Further work is in progress to clarify the relationship between electronic structure and catalytic reactivity.

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Selective Poisoning of Al_2O_3 Catalysts

In connection with fundamental research into the catalytic properties of gamma alumina for the isomerization of the *n*-butenes important information could be obtained from poisoning experiments using triethylamine. An instrument comprising a microreactor with 200 mg of catalyst and a gas-liquid chromatograph was used to determine the activity by means of the pulse technique. With a fresh (conditioned) catalyst three pulses had to be injected into the carrier gas stream before a constant conversion was found. Then small amounts of triethylamine dissolved in cyclohexane were injected in a sequence. After each injection the catalytic activity was measured in the indicated way. The amine strongly poisoned the catalyst while the activity was not affected by the cyclohexane alone.

Typical results obtained with the *n*-butenes on samples of the same catalyst batch are given in Fig. 1a,b,c. In certain parts of the graphs linear relations are found and in some cases the slopes are found to change rather abruptly. The horizontal parts of some curves are due to the fact that interconversion of butene-1 (b-1) and *cis*-butene-2 (c.b-2) is rapid and easily leads to equilibrium compositions. The results seem to show that two points on the horizontal axis are relevant for the different feed materials and reaction products. The original part of the curve valid for formation of *trans*-butene-2 (t.b-2) from b-1 or c.b-2 can be extrapolated to the same end point on the horizontal axis as the curves for conversion of the t.b-2. This seems to indicate that for reactions in which t.b-2 is involved one should distinguish between two types of active centers. The sites which are poisoned selectively from the beginning are active for conversion and formation of t.b-2. The sites which are poisoned in second instance have no activity for t.b-2 conversion and only a limited activity for t.b-2 formation. For the conversion of b-1 and c.b-2 both active centers behave identically.

For the interpretation of the results it seems important to note that t.b-2 because of its structure cannot come with its double bond near to a flat surface. The shortest distance is approximately 1.5 Å as compared to 0.6 Å for the other butenes (*1*). This could mean that certain active centers can easily interact with the π electrons of b-1 and c.b-2 but not with the π electrons of t.b-2. On those sites formation of t.b-2 is

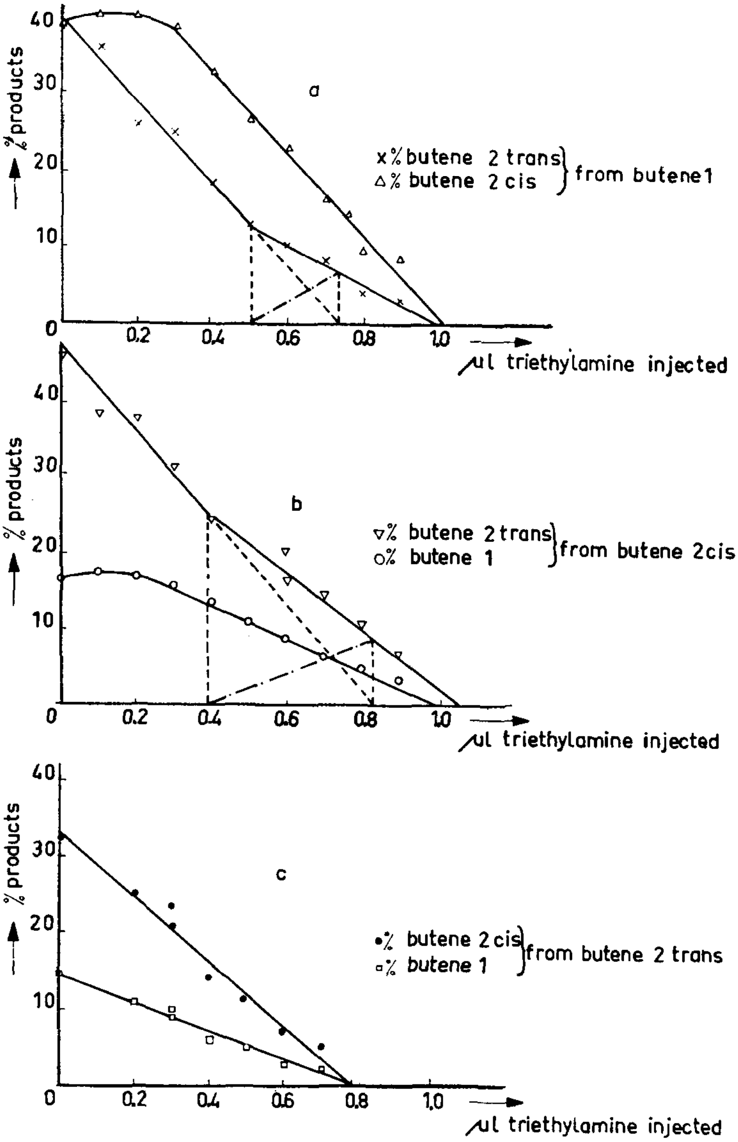

FIG. 1. Products formed on triethylamine-poisoned catalyst as a function of amounts amine introduced. Preheated at 500°C. Reaction temp., 250°C. Pulse experiment. Contact time approx. 1 sec.

perhaps not impossible but will certainly be hampered. Many investigators (*2*) have pointed out that the activity of Al_2O_3 originates from the presence of acid sites with Lewis as well as Brönsted acidic character. Together they form only a small part (approx. 5%) of the surface, the major constituant being oxygen atoms and inactive hydroxyl groups. Because our alumina samples were always brought into equilibrium with water beforehand, the existence in the surface layer of unpaired Al ions with a possible Lewis acid function is highly improbable because they will be covered with water molecules. However, those absorbed water molecules could behave as a type of Brönsted acid sites (type A) which stand out of the surface layer and could be different with respect to acidity from the normal Brönsted acid sites (type

B) which are related to the hydroxyl groups in the surface layer. Moreover, the oxygen atoms will be covered by water at low reaction temperatures (*3*).

