Preparation and Catalytic Property of MoO$_x$ with Meso-porosity

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Abstract: A partially reduced molybdenum oxide (MoO$_x$) with meso-porosity was prepared for the first time and its catalytic performance in *n*-heptane isomerization carried out in a fixed bed flow reactor has been studied.   And the evolvement of MoO$_x$ formation has been characterized by X-ray diffraction and catalytic performance in *n*-heptane isomerization.   The MoO$_x$ catalyst obtained from H$_2$ reduction for 12 h, possessing a maximum pore volume at diameter *ca*. 4.1 nm, exhibited high activity in *n*-heptane isomerization. The composition of this catalyst is of the predominant MoO$_x$ phases, MoO$_2$ phase and trace amount of metal Mo phase.

Keywords: Meso-porosity, MoO$_x$, *n*-heptane isomerization.

Recently, molybdenum oxides (MoO$_x$) treated in H$_2$ at 623~673 K has attracted much attention because of the high catalytic activity and selectivity for *n*-heptane isomerization[1-4] and its microporosity structure[5-7].   Matsuda *et al* have reported that the MoO$_x$ obtained from H$_2$ reduction was more active and selective for isomerization of *n*-heptane compared with 0.5 wt% Pt/USY zeolite[1].   They suggested that the MoO$_x$ possesses a bifunctional property, which is responsible for the high isomerization activity. Furthermore, it is revealed that the active phase and its catalytic performance strongly depend on the reduction conditions, especially the reduction period[1, 4].   On the other hand, T. Matsuda *et al.* have studied the porous structure of MoO$_x$ obtained by H$_2$ reduction at the temperature ranging from 573 K to 673 K[5].   And they have found that the MoO$_x$ produced at the temperature lower than 623 K has the characteristic of microporosity with maximum volume around 0.8 nm in diameter[5-7], and that reduction of MoO$_3$ at 673 K almost cannot produce pores.   In this paper, we report a MoO$_x$ with meso-porosity characteristics obtained by H$_2$ reduction of MoO$_3$, which is more active for *n*-heptane isomerization.

Experimental

In this study MoO$_3$ (Beijing Chemicals) powder with analytical purity was used as the precursor of the MoO$_x$ catalyst.   The MoO$_3$ was made into pellets, crushed, and then sieved (60-80 mesh) for charging into a stainless steel reactor with the diameter of 3.8 mm. The MoO$_x$ catalyst was obtained by reducing the precursor in H$_2$ with a flow rate of 120

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mL/min.   A prescribed amount (0.15 g) of the MoO_3 was packed at the central position of the reactor, and then was reduced at 623 K for the designated time in H_2 which was purified by passing through Pd/Al_2O_3 catalyst and then dried with molecular sieve on line. After being cooled to reaction temperature in H_2, the sample was purged by pure N_2 for 30 min, cooled to room temperature in pure N_2, and then passivated for 3 h with 0.5 % O_2 in N_2 to avoid a bulk oxidation.   The samples thus obtained were designated as $MoO_3(2)$, $MoO_3(6)$, *etc.*, where the values in parentheses represent the period of H_2 reduction. Crystalline phase of the catalysts was characterized in Riguka D/max 2400 X-ray diffractometer using Cu-K_α radiation under 40 KV and 100 mA.   BET surface area and pore size distribution of the catalysts were determined at liquid nitrogen temperature by a micrometritics ASAP-2000 adsorption analyzer.   The isomerization of *n*-heptane was isothermally carried out at 573 K under atmospheric pressure in a conventional fixed-bed flow reactor, in which the catalyst was used *in situ* without passivation.   The composition of effluent gas was analyzed by means of FID gas chromatography using quartz capillary separation column.   The selectivity to *iso*-C_7 was defined as the ratio in terms of moles of *iso*-C_7 products to *n*-C_7 transformed.

Results and Discussion

**Figure 1**   XRD patterns of MoO_x obtained by H_2 reduction at 623 K for various time
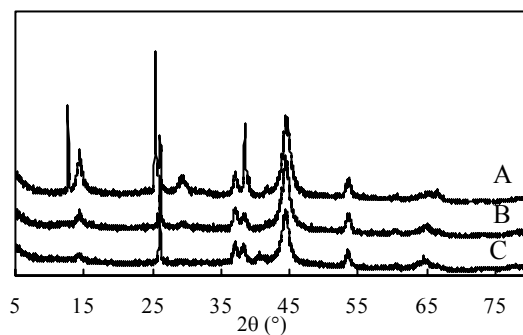
(A) 2 h   (B) 6 h and (C) 12 h (,   and   corresponding to MoO_3, MoO_2, (B) and metal Mo phase, respectively)

