

## Effect of H<sub>2</sub> Flow Rate in Reduction Process on the Catalytic Properties of Reduced MoO<sub>3</sub>

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Catalytic activities of reduced MoO<sub>3</sub> for the conversions of heptane and 2-propanol were markedly enlarged by an increase in the flow rate of H<sub>2</sub> in reduction. The degree of reduction and the surface area were found to depend on the H<sub>2</sub> flow rate. These phenomena seem to be induced by action of H<sub>2</sub>O produced by reduction.

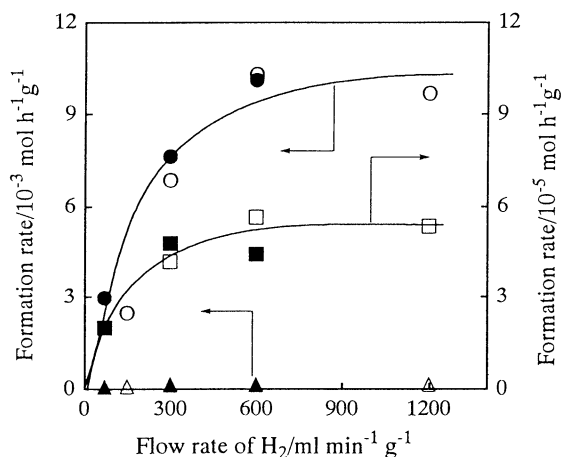
Industrial isomerization processes to convert linear alkane to branched one are usually performed using the bifunctional catalyst consisting of an acidic oxide and a noble metal. Transition metal carbides modified with oxygen have been reported to catalyze alkane isomerization with high selectivity.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

Katrib and co-workers<sup>3,4</sup> showed recently by systematic studies using catalytic reactions in association with spectroscopic techniques that isomerization of alkane was catalyzed by MoO<sub>2</sub> phase. It was shown in our previous paper<sup>5</sup> that H<sub>2</sub> reduction of MoO<sub>3</sub> at 623 K enhanced the activity for heptane isomerization, and the reduced MoO<sub>3</sub> catalyst exhibited a higher isomerization activity than a Pt/USY zeolite. Since the reduced MoO<sub>3</sub> 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<sub>3</sub> was also reported to catalyze the dehydration of 2-propanol.<sup>6</sup> We have found that the catalytic performance of reduced MoO<sub>3</sub> was markedly affected by the flow rate of H<sub>2</sub> in reduction. The main purpose of the present work is to describe the effect of H<sub>2</sub> flow rate in reduction process on the catalytic and physical properties of reduced MoO<sub>3</sub>.

MoO<sub>3</sub> was obtained by calcination of H<sub>2</sub>MoO<sub>4</sub>·H<sub>2</sub>O (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<sub>2</sub> was purified by passage through a molecular sieve and a Mn/SiO<sub>2</sub> 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<sub>3</sub> was diluted with 0.5 g silicon carbide, and then was packed at the central position of a reactor, followed by H<sub>2</sub> treatment at 623 K for 12 h. After cooling to reaction temperature with H<sub>2</sub> still flowing, the reaction gas mixture of H<sub>2</sub>/heptane=40 or H<sub>2</sub>/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<sub>2</sub> adsorption isotherm. The reduced sample was cooled to room temperature in H<sub>2</sub> atmosphere, and then evacuated for 0.5 h, followed by the measurement of N<sub>2</sub> adsorption at 77 K. After reduction procedure, the sample was completely reoxidized to MoO<sub>3</sub> 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<sub>3</sub> as a catalyst. 2-Propanol was converted to propene, diisopropylether (DIPE), and acetone on the reduced MoO<sub>3</sub> 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<sub>3</sub> 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



**Figure 1.** Effect of H<sub>2</sub> flow rate in reduction process on the catalytic activity of MoO<sub>3</sub> for the conversion of 2-propanol. ○ ●, propene; △ ▲, DIPE; □ ■, acetone. Weight of MoO<sub>3</sub>, 0.1 g (open symbols); 0.2 g (solid symbols).

reduced MoO<sub>3</sub> for the conversion of 2-propanol as a function of the flow rate of H<sub>2</sub> in reduction process. The dehydration activity of reduced MoO<sub>3</sub> was much higher than the dehydrogenation activity, irrespectively of the reduction condition. The reduced MoO<sub>3</sub> exhibited a different catalytic activity when reduction condition altered only in the weight of MoO<sub>3</sub>. At the constant flow rate of H<sub>2</sub>, 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<sub>2</sub> based on the weight of MoO<sub>3</sub> into consideration. The catalytic activities for dehydration and dehydrogenation were enlarged by

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

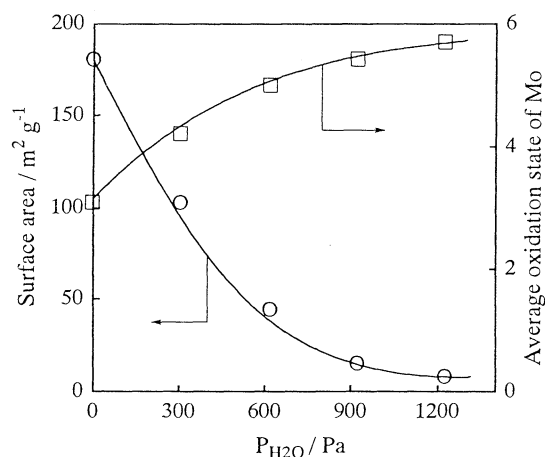
It was shown in our previous paper<sup>5</sup> that  $H_2$  reduction of  $MoO_3$  was accompanied by an increase in the surface area as well as change in the catalytic properties. Hence, the effect of  $H_2$  flow rate on the surface area and the average oxidation state was studied. Typical results 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  $5 \text{ m}^2 \text{ g}^{-1}$ .  $H_2$

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

<sup>a</sup>The rate of heptane isomerization. <sup>b</sup>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  $600 \text{ ml min}^{-1} \text{ g}^{-1}$

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  $180 \text{ m}^2 \text{ g}^{-1}$  at  $H_2$  flow rate larger than  $600 \text{ ml min}^{-1} \text{ g}^{-1}$ . As shown in Table 1,  $MoO_3$  was more deeply reduced at the larger flow rate of  $H_2$ .

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  $NH_3$ .<sup>7,8</sup> 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 =  $600 \text{ ml min}^{-1} \text{ g}^{-1}$ ) yielded a product with surface area of  $150 \text{ m}^2 \text{ g}^{-1}$ , 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  $150 \text{ m}^2 \text{ g}^{-1}$  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.

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