Effect of H_2 Flow Rate in Reduction Process on the Catalytic Properties of Reduced MoO_3

Takeshi Matsuda,* Yasuyoshi Hirata, Masaki Suzuki, Hirotoshi Sakagami, and Nobuo Takahashi
Department of Materials Science, Kitami Institute of Technology, 165 Koen-cho, Kitami, Hokkaido 090-8507

(Received May 21, 1999; CL-990413)

Catalytic activities of reduced MoO_3 for the conversions of heptane and 2-propanol were markedly enlarged by an increase in the flow rate of H_2 in reduction. The degree of reduction and the surface area were found to depend on the H_2 flow rate. These phenomena seem to be induced by action of H_2O produced by reduction.

Industrial isomerization processes to convert linear alkane to branched one are usually performed using the bifunctional catalyst consisting of an acidic oxide and a noble metal. Transition meal carbides modified with oxygen have been reported to catalyze alkane isomerization with high selectivity. Iglesia and co-workers[1] suggested that isomerization reaction of alkane on the oxygen modified WC proceeded via a conventional bifunctional mechanism, with dehydrogenation-hydrogenation steps on WC_x sites with metallic character and isomerization step on WO_x sites with acidic property. In heptane isomerization on the oxygen modified Mo_2C, Ledoux et al.[2] proposed the generation of a new catalytically active phase, molybdenum oxycarbide, and a bond shift mechanism via a metallocyclobutane intermediate.

Katrib and co-workers[3,4] showed recently by systematic studies using catalytic reactions in association with spectroscopic techniques that isomerization of alkane was catalyzed by MoO_2 phase. It was shown in our previous paper[5] that H_2 reduction of MoO_3 at 623 K enhanced the activity for heptane isomerization, and the reduced MoO_3 catalyst exhibited a higher isomerization activity than a Pt/USY zeolite. Since the reduced MoO_3 provided a similar product distribution to Pt/USY, we suggested that isomerization reaction on this catalyst proceeded via a conventional bifunctional mechanism. The reduced MoO_3 was also reported to catalyze the dehydration of 2-propanol.[6] We have found that the catalytic performance of reduced MoO_3 was markedly affected by the flow rate of H_2 in reduction. The main purpose of the present work is to describe the effect of H_2 flow rate in reduction process on the catalytic and physical properties of reduced MoO_3.

MoO_3 was obtained by calcination of $H_2MoO_4 \cdot H_2O$ (Kanto Chemicals) at 673 K for 3 h. Catalyst powder was made into pellets, crushed, and then sieved (30-60 mesh) prior to use. Heptane and 2-propanol were dried using a molecular sieve. H_2 was purified by passage through a molecular sieve and a Mn/SiO_2 oxygen trap. Reactions of heptane and 2-propanol were isothermally carried out at 523 K and 398 K, respectively, under atmospheric pressure in a conventional fixed bed flow reactor. A prescribed amount of MoO_3 was diluted with 0.5 g silicon carbide, and then was packed at the central position of a reactor, followed by H_2 treatment at 623 K for 12 h. After cooling to reaction temperature with H_2 still flowing, the reaction gas mixture of H_2/heptane=40 or H_2/2-propanol=20 was introduced onto catalyst. Concentration of the products in the effluent gas stream was analyzed by means of gas chromatography. The catalytic activity was determined using data at the conversion level below 10%. Specific surface area was calculated from a N_2 adsorption isotherm. The reduced sample was cooled to room temperature in H_2 atmosphere, and then evacuated for 0.5 h, followed by the measurement of N_2 adsorption at 77 K. After reduction procedure, the sample was completely reoxidized to MoO_3 at 773 K using a pulse technique to determine the average oxidation state of Mo.

