Selectivity Changes in Al_2O_3 Catalysts

I. Influence of Heat Treatment and Neutron Irradiation on the Activity for *n*-Butene Isomerization

During our investigations of γ-alumina catalysts, their activity and selectivity for *n*-butene isomerization processes were found to be strongly influenced by heat treatment (Fig. 1) and neutron bombardment (Fig. 2). The catalysts which were brought into equilibrium with water vapor after these treatments, but before use, were also subjected to the ethylamine poisoning experiments described by us elsewhere (*1*). Graphs very similar to those already published were obtained. From them the amounts of A and B sites present in the surface could be calculated assuming that one active site is poisoned by one amine molecule. [The nature of type A and B sites is described in the preceding paper (*1*)]. The results show that the amounts of A and B sites depend on preheating temperature and neutron dose (Fig. 3, Table 1).

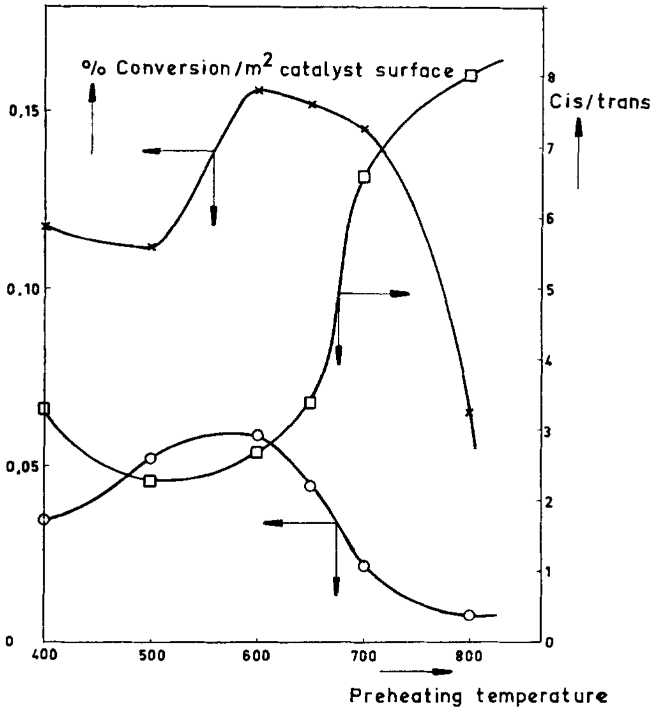

FIG. 1. Influence of preheating temperature on activity and selectivity of γ Al_2O_3 catalyst: ×, butene-1 → *cis*-butene-2; ○, butene-1 → *trans*-butene-2; □, *cis/trans*.

The changes found in the total amount of (A + B) sites with increased preheating temperature are comparable to the changes in amounts of adsorbed ammonia found at low temperatures by MacIver (*2*), who also compared catalysts heated at different temperatures. The general trend in total sites is roughly parallel to the activity changes for the formation of *cis*-butene-2 (c.b.-2) as can be seen by comparing Figs.

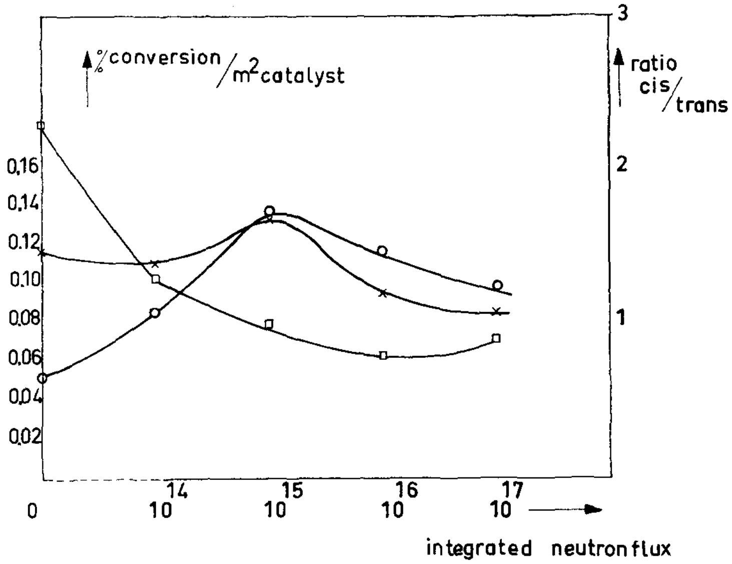

FIG. 2. Influence of neutron irradiation on activity and selectivity of γ-Al_2O_3 catalyst. Reaction temperature, 125°C. Pulse experiment. Preheating temperature, 500°C. ×, Butene-1 → *cis*-butene-2; ○, butene-1 → *trans*-butene-2; □, ratio *cis/trans*.

