

A Promising MoO_x-based Catalyst for *n*-Heptane Isomerization

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Abstract: The SiO₂ and γ -Al₂O₃ supported MoO_x catalyst and a MoO_x-SiO₂ catalyst have been studied in a conventional fixed-bed flow reactor for *n*-alkanes isomerization. It is shown that the MoO_x-SiO₂ catalyst with SiO₂ framework, in which the bulk MoO_x phase is large enough to form typical mesoporous structure, is promising in terms of its advantages of both improved mechanical strength and high catalytic properties over the supported MoO_x and bulk MoO_x catalyst.

Keywords: *n*-Heptane isomerization, molybdenum oxides, SiO₂, mesopore, MoO_x-based.

The increasing demand for higher-octane gasoline and the regulations limiting the amount of aromatics in the fuel motivate the interest in catalytic isomerization of *n*-alkanes. In the last ten years, transition metal oxides or oxycarbides based on molybdenum or tungstate have attracted much attention due to their high activity and isomerization selectivity compared to the conventional bifunctional supported platinum catalyst and high resistance to sulphur and nitrogen catalyst poisons¹⁻⁵. Matsuda *et al*⁴ have shown that bulk MoO_x catalyst obtained from H₂ partial reduction of MoO₃ at 623 K possesses a higher activity and selectivity for *n*-heptane isomerization compared with the 0.5 wt%Pt/USY bifunctional catalyst. In our previous work, it has been shown that apparent activated energy of 49.3 kJ/mol for *n*-heptane isomerization on bulk MoO_x catalyst is much lower than that over conventional bifunctional catalyst⁶. The studied MoO_x catalyst is very loose, while the high mechanical strength of the catalyst is required for large catalyst beds used in industry. Therefore, the aim of our work is trying to find a way to improve the mechanical strength of the catalyst, keeping its catalytic activity for *n*-heptane isomerization. For this purpose, the catalysts obtained by supporting MoO_x on some carriers or adding some inorganic material into MoO_x to form the framework have been studied.

Experimental

The MoO₃/SiO₂ or MoO₃/ γ -Al₂O₃ supported catalyst precursor was obtained by the conventional incipient wetness impregnation method. And the MoO₃-SiO₂ catalyst precursor with SiO₂ as the framework was prepared by the following steps: MoO₃

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powder was mixed with silica sol, dried in air at 393 K, and then crushed to 60~80 mesh. Both types of the catalysts were finally activated *in situ* at 623 K in H₂ flow of 120 mL/min for 6 h, and the reaction was carried out under atmosphere pressure in a conventional fixed-bed flow reactor according to the details described in our previous work⁶⁻⁷. To study the interaction between the support and MoO₃, which has been considered to be unfavorable to the catalytic activity, the specific activity of per gram of MoO₃ of r_m was compared, and different amount of the catalyst was used in order to minimize influence of conversion of *n*-heptane on the r_m results. The charged amount of the catalysts precursor was 0.88 cm³ for the MoO_x/SiO₂ or MoO_x/γ-Al₂O₃ catalyst and 0.27 g for MoO_x-SiO₂ catalyst (0.28 cm³) with the same MoO₃ content (0.15 g) as bulk MoO_x catalyst. Crystalline phase of the catalysts was characterized by a Riguka D/max 2400 X-ray diffractometer using Cu-Kα radiation under 40 kV and 100 mA. The pore size distribution of the catalysts was measured on Micromeritics ASAP-2000 adsorption analyzer. The sample for the measurement was obtained as follows: after being reduced by H₂, the catalyst sample was purged and cooling to room temperature in pure N₂, and then passivated for 3 h with 0.5 % O₂ in N₂ to avoid a strong bulk oxidation.

Results and Discussion

Table 1^a Catalytic performance of the different types of MoO_x-based catalysts

Catalyst precursor	C_{n-C7}^b (mol%)	S_{iso} (mol%)	r_m (mmol- <i>n</i> -C ₇ /h/g-MoO ₃)	r_v (mmol- <i>n</i> -C ₇ /h/cm ³ -cat)
Bulk MoO ₃	48	93	44	82
22.4 wt% MoO ₃ /γ-Al ₂ O ₃	12	73	9.5	1.9
13.1 wt% MoO ₃ /SiO ₂	9	98	24	1.4
20.9 wt% MoO ₃ /SiO ₂	20	96	30	3.1
34.5 wt% MoO ₃ /SiO ₂	37	95	29	6.0
55.4 wt% MoO ₃ -SiO ₂	48	94	44	24

a: The result given in **Table 1** was taken after 1 h of run.

b: C_{n-C7} and S_{iso} mean conversion of *n*-heptane and isomerization selectivity, respectively.

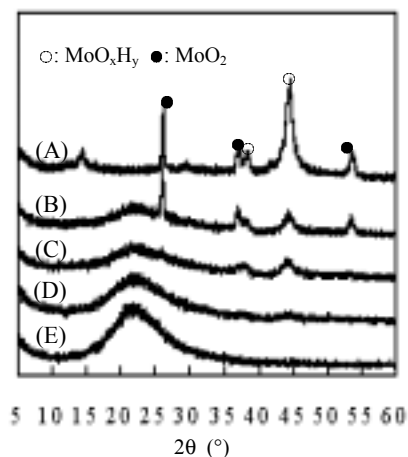
Reaction conditions: reaction temperature=573 K, H₂=120 mL/min and H₂/*n*-C₇=23.

