Effect of Noble Metal Concentration upon the Isomerization Activity of Molecular Sieve Zeolite Catalysts

The mechanism of paraffinic hydrocarbon isomerization over dual-function catalysts has been studied extensively. These catalysts generally consist of noble metals deposited on an acidic support. Only limited published literature, however, is available on the quantity of metal required for optimum isomerization activity. We have investigated the effect of incorporating various quantities of platinum or palladium into a Molecular Sieve isomerization catalyst by an ion-exchange technique. With *n*-hexane feed, a linear relationship exists between isomer yields at conversions up to equilibrium isomer distributions, and quantity of metal.

The preparation of the 45% La^{3+}–45% NH_4^+-exchanged zeolite base used in this study has been previously described (*1*). The noble-metal-containing cations were introduced as follows: To the rapidly stirred aqueous slurries of the base was added, dropwise and over a period of several hours, a very dilute aqueous solution of $Pt(NH_3)_4Cl_2 \cdot H_2O$ or $Pd(NH_3)_4Cl_2$ salt. The quantity of noble metal salt employed was calculated to yield the desired concentration of noble metal in the finished catalyst. For concentrations of up to several weight percent, exchange of $Pt(NH_3)_4^{2+}$ and $Pd(NH_3)_4^{2+}$ ions with zeolite cations is essentially quantitative. Stirring was continued for at least several hours after the addition of the salt solution was complete.

The noble-metal-containing cation-exchanged powder was filtered, washed free of chloride, dried at 120°C, and converted to tablets ⅛-inch long by ⅛-inch diameter in a Stokes Model E tablet press. Prior to use, the tablets were calcined in air at 550°C in an oven, to decompose the noble-metal-containing complex cations and decationize the zeolite base; they were then reduced in hydrogen at 510°C in the test reactor. The test equipment and procedures have been previously described (*2*). Catalysts with less than about 0.2 wt % metal gradually declined in activity. The activities were, therefore, compared at equal times on stream, 24–26 hr. All isomerization tests were carried out under a pressure of 450 psig, H_2-to-hydrocarbon molar ratio of 5, and a weight-hourly-space-velocity of 2.0 g feed per gram catalyst per hour. Temperature was adjusted to give about 5 mole % C_1–C_5 products.

In the isomerization of *n*-hexane the ratio of monomethylpentane isomers to the 2,2-dimethylbutane isomer, 2,2-DMB, depends upon the catalyst activity. The catalyst without noble metal has isomerization activity of its own, producing ~20% monomethyl isomers and 0.5% 2,2-DMB at 340°C. Incorporation of even small amounts of noble metal enhances isomerization activity at otherwise the same cracking level and approximately the same temperature. All the data with the metal-loaded and non-metal-loaded catalysts of this study were obtained in the range of 320–340°C, in which the thermodynamic isomer distribution is not affected to an appreciable extent with the change in temperature.

The effect of metal concentration upon the formation of monomethyl isomers is shown in Fig. 1. For both the Pd- and Pt-containing catalysts, the activity increased linearly with metal concentration until equilibrium isomer concentrations were produced with 0.05 wt % Pd or 0.10 wt % Pt. With further increase in metal concentration, the yield of monomethyl isomers decreased slightly, as conversions to 2,2-DMB increased, and then remained constant. A similar but more pronounced effect was observed for the 2,2-DMB formation (Fig. 2). The activity increased linearly with metal concentration up to 0.25 wt % Pd and ~0.40 wt % Pt. At these metal

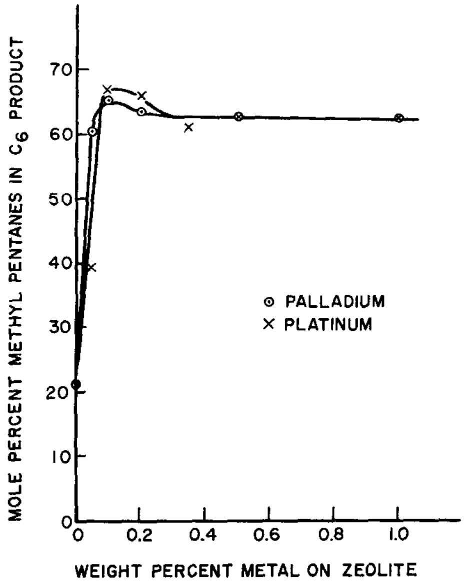

Fig. 1. Effect of metal concentration on methylpentane formation.

concentrations, the isomer yields are essentially equilibrium values.