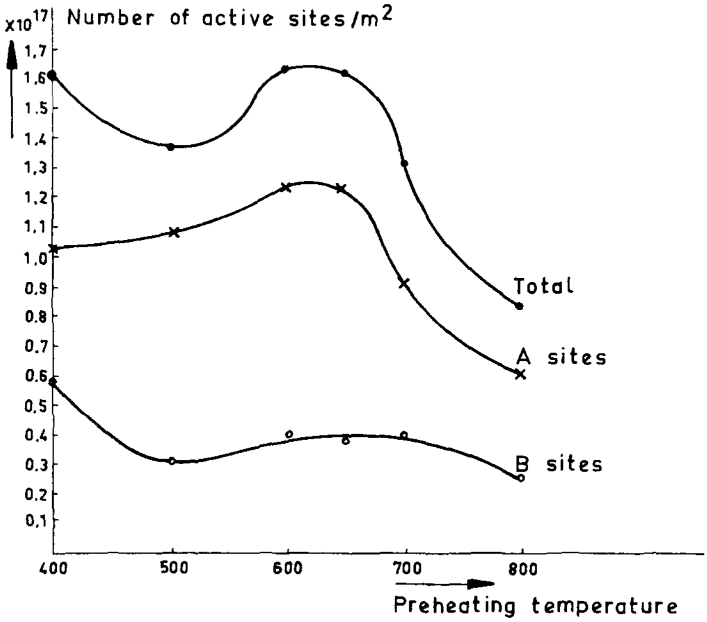

FIG. 3. Influence of preheating temperature of γ-Al_2O_3 on the number of active sites.

1 and 3. On the contrary, the activity changes for the formation of *trans*-butene-2 (t.b-2) with increasing preheating temperature of the catalyst are more in accordance with the trend in the amount of type A sites. This is in complete agreement with earlier conclusions (*1*) that A and B sites behave similarly in reactions between butene-1 (b-1) and c.b-2 but have different activities for reactions where t.b-2 is involved.

As can be seen the indicated similarities

TABLE 1

INFLUENCE OF NEUTRON IRRADIATION ON SELECTIVITY OF γ-Al_2O_3

Pretreatment temperature (°C)	Total flux n.v.t.	Number type A/m²	Number type B/m²	Total (A + B)/m²	% *trans* conversion per A site
500	—	1.1×10^{17}	0.3×10^{17}	1.4×10^{17}	0.34×10^{-17}
500	10^{17}	1.3×10^{17}	0.1×10^{17}	1.4×10^{17}	0.27×10^{-17}
700	—	0.95×10^{17}	0.4×10^{17}	1.3×10^{17}	0.37×10^{-17}
700	10^{17}	1.1×10^{17}	0.2×10^{17}	1.3×10^{17}	0.29×10^{-17}

between curves for activity and amount of sites are only of a rough nature. The activity values for the formation of c.b-2 show a stronger increase in the preheating temperature range between 400° and 600°C than the total amount of sites, indicating that the activity per site increases. This coincides with an increase in acid strength of the active centers as has been found by MacIver (*2*). Above 600°C the activity per site and acid strength (MacIver) decreases. Reasons for both changes in amount and acidity of active sites should be sought in structural changes caused by the heat treatment. Dehydration of the surface at lower temperatures (400–600°C) leads to a decrease of hydroxyl groups and an increase of aluminum atoms in the surface involving a conversion of type B to type A sites. At higher temperatures (>650°C) both types diminish in amount because of recrystallization processes in the surface.

As is shown in Table 1 the conversion of type B to type A sites can also be promoted by neutron irradiation even in a catalyst which was already submitted to a heat treatment by which a nearly optimal formation of type A sites was obtained. Obviously this leads to an increase in total activity (Fig. 2). However, it was found (compare last column in Table 1) that the activity per A site decreases at the same time. Though the irradiation was done with a mixture of slow and fast neutrons in combination with γ radiation it seems most plausible that fast neutrons are responsible for knocking out more oxygen atoms and hydroxyl groups from the surface. The resulting increase of type A sites leads to a higher activity for t.b-2 formation and to an extremely low value for the *cis/trans* ratio. The latter is not changed any more at higher radiation dose, indicating that an equilibrium mixture of the two active sites has been formed.

REFERENCES

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2. MACIVER, D. S., TOBIN, H. H., AND BARTH, R. T., *J. Catalysis* **2**, 485 (1963).

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Surface Properties of Nickel Oxide

The qualitative electronic theory of catalysis, as developed by Volkenstein (*1*), predicts that the position of the Fermi level of a semiconducting catalyst and also its adsorptive capacity depend upon the particle or crystallite size below a certain critical dimension. This Note reports the results of electrical measurements on a series of small particles of NiO and the effect of adsorbed water on these properties.