JOURNAL OF SOLID STATE CHEMISTRY 12, 289–290 (1975)

Catalysis over Oxides*

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Received July 3, 1974

It is convenient to classify oxides (loosely) according to their acidic or basic characteristics because these are reflected in their catalytic behavior. Acid catalysis, because of its vast industrial importance, has been more extensively studied than any other single area of catalysis, and is perhaps the best understood. Partly, this is because the reactions fit neatly into the general scheme of carbonium ion chemistry so that the results of an investigation can be cross compared with the vast amount produced by the organic chemist in homogeneous media.

Zeolites and other aluminasilicates are strongly acidic and capable of donating protons to unsaturated hydrocarbons to form carbonium ions. This can be readily demonstrated by their ability to effect the formation of stable ions from substrates such as triphenylmethane or triphenylcarbonol. With the former, the mechanism of this reaction is analogous to a common test reaction used for kinetic studies, i.e., the dealkylation of cumene.

Selectively for gasoline production in the worlds largest catalytic operation, catalytic cracking, depends on the unique limitations of the carbonium ion mechanism. In this operation, a large variety of reactions appear, i.e., all those permitted by carbonium ion chemistry. Thus, the general reaction schemes are known and in recent years studies have been directed towards more subtle questions such as the details of carbonium ion formation, the nature of the acid sites, and the way the reaction coordinates (and therefore the selectivity for product formation) can be altered by changing the composition of the oxide. For this work, simpler reaction systems have been found useful. These include the isomerization of cyclopropane to propylene and the *cis-trans* and double bond isomerization of the *n*-butenes. Tracer experiments with the former have provided a clear picture of the reaction mechanism including all of the steps: adsorption, activation, isotope exchange, and isomerization. With the latter, product selectivity and relative reactivity of the three isomers have been shown to depend on the reaction coordinates. Even the thermodynamic equilibrium constants could be approximated from a rather simple model. Thus, with this reaction, certain criteria for a reaction involving intermediate carbonium ions have been developed. When these were applied to alumina catalysts, it was found that this mechanism cannot apply. For example, in the isomerization of 1-butene, the *cis-trans* product ratios for a carbonium ion reaction cannot vary very much from unity. Over alumina, ratios as high as ten have been reported, and still higher ones have been obtained over ZnO and MgO. In a carbonium ion mechanism, one intermolecular transfer of H must occur in each isomerization step; this was found for aluminasilicates, but over alumina the transfer is intramolecular. Recent experiments by R. J. Kokes with ZnO and alumina suggest that here the mechanism involves an allylic intermediate, and the high *cis–trans* ratios can be explained on this basis. On the other hand, alumina can function as a proton donor when it is required to do so by the reaction mechanism, but only at much higher temperatures than with silica alumina. The isomeriza-

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* Invited paper.

Printed in Great Britain

tion of cyclopropane and the dealkylation of cumene are two such examples.

Alumina also catalyzes another set of characteristic reactions not shown by alumina-silicates. These are the isotope exchange reactions of hydrocarbons and of D_2 with hydrocarbons. Thus, CH_4 will exchange with CD_4 at room temperature and perdeuterio-cyclopropane can be produced by repeated exchange of $c\text{-}C_3H_6$ with D_2 without opening the ring. It has been shown by selective poisoning with CO_2 that these reactions occur on a very small fraction of the surface (~1%) on sites which also catalyze the H_2–D_2 exchange at temperatures as low as −150°C and the ortho–para H_2 conversion at 195°C. These findings, together with results of Plisken and Eischens and of Kokes and co-workers provide some insight into the important problem of the dissociation of H_2 on oxides.