The comparison of the catalytic activity of the different types of MoO_x-based catalysts for *n*-heptane isomerization was shown in **Table 1**. The MoO_x/γ-Al₂O₃ catalyst possessed a poor r_m and isomerization selectivity compared with bulk MoO_x catalyst and the MoO_x/SiO₂ catalyst. These results can be explained well from the interaction between the support and the MoO₃. It is widely known that the strong metal-support interaction between the MoO₃ and the alumina support surface made MoO₃ to be hardly reduced to the active state⁸. And the lower selectivity to isomerization of the MoO_x/γ-Al₂O₃ catalyst may result from the naked alumina surface. It confirmed that γ-Al₂O₃ is not a proper support.

Over the MoO_x/SiO₂ catalyst, the reaction specific activity of per g-MoO₃, r_m , increased when the MoO₃ loading increased from 13.1 wt% to 20.9 wt% in the precursor and then kept almost constant as further increasing the loading, while the isomerization selectivity remained as high as that of unsupported bulk MoO_x catalyst. As the

MoO_x/SiO₂ catalyst with higher MoO₃ loading has a larger of r_m , it can be suggested that the MoO_x site dispersed on the SiO₂ surface is less active than bulk phase of MoO_x in the SiO₂ pores though the interaction between the MoO₃ and SiO₂ is weaker⁹. This suggestion is also supported by the XRD results shown in **Figure 1**, that the intensity of the diffraction lines at $2\theta=38.1^\circ$ and 44.6° attributed to MoO_xH_y phase, as well as those at $2\theta=26.1^\circ$, 37.0° and 53.5° attributed to MoO₂ phase¹⁰⁻¹² became stronger as MoO₃ loading in the MoO_x/SiO₂ catalyst precursor increased from 13.1 wt% to 34.5 wt%.

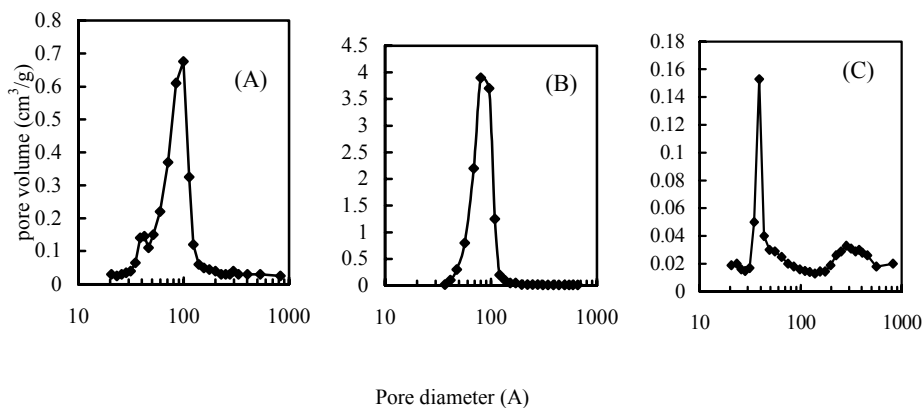
Figure 1 XRD patterns of MoO_x-SiO₂, MoO_x/SiO₂ and bulk MoO_x catalysts



The corresponding precursors are (A) bulk MoO₃; (B) 55.4 wt% MoO₃-SiO₂; (C) 34.5 wt% MoO₃/SiO₂; (D) 13.1 wt% MoO₃/SiO₂; (E) SiO₂.

To obtain a catalyst with both enough mechanical strength and more proportional bulk phase of MoO_x, we studied the MoO_x-SiO₂ catalyst, in which SiO₂ acted as the framework. As shown in **Figure 1**, the XRD pattern of the MoO_x-SiO₂ catalyst was similar to that of bulk MoO_x catalyst, indicating that it contained more bulk phase of MoO_x. Furthermore, the framework structure was well characterized by the pore-size distribution curves shown in **Figure 2**. The MoO_x-SiO₂ catalyst possessed two types of pores, one type with pore diameter of about 4 nm and the other with 10 nm. By comparing the pore-size distribution curves with those of bulk MoO_x catalyst and the SiO₂ support, it is reasonable to attribute the pores with the diameter of 4 nm to that formed by the bulk MoO_x phase and that with diameter of about 10 nm to that formed by the SiO₂ phase in the MoO_x-SiO₂ catalyst. From the pore-size distribution curves, it could be considered that the MoO_x-SiO₂ catalyst had the framework of SiO₂, in which the bulk MoO_x phase could be large enough to form own typical pore structure.

Interestingly, the MoO_x-SiO₂ catalyst exhibited an almost unchanged specific activity of r_m compared with that of bulk MoO_x catalyst as shown in **Table 1**.

Figure 2 Pore-size distribution curves for MoO_x-SiO₂, MoO_x/SiO₂ and bulk MoO_x catalysts

The corresponding precursors are (A) 55.4 wt% MoO₃-SiO₂; (B) SiO₂; (C) bulk MoO₃.

By comparing the different catalysts listed in **Table 1** with the reaction specific activity of per cm³-catalyst, r_v , it can be seen that the activity of these catalysts is in the order: bulk MoO_x > MoO_x-SiO₂ > MoO_x/SiO₂ > MoO_x/γ-Al₂O₃. However, from practical application standpoint, MoO_x-SiO₂ catalyst is very promising in terms of its advantages of both improved mechanical strength and high catalytic properties over the bulk MoO_x catalyst and supported MoO_x catalyst.

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