Catalytic Properties of Ni-MoO_3 for the Isomerization of Heptane

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The catalytic properties of Ni-MoO_3 for the isomerization of heptane were investigated. After treatment with a mixture of H_2 and heptane, Ni-MoO_3 catalysts became active and selective for this reaction. The isomerization activity increased with increasing amount of Ni loading onto MoO_3, indicating that Ni was an effective additive to enhance the catalytic performances of MoO_3 for the isomerization of heptane.

The use of transition metal carbides as catalysts has received a great deal of interest due to their similarity with noble metals in heterogeneous catalysis. Their effectiveness as catalysts was first demonstrated by the work of Muller and Gault.[1] Many catalytic reactions have been investigated on the carbides of Group IV-VI metals, including hydrogenolysis, hydrogenation, dehydrogenation, isomerization, and hydrodenitrogenation.

Iglesia et al.[2-5] and Ledoux et al.[6,7] showed that the oxygen modified WC and Mo_2C catalyzed heptane isomerization without cyclization and excessive hydrocracking. Iglesia and co-workers proposed from the results of kinetic, isotopic and deuterium-exchange measurements that isomerization reaction on this catalyst proceeded via the conventional bifunctional mechanism. On the other hand, Ledoux et al. proposed the formation of a new catalytically active phase, an oxicarbide consisting of a Mo_2C lattice where oxygen replaces some carbon atoms in the interstitial voids, and a bond-shift mechanism via a metallocyclobutane intermediate since the oxygen modified Mo_2C exhibited different catalytic behavior from Pt/zeolite catalyst. They also reported[8,9] that treatment of MoO_3 with a mixture of hexane and H_2 provided molybdenum oxicarbide phase, and this carbon modified MoO_3 was active and selective for the isomerization of hexane and heptane.

We have studied the catalytic properties of MoO_3 for the isomerization of heptane, and have found that loading of Ni onto MoO_3 enhanced its catalytic activity. The main purpose of the present work is to investigate the catalytic properties of Ni-MoO_3 for the conversion of heptane.

MoO_3 used in this study was obtained by calcination of H_2MoO_4 (Kanto Chemical Inc.) at 673 K for 3 h. Ni-MoO_3 was prepared by impregnation of MoO_3 with an aqueous solution of $Ni(NO_3)_2$. Thus obtained Ni-MoO_3 was dried overnight at 393 K, and then calcined at 673 K for 3 h. The catalyst powder was made into pellets, crushed, and then sieved (250-500 μm) for charging into a reactor. Heptane(Kanto Chemical Inc.) was dried using molecular sieve. H_2 were purified by passage through an oxygen trap.

Reaction was isothermally carried out under atmospheric pressure in a conventional fixed bed flow reactor equipped with a gas sampling valve for gas chromatographic analysis. A catalyst was heated to 623 K at a rate of 5 $K{\cdot}min^{-1}$ in a stream of H_2 and kept for 2 h, followed by an introduction of heptane onto the catalyst at the pressure of 2471 Pa with H_2 as complement to the atmospheric pressure. The composition of effluent gases was analyzed by means of FID gas chromatography using TC-1 glass capillary separation column with temperature programmed heating from 303 to 393 K.

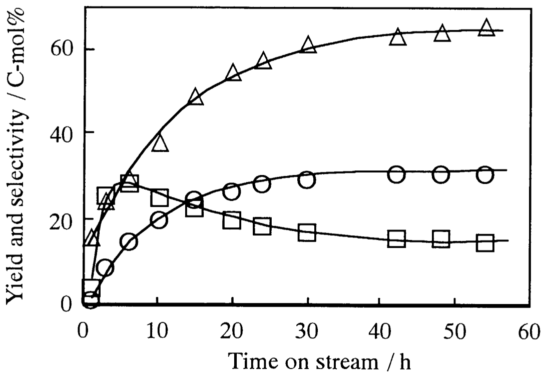

Figure 1. Variation in the catalytic activity of 1 mol%Ni-MoO_3 for the conversion of heptane. ○, yield of isomerization products; □, yield of cracking products; △, selectivity for isomerization. Temperature, 623 K; W/F, 300 cat-g h/C_7-mol; H_2/C_7 molar ratio, 40.

Figure 1 shows the catalytic activity of 1 mol%Ni-MoO_3 for the conversion of heptane at 623 K. At the initial stage of run, this catalyst exhibited no activity both for isomerization and hydrocracking reactions. The hydrocracking activity increased with time on stream, and then reached to maximum at about 6 h of run. The stable hydrocracking activity was obtained after about 42 h of run. This catalyst showed a longer induction period for isomerization than for hydrocracking. The isomerization activity and selectivity became stable after about 42 h of run. The cyclization of heptane to give methylcyclohexane and toluene was negligible over this catalyst.

Ledoux and co-workers reported[8] that the oxygen modified Mo_2C and MoO_3 showed an induction period in the isomerization of heptane. They suggested the formation of a new catalytically active phase, $Mo_xO_yC_z$, in the course of reaction. Delporte et al.[9] showed by XRD and XPS measurements that a part of MoO_3 was transformed to $Mo_xO_yC_z$ by treatment with a mixture of H_2 and hexane at 623 K. In this study, however, the formation of $Mo_xO_yC_z$ was hardly observed even after 54 h run, and only MoO_2 was detected by XRD measurement. This difference is not clear at present, and the surface analysis is required to clarify what proceeded during the induction period.

