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Isomerization of n-hexane over Platinum loaded zeolite catalysts

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Abstract

The isomerization of n-hexane over Pt-loaded Hβ, H-ZSM-5 and H-dealuminated mordenite was studied at temperatures lower than 573 K under atmospheric pressure. It was found that Pt loaded Hβ showed the highest activity and selectivity of these three catalysts. Namely, the conversion of hexane was 76 C-% and selectivities to dimethylbutanes, methylpentanes and cracking products were 19.4, 76.2 and 4.4 C-%, respectively, under the following conditions: reaction temperature, 548 K; W/F, 5 g h mol^{-1}; molar ratio of hydrogen to n-hexane, 4. Pt/Hβ catalyst showed a good stability, because Hβ has acid sites with medium strength and three-dimensional large pores. We can adjust the balance between metallic sites and acid sites to obtain right catalyst which has the highest activity and the highest selectivity for the isomerization of hexane.

Keywords: Pt catalysts; Isomerization of hexane

1. Introduction

A tendency to eliminate benzene and other aromatic hydrocarbons from gasoline with a high octane number is shown lately. Therefore, the isomerization of straight chain paraffins to branched chain paraffins without cracking should be one of the key reactions for the production of high octane gasoline.

It has been known that the dual functional catalysts or the super acid catalysts promote effectively the isomerization of paraffins. Zeolites are perfectly adapted to the preparation of bifunctional catalysts: their acid sites are numerous and highly active; moreover a high dispersion and a high activity of hydrogenating sites can be obtained when introducing the metal by an ion-exchange process. Platinum-hydrogen-mordenite (Pt/HM) catalysts have been used commercially for isomerization of C_5–C_6 normal alkanes to higher-octane branched isomers [1]. However, the selectivity and the stability of Pt/HM catalysts are very low. On the other hand, the highly siliceous zeolites are profitable in the heat resistance and the depression of coke formation. We challenge the preparation of a good catalyst for the isomerization of paraffins by using highly siliceous zeolites and Pt. We discuss on the properties of good catalysts for the isomerization of paraffins.

2. Experimental

ZSM-5, β and mordenite were synthesized hydrothermally. The structure of synthesized zeolites was determined by XRD. The synthesized mordenite was dealuminated with nitric acid at

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373 K for 3 h. The atomic ratios of Si to Al in ZSM-5, β and dealuminated mordenite were 30, 23 and 11, respectively. The parent zeolites were converted into the NH_4^+ form by ion-exchange with ammonium nitrate solution. Their hydrogen form was obtained by calcining them at 813 K. Pt was introduced by ion-exchange with $Pt(NH_3)_4Cl_2$ aqueous solution. All catalysts were pretreated with oxygen diluted in helium by multistage, then reduced with hydrogen at 673 K for 2 h and at 723 K for 1.5 h before reaction.

The isomerization of hexane was carried out in a continuous flow fixed-bed reactor system under atmospheric pressure. The mixture of hydrogen and hexane with molar ratio of 4 was fed into the reactor. Products were analyzed by gas chromatography equipped with Petrocol™ DH fused silica capillary column.

3. Results and discussion

3.1. Comparison of various zeolites

The results of n-hexane isomerization on various Pt-loaded zeolite catalysts are shown in Table 1. Data were collected at 1 h on stream. Products are cracking products ($< C_6$), 2,2-dimethylbutane (2,2-DMB), 2,3-dimethylbutane (2,3-DMB), 2-methylpentane (2-MP) and 3-methylpentane (3-MP). Pt/Hβ showed the highest conversion and selectivity for isomerization, while Pt/HM catalyst showed the lowest.

The acid strength of zeolites was estimated by measuring the differential adsorption heat of ammonia. The main acid sites on Hβ showed medium strength (100–80 kJ mol^{-1}). H-dealuminated mordenite had strong acid sites (125–100 kJ mol^{-1}). The amount of adsorbed NH_3 on H-dealuminated mordenite (> 80 kJ mol^{-1}, 0.75 mmol g^{-1}) was larger than that on Hβ (> 80 kJ mol^{-1}, 0.46 mmol g^{-1}). From these results it is suggested that the cracking of hexane would be promoted by the strong acid sites and the highly dense acid sites. The activity of Pt/HM rapidly decreased with time on stream (26%, from 15 min to 1 h on stream). The lower activity of Pt/HM may be due to its faster deactivation which is probably related to its uni-dimensional pore system and the higher acid site density of the catalyst [2,3].

Dimethylbutanes have high octane number. Therefore from the view point of gasoline manufacture, it is desired to form dimethylbutanes effectively by isomerization of hexane. The selectivities for dimethylbutane formation on Pt/Hβ and Pt/HM were much higher than that on Pt/H-ZSM-5, because the pore window size of ZSM-5 is smaller than the molecular size of dimethylbutanes.

