected by the reduction temperature. The surface composition seems to play an important role to generate the active sites for the isomerization of heptane, although we have no information concerning the surface states at present. In further studies, we will show the relation between the isomerization activity and the surface composition of MoO_3 in detail.

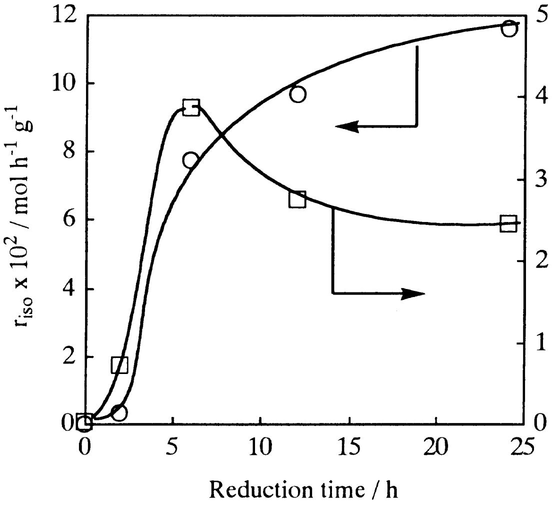

Figure 4. Effect of reduction time on the isomerization activity of MoO_3 reduced at 623 K.

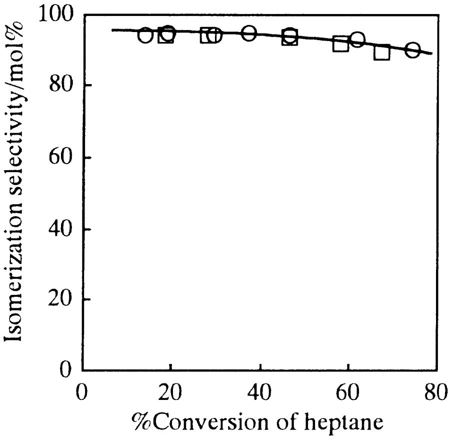

Figure 5. Relationship between the isomerization selectivity and the conversion level on $MoO_3(24)$ reduced at 623 K (○) and 0.5 wt% Pt/USY (□) catalysts.

Figure 5 shows the variation in isomerization selectivity with the conversion level of heptane. There was no appreciable difference in the isomerization selectivity between $MoO_3(24)$ reduced at 623 K and 0.5 wt% Pt/USY catalysts. The isomerization selectivity decreased slightly with increasing conversion level, but the high selectivity was preserved even at high conversion level on both catalysts. Figures 6 and 7 indicate the distribution of isomerization products on $MoO_3(24)$ reduced at 623 K and Pt/USY as a function of the conversion level. These two catalysts provided almost the same products distribution. At low conversion levels, heptane was isomerized to 2- and 3-methylhexanes in equal amount. With increasing conversion level, dimethylpentanes were formed at the expense of methylhexanes. We suggest from these results that isomerization of heptane on MoO_3 reduced at 623 K proceeded via the conventional bifunctional mechanism, with dehydrogenation–hydrogenation steps on sites with a metallic character and isomerization step on sites of acidic type.

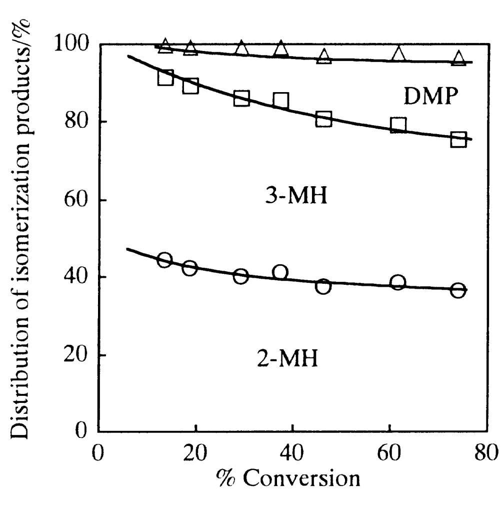

Figure 6. Variation in distribution of isomerization products as a function of the conversion level on $MoO_3(24)$ reduced at 623 K.

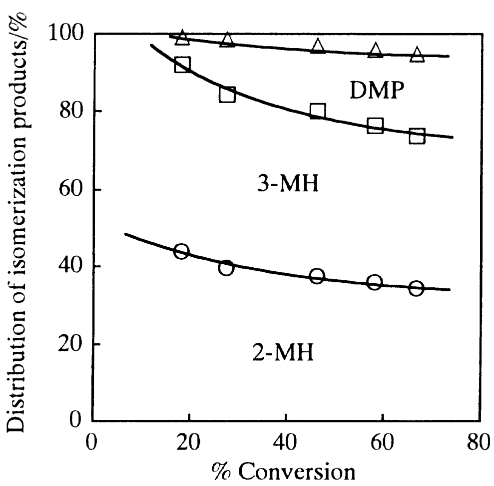

Figure 7. Variation in distribution of isomerization products as a function of the conversion level on 0.5 wt% Pt/USY catalyst.

4. Conclusion

The isomerization activity of MoO_3 at 573 K was enhanced by an increase in the period of H_2 reduction at 623 K, and became almost constant after 24 h reduction. The reduction of MoO_3 to MoO_2, which was accompanied by an increase in the surface area, was a slow process at 623 K, and MoO_3 was completely converted to MoO_2 after 48 h reduction. The reduced MoO_3 catalysts exhibited higher isomerization activity than 0.5 wt% Pt/USY zeolite, although the isomerization activity of the reduced MoO_3 catalysts became deactivated with time on stream. The activity of reduced MoO_3 catalyst was strongly affected by the reduction temperature. MoO_3 reduced at 623 K was more active than MoO_3 reduced at 673 K. The MoO_3 reduced at 623 K provided almost similar isomerization selectivity and products distribution to 0.5 wt% Pt/USY. We deduce from these results that MoO_3 reduced at 623 K was active and selective for heptane isomerization, and it had both sites with metallic character and sites of acidic nature.

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