JOURNAL OF CATALYSIS 6, 458–459 (1966)

LETTER TO THE EDITORS

Catalytic Selectivity and Electron Shell Deformation

In a paper (*1*) presented at the Third International Congress on Catalysis the results on decomposition reactions of isopropanol on pure and doped oxides were given. A very marked change in selectivity was already caused by a relatively small amount of sulfate ions. Considering also other experimental data it could be stated as a rule that the more ionic character a catalyst oxide possesses, the more it dehydrogenates, and the nearer the oxide approaches the covalent character, the greater is its dehydrating effect.

The variation of selectivity can be interpreted so that the strength of the hydrogen coupling to nondeformed oxygen ions, in oxides of more positive metals, is great, thus dehydrogenation prevails, while with deformed oxygen ions, in oxides of less positive elements (acidic oxides) it is weak, but strong hydroxyl coupling is possible. Consequently dehydration takes place.

The deformation of the electron shell of oxygen ions is a function of the polarizing power of the cation, which in turn is greater the higher is the charge and the smaller the radius of the cation.

These statements can and must be confined to the surface layer of catalyst only. This follows from the experiments carried out with alumina prepared properly.

Aluminum hydroxide was precipitated from a solution of aluminum nitrate by ammonia. The precipitate was washed most intensively with conductivity water and divided in three parts. The first part was ignited at 450°C, the second at 800°C, finally the third portion at 1200°C. The first sample exerted a full dehydrating effect, with the second the selectivity turned out as 50–50%, and the third catalyst dehydrogenated up to 100%.

The X-ray pattern of the first catalyst showed an amorphous structure without any crystalline phase, while the diffractograms of the second and third samples were fully identical, proving the very same crystalline structure. The variation in catalytic activity resides in the surface layer only.

This was proved by taking the reflection spectra in the far ultraviolet. Although the total amount of reflection, i.e., the full fluorescence light, was measured by Unicam SP 500 spectrophotometer, the difference in reflectivity shows unequivocally that a smaller amount of reflected light, i.e., greater absorption and thus greater deformation of electron orbitals of the dehydrating sample, is a direct proof of the above considerations on the origin of selectivity.

These experimental results point to the fact that besides the electronic factor which is based on the theory of disorder of semiconductors another mechanism must also be considered which is controlled by the deformation of the electron shell, i.e., by the affinity to the proton. These are the Lewis-type acid-base catalysts. Assuming this difference in electron surface densities there is no need to be concerned with the concept of Bronsted's acids.

A throughout examination of these effects is now in progress.

REFERENCE

1. BATTA, I., BÖRCSÖK, S., SOLYMOSI F., AND SZABÓ, Z. G., *Proc. Intern. Congr. Catalysis, 3rd, Amsterdam, 1964,* pp. 1340 (1965).

Z. G. SZABÓ

Reaction Kinetical Research Group
Hungarian Academy of Sciences
Szeged, Hungary

Received August 16, 1966