3.2. Effect of reaction temperature

The principal dependence of n-hexane transformation over Pt/Hβ on reaction temperature is illustrated in Fig. 1. The conversion of n-hexane increased with reaction temperature. The total yield of all isomers passed through a maximum at 548 K, indicating the consumption of the isomerized products in consecutive hydrocracking reactions. In this case the isomer distri-

Table 1
Isomerization of n-hexane on Pt-loaded zeolite catalysts

Catalyst	Conversion (C-%)	Selectivity to Isomerization (C-%)	Product distribution (C-%)				
			$< C_6$	2,2-DMB	2,3-DMB	2-MP	3-MP
Pt/Hβ	72.4	95.6	4.4	8.7	10.7	46.8	29.4
Pt/HM	14.2	81.3	18.7	6.0	10.9	40.4	24.0
Pt/H-ZSM-5	46.0	89.4	10.6	0.1	0.9	69.1	19.3

Reaction temperature: 548 K, H_2/C_6 molar ratio: 4, W/F: 5 g h mol^{-1}.
Content of platinum: 0.5 wt.-%.

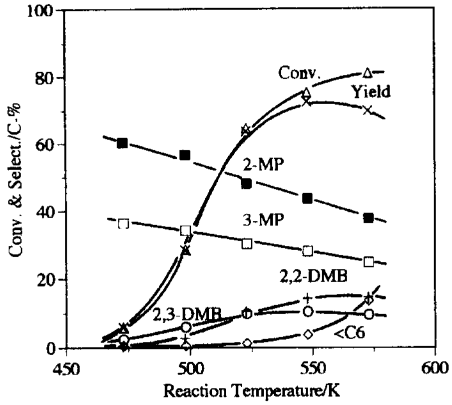

Fig. 1. Effect of reaction temperature on n-hexane conversion and product distribution. Catalyst: 1.0 wt.-% Pt/Hβ, W/F: 5 g h mol^{-1}, H_2/C_6 molar ratio: 4.

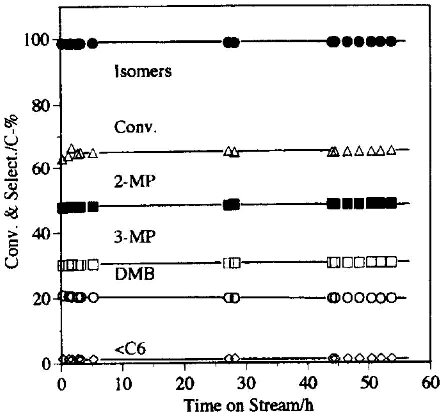

Fig. 2. Effect of time on stream on n-hexane conversion and product distribution. Catalyst: 1.0 wt.-% Pt/Hβ, Reaction Temperature: 523 K, H_2/C_6 molar ratio: 4, W/F: 5 g h mol^{-1}.

bution is also markedly dependent on the conversion rate, as suggested by Guisnet et al. [4]. The branching occurs by consecutive reactions:at low conversion monobranched alkanes (2-MP and 3-MP) are formed almost exclusively (at least 96%); by increasing the conversion rate, the content of doublebranched alkanes (2,2-DMB and 2,3-DMB) increases.

3.3. Effect of time on stream

The acid sites on Hβ have mainly medium strength, so that the selectivity to cracking can be depressed at a reaction temperature lower than 573 K. Effect of time on stream on n-hexane conversion and product distribution are shown in Fig. 2. Conversion of hexane and selectivities to products showed no obvious change in up to ca. 55 h on-stream runs. Namely, Pt/Hβ showed a good stability.

3.4. Effect of contact time (W/F)

Hexane conversion and product distribution as a function of contact time are shown in Fig. 3. An increase in contact time results in a longer residence time of hexane and monobranched isomers inside the β zeolite pores, and consequently the yields of mono- and double-branched

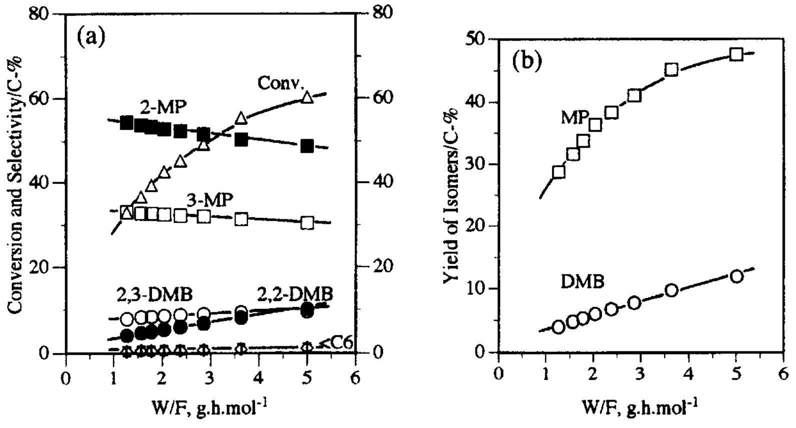

Fig. 3. Effect of contact time (W/F) on n-hexane conversion and product distribution. Catalyst: 1.0 wt.-% Pt/Hβ, Reaction Temperature: 523 K, H_2/C_6 molar ratio: 4.