The induction period was observed in all of the catalysts used, and the stable isomerization activity and selectivity was obtained after about 42 h of run, independently of the amount of Ni loading. Hence, the catalytic properties of Ni-MoO_3 for the conversion of heptane were measured after the treatment with a mixture of H_2 and heptane at 623 K for 54 h. Figure 2 demonstrates the yields of isomerization products over Ni-MoO_3 catalysts as a function of reaction temperature. Here, the results

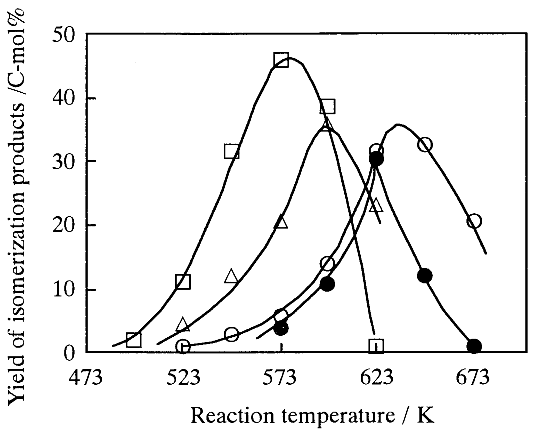

Figure 2. Effect of Ni loading on the isomerization activity of MoO_3 catalyst for the conversion of heptane. ○, 1 mol% Ni; △, 5 mol%Ni; □, 10 mol%Ni; ●, MoO_3; W/F, 300 cat-g h/C_7-mol; H_2/C_7 molar ratio, 40.

Table 1. Catalytic properties of Ni-MoO_3 for the conversion of heptane

Ni content/mol%	0	1	5	10
W/F cat-g h /C_7-mol	900	900	150	75
% Conversion	15.1	19.8	15.7	21.6
Selectivity/C-mol%				
Isomerization	80.3	76.2	76.4	79.6
Cracking	18.5	22.3	21.6	19.0
Cyclization	1.2	1.5	2.0	1.4
Distribution/C-mol%				
Isomerization products				
2-MH	40.5	40.3	40.0	41.1
3-MH	47.6	47.6	44.6	43.5
DMP	10.2	11.1	13.8	13.9
others	1.7	1.0	1.6	1.5
Cracking products				
C_1	2.0	16.8	24.3	25.5
C_2	3.6	6.0	3.2	3.5
C_3	32.3	11.7	9.0	10.6
C_4	41.8	16.2	13.5	15.6
C_5	6.9	15.9	13.8	13.5
C_6	13.4	33.4	36.2	31.3

Temperature, 573 K; H_2/C_7 molar ratio, 40.

on MoO_3 were also shown for comparison. The yields of isomerization products on 1 mol%, 5 mol%, and 10 mol%Ni-MoO_3 catalysts reached to maximum at 635 K, 598 K, and 573 K, respectively. Above these reaction temperatures, excessive hydrocracking occurred on Ni-MoO_3. MoO_3 catalyst gave the maximum isomerization yield at 623 K. This is caused by catalyst deactivation, not by excessive hydrocracking, because the level of heptane conversion as well as the isomerization yield dropped at higher reaction temperatures than 623 K. These results suggest that Ni loaded onto MoO_3 has an effect to suppress catalyst deactivation. This effect will be described elsewhere. When compared at lower temperatures than 598 K, the yield of isomerization products was enlarged by an increase in the amount of Ni loading, showing that the isomerization reaction on MoO_3 was promoted in the presence of Ni. 10 mol%Ni-MoO_3 catalysts provided the highest yield of hydrocracking products among the catalyst tested, irrespectively of reaction temperature.

Supported Ni catalysts are widely used for hydrocracking reaction, due to the high ability of Ni for C-C bond cleavage. Loading of Ni onto MoO_3 is considered to lower the isomerization selectivity. Hence, the selectivity of Ni-MoO_3 for isomerization and products distribution were compared at 573 K. Typical results are shown in Table 1. Here, the conversion level was adjusted to be about 20 % by controlling W/F. There was no appreciable difference in the isomerization selectivity and distribution of isomerization products among the catalysts tested. 2- and 3-methylhexanes were mainly produced by isomerization. 10 mol%Ni-MoO_3 gave a slightly high selectivity for dimethylpentanes compared with other catalysts.

Distribution of hydrocracking products was affected by the amount of Ni loading. The major hydrocracking products on the parent MoO_3 were C_3 and C_4, whereas C_1 and C_6 were mainly formed on Ni-MoO_3. The C_1 selectivity increased with increasing amount of Ni loading, at the expense of C_2-C_5 hydrocarbons. This behavior seems to reflect the catalytic nature of Ni. It is well known, however, that Ni has a large affinity for carbon and Ni catalysts deactivate easily due to coke formation in hydrocarbon reactions. In addition, the selectivity for isomerization was independent of the amount of Ni loading, as shown in Table 1. Therefore, we consider that the change in the carbon-number distribution is not attributed to the nature of Ni. Blekkan and co-workers[7] showed that the major products for hydrocracking were shifted from C_3+C_4 to C_1+C_6 in the course of the formation of a catalytically active phase, $Mo_xO_yC_z$. Thus, the formation of $Mo_xO_yC_z$ seems to be promoted in the presence of Ni, resulting in a high isomerization activity, although the formation of $Mo_xO_yC_z$ was not detected even on 10 mol%Ni-MoO_3 by XRD measurement.

It is to be noted that the catalytic activity of MoO_3 for the isomerization of heptane was enhanced without change in the isomerization selectivity by loading a large amount of Ni.

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