

Effect of Ni Loading on the Catalytic Properties of Molybdenum Oxides for the Isomerization of Heptane

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Abstract: The catalytic properties of MoO_x and incorporation Ni onto the MoO_x for the isomerization of heptane have been investigated under atmospheric pressure at different conditions such as different flow rate of H_2 , different reaction temperature *etc.*. Compared with MoO_x , the Ni addition to the MoO_x markedly improved the isomerization activity of heptane by improving the reducibility of MoO_3 and activation of H_2 in reaction.

Keywords: Molybdenum oxides, nickel, isomerization, heptane.

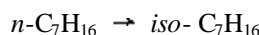
The isomerization of straight chain hydrocarbons to branched isomers is an important reaction in the process of crude oil refining industry for producing superior quality fuels with higher octane ratings. The conventional catalyst for the reaction is the bifunctional platinum supported on zeolite. However, recently Matsuda and colleagues¹⁻³ have demonstrated that the MoO_x are also excellent catalyst for the isomerization of alkanes. They have showed that MoO_x at 623 K exhibited a higher isomerization activity than a typical bifunctional catalyst, Pt/USY zeolite, for heptane isomerization, but the catalyst has some disadvantages such as longer reduction time, higher reaction temperature, and higher flow rate of H_2 *etc.*. In this paper, we report for the first time the result of the isomerization of heptane over a Ni modified MoO_x catalyst. It was found that the incorporation of Ni markedly improved the isomerization activity of heptane.

The Ni/ MoO_3 containing 5% of Ni by weight was prepared by impregnation of MoO_3 with an aqueous solution of $\text{Ni}(\text{NO}_3)_2$. The isomerization reaction was carried out in a conventional fixed bed flow reactor under atmospheric pressure. A prescribed amount of MoO_3 or NiO- MoO_3 was reduced *in situ* in a stream of H_2 and kept for 12 h at certain temperature before reaction. In the heptane isomerization reaction, all experiments were performed using 0.15 g of the catalyst and 9.0 h^{-1} of heptane WHSV. The products were analyzed by GC using quartz capillary separation column and FID detector.

Figure 1 shows the variation in activity and isomerization selectivity of MoO_x (623) and Ni/ MoO_x (623) for the isomerization of heptane, in parenthesis is the temperature, at which the reduction takes place. The flow rate of H_2 changed in the reaction process at 573 K. The flow rate of H_2 directly affected the isomerization of heptane, although it

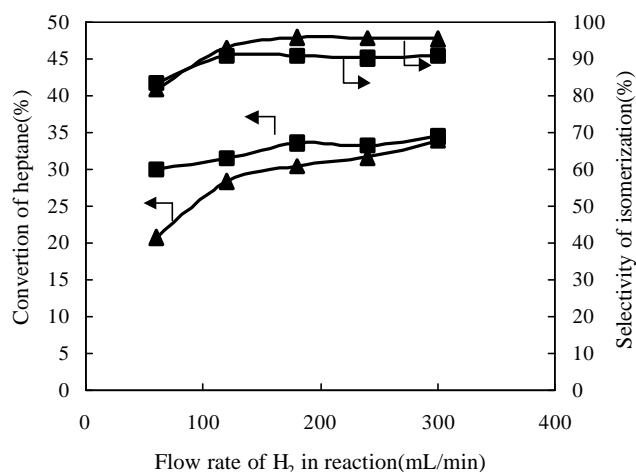
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does not appear in the isomerization equation:



The catalytic activity of MoO_x (623) was markedly enhanced by the increase of the hydrogen flow rate, this behavior is very similar to the other reports^{4,5}. The dependence of the catalytic activity of Ni/MoO_x upon the hydrogen flow rate was markedly reduced after Ni loading on the MoO_x catalyst. The slower hydrogen flow rate is, the clearer this behavior is. So it could be considered that the component of Ni in the Ni/MoO_x improved the isomerization activity of heptane through activating H_2 .

Figure 1 Variation in %conversion of heptane and isomerization selectivity



on MoO_x (▲) and Ni/MoO_x (■) with changing the flow rate of H_2 in reaction
Reaction temperature 573K; Data were taken after 6h of run.