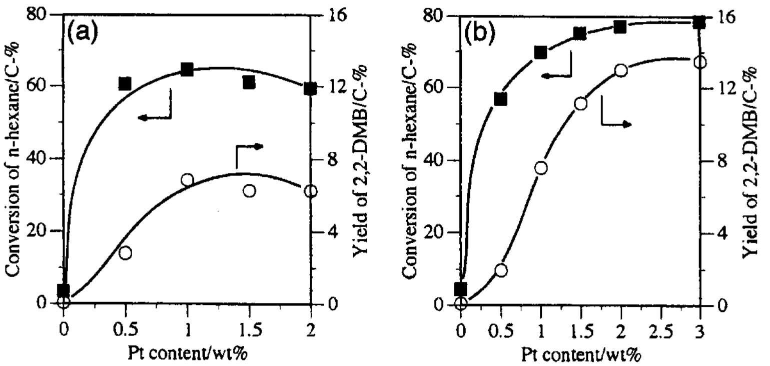

Fig. 4. Variation of the total conversion and the yield of 2,2-DMB as a function of platinum content (a) Pt/Hβ, (b) Pt/Hβ'. Reaction Temperature: 523 K, W/F: 5 g h mol^{-1}, H_2/C_6 molar ratio: 4.

isomers are improved. The increase of the latter is almost linear (Fig. 3, right) and at the expense of the monobranched ones (Fig. 3, left). From Fig. 3 (left), it can be observed that the isomer distribution is markedly dependent on the conversion rate.

3.5. Balance of dual function

The balance between acid sites and metallic sites is important for getting the optimum isomerization activity. We have investigated the effect of incorporating various quantities of platinum into β zeolite by an ion-exchange technique. Isomerization results of hexane on Pt/Hβ and Pt/Hβ' catalysts with various contents of Pt are shown in Fig. 4. The acidity of Hβ is lower than that of Hβ'. A platinum content increase causes a rapid increase of the conversion and the yield of 2,2-DMB, up to about 1.0 wt.-% Pt; a plateau is then reached for Pt/Hβ catalyst. A platinum content increase causes a rapid increase of the conversion and the yield of 2,2-DMB, up to about 2.0 wt.-% Pt; a plateau is then reached for Pt/Hβ' catalyst. At these metal concentrations, the selectivity to 2,3-DMB is at an essentially equilibrium value. We can conclude that the selectivity to 2,2-DMB is markedly dependent upon the catalytic activity. These results are consistent with that on Pt/HM [5] which optimum Pt content is lower than ours. This may suggest that Pt dispersion is lower in β zeolite than in mordenite. Our results are consistent with a bifunctional mechanism(acid and metallic) for n-hexane isomerization [6]. On low platinum content catalysts, the limiting step is the n-hexane dehydrogenation or the methylpentene hydrogenation on the metallic sites; under these conditions, the isomerization activity increases with the platinum content. On high platinum content catalysts, the limiting step is the skeletal isomerization of olefins on acid sites; under these conditions the activity of the bifunctional catalysts no longer depends on their metal contents but only on their acidity. Thus, the activity of bifunctional catalysts with a given acid carrier remains content beyond a certain content of metal. Moreover, the greater the acidity of the carrier, the higher the maximum value of the activity of the bifunctional catalysts (Fig. 4). Therefore, it is important to adjust the balance between the metallic sites and acid sites to obtain a good catalyst for the isomerization of paraffins. We suppose that Pt/Hβ^* with greater acidity than Hβ' may show higher maximum value of activity than Pt/Hβ'.

4. Conclusion

We draw the following conclusions:

(1) Pt/Hβ showed higher isomerization activity of hexane and selectivity to isomers than

Pt/HM and Pt/H-ZSM-5. The conversion of hexane was 76%, and selectivity to isomers was 95.6% over Pt/Hβ.

(2) Pt/Hβ catalyst showed a good stability.

(3) The lower selectivity to dimethylbutanes (2,2-DMB and 2,3-DMB) over Pt/H-ZSM-5 catalyst was attributed to the hindered formation of more branched isomers in the medium-sized pore.

(4) The high activity of hexane isomerization and the high selectivity to isomers (esp. dimethylbutanes) can be obtained by adjusting the balance between the acidity of Hβ and the content of loaded platinum.

References

[1] H.W. Kouwenhoven, Am. Chem. Soc., Adv. Chem. Ser., 121 (1973) 529.

[2] H.G. Karge and E.P. Boldingh, Catal. Today, 3 (1988) 53.

[3] B.T. Carvill, B.A. Lerner, B.J. Adelman, D.C. Tomczak and W.M.H. Sachtler, J. Catal., 144 (1993) 1.

[4] M. Guisnet and G. Perot, in F.R. Ribeiro, A.E. Rodrigues, L.D. Rollman and C. Naccache (Editors), Zeolites: Science and Technology, Nijhoff, The Hague, 1984, p. 397.

[5] M.A. Lanewala, P.E. Pickert and A.P. Botton, J. Catal., 9 (1967) 95.

[6] P.B. Weisz, Adv. Catal., 13 (1962) 137.