Conversion of 2-propanol was performed at 398 K using the reduced MoO_3 as a catalyst. 2-Propanol was converted to propene, diisopropylether (DIPE), and acetone on the reduced MoO_3 under reaction condition employed. Hence, the activity for dehydration was evaluated using the rates of propene and DIPE formations, and the dehydrogenation activity was estimated by the rate of acetone formation. The catalytic activity of reduced MoO_3 declined slightly with time on stream. However, there was no appreciable difference in the degree of deactivation among the catalysts tested. Here, the data after 6 h run were adopted. Figure 1 shows the catalytic activity of reduced MoO_3 for the conversion of 2-propanol as a function of the flow rate of H_2 in reduction process. The dehydration activity of reduced MoO_3 was much higher than the dehydrogenation activity, irrespectively of the reduction condition. The reduced MoO_3 exhibited a different catalytic activity when reduction condition altered only in the weight of MoO_3. At the constant flow rate of H_2, the smaller mass yielded a catalyst with higher activity. As shown in Figure 1, this effect can be understood by taking the flow rate of H_2 based on the weight of MoO_3 into consideration. The catalytic activities for dehydration and dehydrogenation were enlarged by

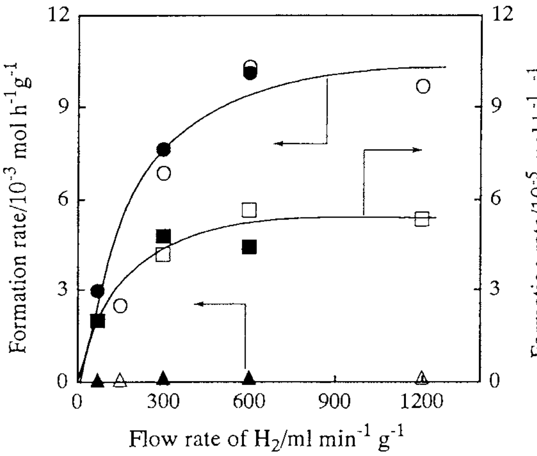

Figure 1. Effect of H_2 flow rate in reduction process on the catalytic activity of MoO_3 for the conversion of 2-propanol. ○ ●, propene; △ ▲, DIPE; □ ■, acetone. Weight of MoO_3, 0.1 g (open symbols); 0.2 g (solid symbols).

an increase in the flow rate of H_2 in reduction, and became almost constant at H_2 flow rate larger than 600 ml min^{-1} g^{-1}.

It was shown in our previous paper[5] that H_2 reduction of MoO_3 was accompanied by an increase in the surface area as well as change in the catalytic properties. Hence, the effect of H_2 flow rate on the surface area and the average oxidation state was studied. Typical results are demonstrated in Table 1, where the catalytic results for heptane isomerization are also indicated. A catalyst with higher isomerization activity was produced at larger flow rate of H_2. This is in analogy with the results obtained in the conversion of 2-propanol. Isomerization selectivity was slightly dependent on the flow rate of H_2. The catalytic results of 2-propanol and heptane conversions obviously indicate that bifunctional properties of reduced MoO_3 were affected by the flow rate of H_2.

The parent MoO_3 had a surface area of about 5 m^2 g^{-1}. H_2 reduction at 623 K for 12 h enlarged the surface area remarkably. Change in the surface area was induced when reduction condition differed only in the flow rate of H_2. Surface area increased with increasing H_2 flow rate and reached to a constant value of 180 m^2 g^{-1} at H_2 flow rate larger than 600 ml min^{-1} g^{-1}. As shown in Table 1, MoO_3 was more deeply reduced at the larger flow rate of H_2.

Table 1. Effect of H_2 flow rate in reduction process on the catalytic and physical properties of reduced MoO_3

H_2 flow rate /ml min^{-1} g^{-1}	r_{iso}[a] /mol h^{-1} g^{-1}	S_{iso}[b] /%	Surface area /m^2 g^{-1}	Oxidation state of Mo
75	1.33×10^{-3}	91	67	4.0
150	2.33×10^{-3}	95	142	3.5
300	3.39×10^{-3}	96	170	3.2
600	4.51×10^{-3}	98	180	3.1
1200	4.74×10^{-3}	97	185	2.9

[a]The rate of heptane isomerization. [b]Selectivity for heptane isomerization.