It has been suggested (*4*) that double bond shift proceeds in a surface complex through a hydrogen switch mechanism, in which acid sites play an important role in donation and acceptance of protons. Though the proposed mechanism suggests the necessity of two oxygen atoms, it should be indicated that a hydrogen switch under suitable conditions (bond lengths, etc.) could also occur through only one oxygen atom (see Fig. 2). However, from stereo models it can be deduced (*1*) that a hydrogen switch on one oxygen atom can easily occur when starting from b-1 or c.b-2 but not when starting from t.b-2 because of the large distance to the hydrogen atoms involved. This is less so when the oxygen atom in the intermediate stages carries three hydrogen atoms (type A) instead of two (type B). Thus, for the double bond shift of t.b-2 to b-1 two arguments lead to a higher activity of type A when compared to type B centers. For the *trans*-to-*cis* isomerization only the difficulty of approach remains because for this type of isomerization no switch mechanism is necessary (*5*).

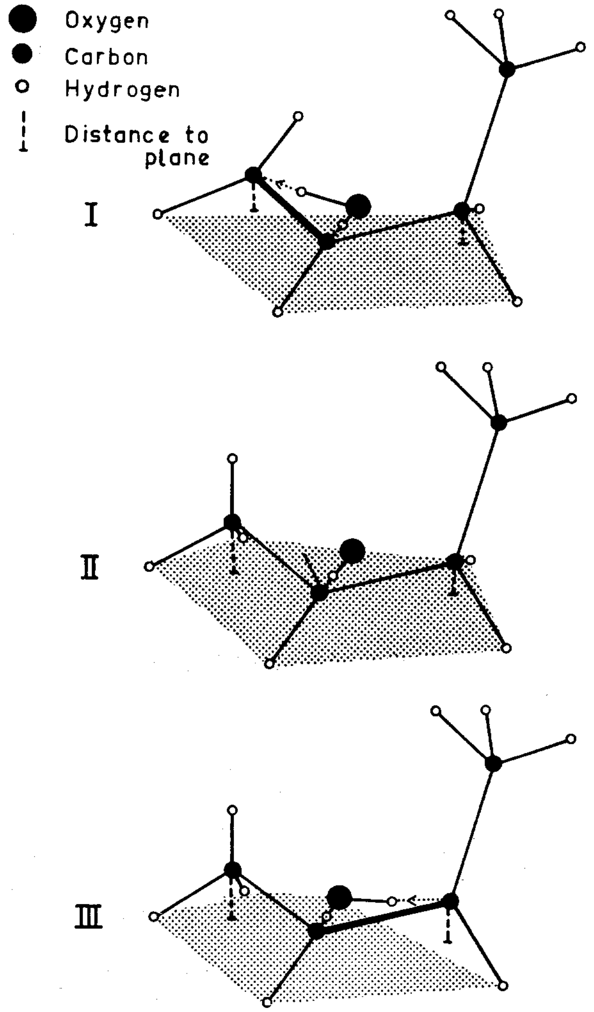

FIG. 2. Hydrogen switch mechanism on one oxygen atom.

In fact this single argument seems to be sufficient for preventing the reaction of t.b-2 on type B sites. On the other hand both arguments seem only to lead to a hampering of the formation of t.b-2 from b-1 on these sites.

Additional experiments were carried out with dried alumina catalysts in which no type A sites should be available. To ensure the exclusion of moisture they were carried out as static experiments necessarily involving high contact times. Under these circumstances the catalyst is not completely inactive for the conversion of t.b-2 as would be expected from the data of Fig. 1c. However, from Fig. 3 it can be seen that the ratio c.b-2/b-1 in the reaction product is extremely high at the relatively short contact times, indicating that the formation of c.b-2 is strongly favored on type B sites. This formation of c.b-2 may either result from longer contact times or from the fact that the surface is stripped of water molecules (preheating temperature 650°C) thus diminishing the difficulty of approach to type B sites. The formation of more b-1 at higher contact times may result from a secondary reaction of c.b-2.

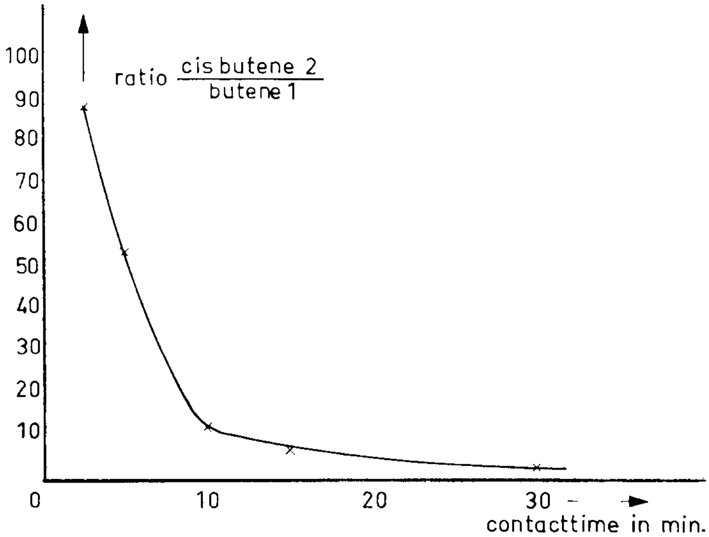

FIG. 3. Conversion of *trans*-butene-2 on a nonwetted catalyst preheated at 650°C. Reaction temperature 100°C. Static experiment.

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