The second role of Ni is to promote the reduction of MoO_3 to lower valence states of Mo, which was considered to be the active site for the heptane isomerization¹. As shown in **Table 1**, the activity of the catalyst MoO_x (573) was much lower than that of catalyst MoO_x (623). Moreover, the activity of MoO_x (573) catalyst slightly increased with time on stream, while on MoO_x (623) catalyst at the reaction conditions presented in **Table 1** no similar phenomenon was observed. These results indicate that the reduction of the parent MoO_3 to the active MoO_x is insufficient at 573 K. On the other hand, the Ni/MoO_x catalyst was always more active than the MoO_x catalyst, and the difference of the activities was much more at the lower reduction temperature. The Ni/MoO_x (623) was about 1.2 times as active as the MoO_x (623), and the activity of the Ni/MoO_x (573) was about 3.7 times that of the MoO_x (573). It is indicated that the diffraction lines corresponding to the metallic crystal of nickel was obvious in the XRD pattern of the Ni/MoO_x (623) catalyst. Thus we deduce that the nickel exists as metal state in the Ni/MoO_x (623). Therefore, it can be suggested that the incorporation of metal state Ni onto the MoO_x to form Ni-MoO_x not only improves the isomerization reactions of

heptane but also benefits for activating hydrogen.

Table 1 Catalytic activities and selectivities of MoO_x and Ni/MoO_x for the isomerization of heptane at different reduction temperature

Reduction ^a temperature (K)	Conv.% (Sel.iso%) ^b	
	MoO _x	Ni/MoO _x
573	7.5 (83.7)	27.5(85.1)
623	36.5(91.1)	42.9(91.0)

a: the flow rate of H₂ in reduction, 120 mL/min; b: reaction temperature, 573 K.

The heptane isomerization reaction was carried out at temperatures in the range from 523 K to 623 K. Typical results are demonstrated in **Table 2**. Loading Ni onto the MoO₃ enhanced the activity at all tested reaction temperature. Especially, the promoting action was much strong at the lower reaction temperature. There was no appreciable difference in the catalytic activity between the Ni/MoO_x (623) and MoO_x (623) at 623 K, but the Ni/MoO_x (623) was about 2.0 times as active as the MoO_x (623) at 523 K. This result indicates that using Ni/MoO_x as the catalyst is beneficial to heptane isomerization at lower reaction temperature.

Table 2 Catalytic activities and selectivities of MoO_x and Ni/MoO_x for the isomerization of heptane at different reaction temperatures

Reaction Temperature ^a (K)	Conv.% (Sel. _{iso} %) ^b	
	MoO _x	Ni/MoO _x
523	2.26 (91.4)	4.65 (91.0)
573	36.5 (91.1)	42.9 (91.0)
623	39.3 (80.6)	41.8 (77.9)

a : reduction temperature, 623K; b: Data were taken after 6 h of run.

From the above results it is very clear that the incorporation of Ni on the MoO_x enable the heptane isomerization reaction to be proceeded at moderate conditions. The results can be explained as follows: the Ni generated at earlier stage in the reduction process made the MoO₃ to be reduced easily to its active state, H₂ was activated at the lower temperature, so that the Ni/MoO_x catalyst exhibited higher activity for the isomerization of heptane at lower reaction temperature and at lower H₂ flow rate. The action of Ni might be attributed to the formation of the activated hydrogen on the surface of Ni and spillover of hydrogen from Ni to the MoO₃ or MoO_x. Matsuda *et al.*² have suggested that isomerization of heptane on MoO₃ (623) proceeded *via* the conventional bifunctional mechanism, with dehydrogenation-hydrogenation steps on site with a metallic character and isomerization steps on sites of acidic type. We suggest here that the incorporation of Ni onto the MoO_x facilitate dehydrogenation-hydrogenation step by the action of spillover hydrogen, and the dehydrogenation-hydrogenation step might be the rate determining step for the isomerization of heptane on MoO_x, hence, the incorporation of Ni onto the MoO₃ markedly improved the catalytic properties of the reduced MoO₃ for the isomerization reaction of heptane.

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