The Isomerization of Cyclopropane on Zeolites. A Second Mechanism

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Summary Evidence is provided for the existence of a second mechanism for the isomerization of cyclopropane on zeolites, in addition to the Brønsted-acid carbonium-ion mechanism previously postulated.

THE isomerization of cyclopropane to propylene in acids[1] and at the surface of a number of acidic solids,[2] including some zeolites,[3] has been intensively studied in recent years. In all these cases the reaction is believed to be acid-catalysed and to involve proton-donor or Brønsted-acid sites, which are responsible for the formation of a carbonium-ion intermediate.

We have now found that when Linde NaY zeolite, partially exchanged with ammonium ion, is calcined at temperatures between 200° and 700°, two distinct regions of catalytic activity are observed. In the Figure the first-order rate constant for the isomerization of cyclopropane to propylene at 70° is plotted against the activation temperature of the zeolite. Catalyst samples were prepared by exchange with ammonium ion at 80° using standard

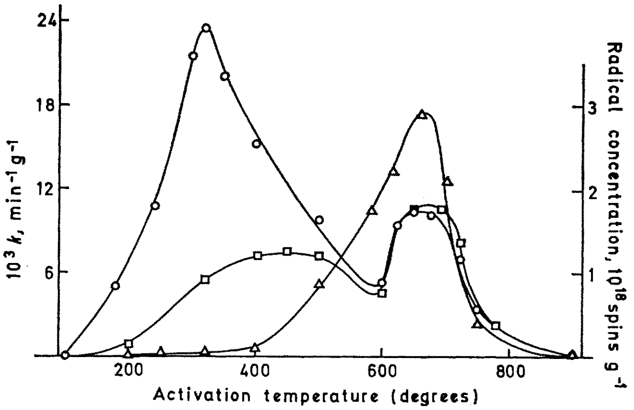

FIGURE. *Rate constant for the isomerization over Y-type zeolite as a function of activation temperature*: 90% *exchanged* (○); 50% *exchanged* (□).

Radical-forming activity of 90% *exchanged zeolite as a function of activation temperature with s-trinitrobenzene as adsorbate* (△).

procedures; over 90% of the ammonia is removed by heating at temperatures above 280° (ref. 4). The lower temperature range, with a maximum at 320°, corresponds to that at which the catalysts possess maximum Brønsted acidity[4] and the mechanism here clearly involves protonic centres. In the higher-temperature range (maximum isomerization activity at 660°), where the Brønsted acidity is low, a different mechanism must operate. The nature of the catalytic site responsible for the activity in samples heated at 660° is uncertain, but it may be significant that at this temperature of activation the electron-donor power, as measured by the formation of trinitrobenzene anion radicals from the adsorbed parent molecule, also reaches a maximum (Figure). The active site may therefore be a Lewis-acid centre or possibly an electron-transfer site of the type responsible for the redox activity of the zeolites.

Support for the view that a second mechanism for the isomerization is involved over zeolite catalysts is found in the values obtained for the activation energy. For samples activated at 320° the Arrhenius activation energy was 16 kcal mole^{-1}, in close agreement with the value obtained for the isomerization over a silica–alumina (12·5% Al_2O_3) catalyst (16 $\pm$ 1 kcal mole^{-1}),[5] whereas on the zeolite samples activated at 660° the apparent activation energy was only 7 kcal mole^{-1}. At temperatures above 700° the crystalline structure of the zeolite is rapidly destroyed, as shown by X-ray examination, and the isomerization activity and electron-transfer power also fall rapidly to zero. The unexchanged sodium Y zeolite was inactive for the isomerization reaction at 70° under any condition of activation. Details of these experiments will be presented elsewhere.

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