As shown in **Figure 1**, almost all of the MoO_3 phase in the $MoO_3(2)$ sample was converted to other phases, though the diffraction lines(2θ=12.7º, 25.4º and 38.5º) corresponding to MoO_3 phase were still obvious.   By comparing the diffraction pattern of $MoO_3(2)$ with those of a series of MoO_3-MoO_2 mixtures composed of different MoO_3 content, less than 1/30 of the MoO_3 in the sample $MoO_3(2)$ in weight could be determined.   When reduction period increased to 6 h, the MoO_3 phase was completely disappeared and the $MoO_3(6)$ sample consisted of MoO_2 as well as some MoO_x phases, which are unascertained thoroughly in their composition and structure of crystalline phase, corresponding to the diffraction lines at 2θ=14.4º, 29.3º, 38.3º, and 44.4º.   The results indicate that MoO_3 are easily reduced in the early stage.   When the reduction period was prolonged to 12 h, a

weak peak ($2\theta=40.8°$)[8] assigned to metal state of Mo was observed, accompanied by the essential disappearance of the diffraction lines at $2\theta=14.4°$ and $29.3°$. Thus it can be considered that the catalyst of $MoO_3(12)$ is composed of the predominant MoO_x phases, MoO_2 phase and trace amount of metal Mo phase.

Figure 2   Pore-size distribution curves based on N_2 desorption data
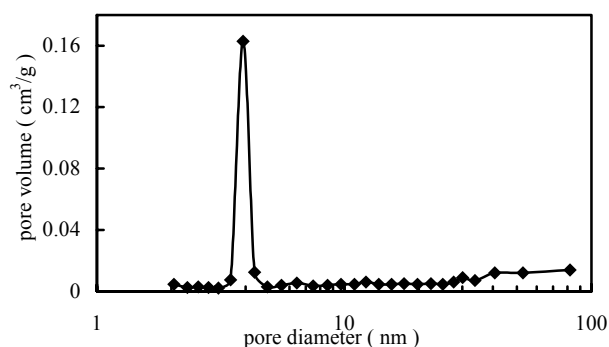
BET equation provided BET surface area of 36.2 m^2/g for $MoO_3(6)$ and 41.6 m^2/g for $MoO_3(12)$.   The corresponding pore-size distribution curve of $MoO_3(12)$ sample showed a maximum pore volume at the diameter of 4.1 nm, as shown in **Figure 2**.   This result is quite different from that reported in the literatures, in which T. Matsuda *et al* obtained the maximum pore volume at the diameter of *ca.* 0.8 nm, and no maximum pore diameter could be observed in the mesoporous region[5-7].   In our experiments, the $MoO_3(6)$ showed also the maximum pore volume at the diameter of 4.1 nm, indicating that the mesopore formation begins at the early stage of the MoO_3 reduction.

Figure 3   Variation of catalytic property of MoO_3 treated with different H_2 reduction period
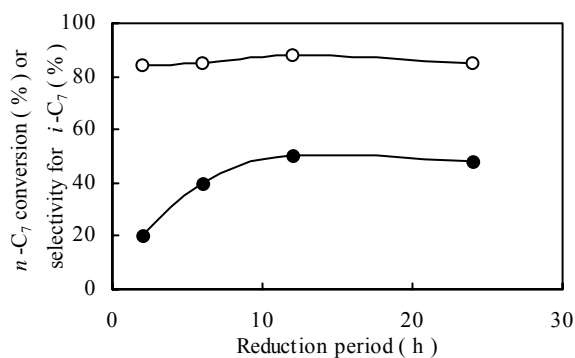
(: selectivity for *i*-C_7;   : *n*-C_7 conversion)

The bifunctional catalytic activity of MoO_x catalysts was characterized by *n*-heptane isomerization reaction that was carried out at 573 K under atmospheric pressure. Typical results taken after 4 h of run are shown in **Figure 3**. The parent MoO_3 was almost inactive for both isomerization and cracking of heptane. And on the MoO_x catalyst, the conversion of *n*-heptane greatly increased with the reduction period when the reduction time was less than 6 h. The activity of the MoO_x catalyst could be further enhanced by prolonging the reduction period for more than 6 hours, but it reached a constant after 12 h. At the conditions of 573 K, 11.0 g-cat·h·mol-C_7^{-1} of *W/F* and 23 of H_2/*n*-heptane in volume, the conversion of *n*-heptane reached 51% on the $MoO_3(12)$ catalyst, which is more active compared with that reported in the literature[1], especially at the lower H_2/*n*-heptane ratio conditions. Here we suppose that the mesopores may be more important than the micropores for *n*-heptane isomerization reaction, for the mesoporous MoO_x with a surface area of 41.6 m^2/g exhibits a higher activity than that of microporous MoO_x with a surface area of 170-180 m^2/g[1-4].

Moreover, it is interesting to compare the maximum pore volume of the $MoO_3(12)$ sample prepared by H_2 reduction to that of Mo_2N synthesized by NH_3 reduction, on which the maximum pore volume at the diameter ranging from 3 to 5 nm was determined,[9] indicating that the meso-porosity of Mo_2N is also created at the early stage of MoO_3 reduction other than exclusively formed at the nitriding step, though it is another kind of material.

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