The ability of the multivalent cation-exchanged zeolite without metal to isomerize *n*-paraffin hydrocarbons in a manner similar to conventional dual-functional catalysts suggests a different reaction mechanism. Pickert *et al.* (*3*) have proposed a mechanism, which involves the strong polarizing influence of the zeolite cation; this postulated mechanism does not require an actual cleavage of H^- ion to form a full carbonium ion. The incorporation of noble metals with selective dehydro–hydrogenation type activity appears to facilitate this partial polarization of C–H bonds, resulting in greater isomerization activity. The technique of metal loading by ion exchange yields very uniform and finely dispersed metal deposits (*3*). It has been shown that catalysts prepared in this manner are considerably more stable in the presence of sulfur in contrast to similar catalysts prepared by conventional impregnation techniques (*4*). The linear increase in the activity with increased metal loading suggests that with each increment of noble metal introduced by ion exchange, the metal atoms are equally effective until an optimum metal concentration is reached. From Figs. 1 and 2 at the optimum metal loadings for both the monomethyl and dimethyl isomers, palladium appears to be about twice as effective as platinum, on a weight basis. However, when these metals are compared on the basis of atomic weight percent they appear to be about equally effective since the atomic weight of platinum (195) is about twice that of palladium (106). The more or less direct proportionality between the metal concentration and activity as well as the ratio of about 1 for the activity of these noble metals on an atomic percent basis supports the postulate that the incorporation of small amounts of noble metal by ion exchange gives a very high, perhaps atomic, dispersion of metal.

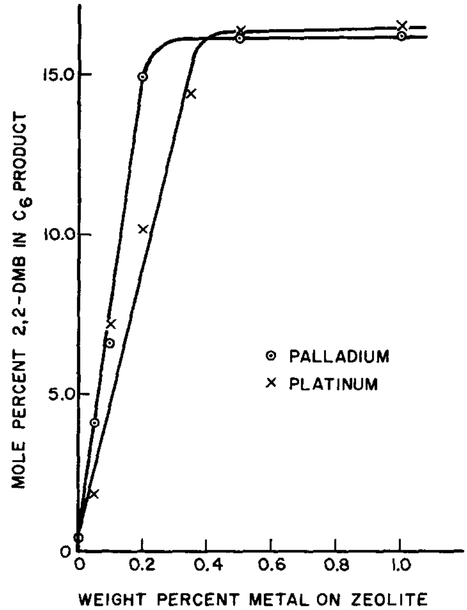

Fig. 2. Effect of metal concentration on dimethylbutane formation.

References

1. Pickert, P. E., paper presented at The International Symposium on Catalysis, Columbus, Ohio, May, 1966.
2. Rabo, J. A., Pickert, P. E., Stamires, D. N., and Boyle, J. E., *Actes Congr. Intern. Catal-*

yse, 2ᵉ Paris 1960 **2**, 2055 (Editions Technip, Paris, 1961).

3. Pickert, P. E., Rabo, J. A., Dempsey, E., and Schomaker, V., *Proc. Intern. Congr. Catalysis, 3rd. Amsterdam, 1964* **1**, 714 (North-Holland Publ. Co., Amsterdam, 1965).
4. Rabo, J. A., Schomaker, V., and Pickert, P. E., *Proc. Intern. Congr. Catalysis, 3rd, Amsterdam 1964* pp. 1264–1276 (North-Holland Publishing Co., Amsterdam, 1965).

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