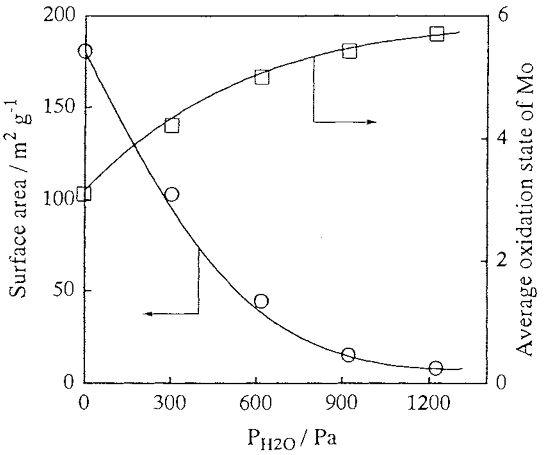

Figure 2. Surface area and average oxidation state of Mo as a function of partial pressure of H_2O. MoO_3 was reduced at 623 K for 12 h at H_2 flow rate of 600 ml min^{-1} g^{-1}

It was reported that Mo_2N with a larger surface area was produced at the higher space velocity of NH_3 by temperature-programmed reaction of MoO_3 and NH_3.[7,8] The concentration gradient of NH_3 in MoO_3 bed and the accumulation of H_2O produced by reaction were suggested to affect the surface area of resultant Mo_2N. Reduction of MoO_3 with gas mixture of 33% H_2 and 67% N_2 (H_2 flow rate=600 ml min^{-1} g^{-1}) yielded a product with surface area of 150 m^2 g^{-1}, indicating that the effect of H_2 gradient was small. In order to study the effect of H_2O, reduction of MoO_3 was performed in the presence of H_2O. Typical results are shown in Figure 2. Surface area was markedly lowered by an increase in the partial pressure of H_2O. H_2O is considered to promote sintering. The surface area of reduced MoO_3 changed from 180 to 150 m^2 g^{-1} by treatment with H_2O-N_2 gas mixture (P_{H_2O}=1227 Pa) at 623 K for 12 h. This indicates that a high surface can be retained even in the presence of H_2O. As shown in Figure 2, reduction of MoO_3 was suppressed in the presence of H_2O. There was a relationship between the surface area and the degree of reduction. We deduce from these results that the smaller flow rate of H_2 produces higher concentration of H_2O, leading to the formation of a product with the small surface area due to suppression of reduction.

Consequently, reduction of MoO_3 at larger flow rate of H_2 yielded a catalyst with larger surface area and with higher activities for the conversions of 2-propanol and heptane due to promotion of reduction.

This work was supported in part by a Grant-in-aid for Encouragement of Young Scientists from the Japanese Ministry of Education, Science, Sports and Culture.

References and Notes

1 E. Iglesia, F.H. Ribeiro, M. Boudart, and J.E. Baumgartner, *Catal. Today*, **15**, 307 (1992).
2 E.A. Blekkan, C.P. Huu, M.J. Ledoux, and J. Guille, *Ind. Eng. Chem. Res.*, **33**, 1657 (1994).
3 A. Katrib, P.Leflaive, L. Hilaire, and G. Maire, *Catal. Lett.*, **38**, 95 (1996).
4 A. Katrib, V. Logie, N. Saurel, P. Wehrer, L. Hilaire, and G. Maire, *Surface Sci.*, **337-379**, 754 (1997).
5 T. Matsuda, H. Shiro, H. Sakagami, and N. Takahashi, *Catal. Lett.*, **47**, 99 (1997).
6 T. Matsuda, Y. Hirata, H. Sakagami, and N. Takahashi, *Chem. Lett.*, **1997**, 1261.
7 S.T. Oyama, J.C. Schlatter, J.E. Metcalf, and J.M. Lamberg, *Ind. Eng. Chem. Res.*, **27**, 1639 (1988).
8 E.J. Markel and J.W. Van Zee, *J. Catal.*, **126**, 643 (1990).