Hydroisomerization of Normal Paraffins Over Synthetic Zeolites

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The hydroisomerization of n-pentane, n-hexane and n-heptane has been studied over the faujasite and mordenite types of zeolite. The hydroisomerization activity of zeolites in the case of n-pentane increases to a limiting value with the increase in SiO$_2$ : Al$_2$O$_3$ mole ratio from 2.5 to 10.57. Ca$^{2+}$ ions increase the hydroisomerization activity of mordenite, while Li$^+$ and K$^+$ ions decrease it. The optimum concentration of Pt in HM type of zeolite for the hydroisomerization is 0.5 wt %.

Results and Discussion

Silica-to-alumina ratio — The effect of SiO$_2$ : Al$_2$O$_3$ mole ratio of zeolite on the isomerization of n-pentane was studied using NaX, NaY and NaM type of zeolite catalysts. The n-pentane conversion into isopentane increases to a limiting value with the increase of SiO$_2$ : Al$_2$O$_3$ ratio from 2.5 to 10.57.

Results were reported for the zeolites A, X and Y in the oligomerization reaction of propylene. Also the catalytic activities for isomerization of o-xylene and cracking of cumene were found to increase with the increase in SiO$_2$ : Al$_2$O$_3$ ratio in the faujasite type of zeolites.

The increase in the isomerization activity of zeolites with the increase in SiO$_2$ : Al$_2$O$_3$ ratio may be related to the silicon-aluminium ordering changes in the zeolite framework and consequent change of the acidity. Eberly et al. found that acidity is the dominant factor for the hydroisomerization of n-pentane over Pt/HM catalysts.

Type of cation — Although all exchanged mordenites were prepared under similar conditions the extent of ion-exchange is not the same in all the cases (Table 1). Among all exchanged mordenites HM possesses the highest isomerization activity. Although conversion was lower for the other cation exchanged mordenites the following order of activity was obtained: Ni$^+$ > Ca$^+$ > Mn$^+$ > Na$^+$ > K$^+$ > Li$^+$. Both Ni$^{2+}$ and Ca$^{2+}$ increase the hydroisomerization activity of the parent NaM while the monovalent K$^+$ and Li$^+$ decrease it.

Platinum concentration — Three catalysts containing 0.3, 0.5 and 0.7 wt % Pt were prepared and compared with the parent HM catalyst with regard to the performance of the catalyst.

Materials and Methods

Catalyst preparation — The Na-form zeolites used were NaX and NaY, which are Linde Molecular Sieve samples SK-20 and SK-40 respectively. NaM showed the following chemical analysis (wt %): SiO$_2$, 69.82; Al$_2$O$_3$, 11.23; Na$_2$O, 6.36; SiO$_2$/Al$_2$O$_3$, 10.57 (mole); Na$_2$O/Al$_2$O$_3$, 0.93 (mole). Cation-exchanged mordenites were prepared by treatment of the sodium mordenite with neutral aqueous solution of the corresponding metal chloride (IN) in a dynamic system. The percent exchange of sodium was determined by flame emission studies.

Ammonium mordenite was calcined in a stream of dry air at 400° for 4 hr to obtain the hydrogen form (HM).

The Pt/HM catalysts were prepared by impregnation of HM with aqueous solution of chloroplatinic acid.

All catalyst tests were performed under atmospheric pressure using 10 ml of catalyst in a fixed bed reactor of conventional design as described elsewhere.

The paraffin was charged at 300° using a micro-dosing pump. Space velocity of 4 ml n-paraffin (ml catalyst/hr) and hydrogen flow rate of 3.5 litre hr$^{-1}$ were used.

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to the hydroisomerization activity of n-pentane. The products of n-pentane conversion over all these catalysts contain C$_1$-C$_4$ hydrocarbons in addition to isopentane. This indicates that the hydroisomerization of n-pentane is accompanied by a hydrocracking side reaction. As the platinum concentration increases to 0.5 wt %, the hydroisomerization as well as the hydrocracking activity of the catalyst increase (Fig. 1). Further increase in the platinum concentration (to 0.7 wt %) decreases only the hydroisomerization activity, while hydrocracking continues to increase continuously. Consequently, at this platinum concentration, the catalyst undergoes some deactivation process decreasing the number of only hydroisomerization active sites. This behaviour can be explained on the basis of the active ensembles and multiplet theories of catalysis.

On the basis of the data of the present work it can be concluded that the platinized hydrogen mordenite catalysts of platinum content up to 0.5 wt % have a relatively large number of catalytic active sites which are more sterically conformance to the isomerization of n-pentane. Further increase in the platinum content on the hydrogen mordenite may lead to a decrease in the number of these active sites but may lead to conditions conducive to the occurrence of the side reaction such as cracking.

**Chain length of n-paraffins** — n-Pentane, n-hexane and n-heptane have been used within the temperature range 150-375°C and space velocity of 4 ml n-paraffin (ml catalyst)$^{-1}$ hr$^{-1}$ using the 0.5% Pt/HM catalyst.

As can be seen from Fig. 2, the total conversion for all the n-paraffins increases continuously with increase in the reaction temperature. Below 250°C...
the conversion of n-pentane is the highest but above 250° n-hexane and n-heptane are converted in larger amounts than n-pentane.

Analysis of the conversion products of n-paraffins indicates also that two reactions, hydroisomerization (Fig. 3) and hydrocracking (Fig. 4) take place over the Pt/HM catalyst. The hydroisomerization is the predominant reaction in case of n-pentane, while the hydrocracking is the main reaction in the case of n-hexane and n-heptane.

The hydroisomerization ability of n-paraffins decreases with the increase in chain length (Fig. 3), while their hydrocracking ability increases with the increase in chain length (Fig. 4).

Comparison between the curves of Fig. 3 and Fig. 4 indicates that on increasing the reaction temperature the hydroisomerization activity of the catalyst reaches a maximum value thereafter it decreases, while the hydrocracking activity goes on increasing.

It is worth noting that the products of hydrocracking of presently studied n-paraffins contain very low yields of C₁ and C₂ products as compared to C₃ and C₄ products. They also contain high yields of isobutane indicating carbonium ion mechanism of the cracking reaction.

References
10. Shao Tong, E. & McIninch, E., J. Catalysis, 10 (1968), 166.