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LETTERS TO THE EDITORS

Redox Processes and Lewis Acid–Lewis Base Reactions on Oxide Surfaces

Lewis (*1*) defined acid–base reactions as those in which an unshared electron pair in the base molecule is accepted by the acid molecule with the formation of a coordinate covalent bond. The reaction of boron trifluoride with ammonia to form the complex H_3N–BF_3 provides the classical example of a Lewis acid–Lewis base reaction. The equivalent reaction on an alumina surface would be the adsorption of ammonia when a dative covalent bond binds the adsorbed molecule to the oxide surface (*2*). No unpairing of electrons occurs in this adsorption process and no electron spin resonance (ESR) signal is observed.

Strong ESR absorption has been detected when various aromatic hydrocarbons and amines are adsorbed on certain oxide surfaces, indicating the presence of radical species [see, for example, refs. (*3*, *4*)]. The active centers in these reactions have usually been referred to as Lewis acids (*3*, *5*). This broadening of the original acid–base concept, as proposed by Lewis, is not only undesirable but also confusing. We believe that in the field of adsorption chemistry a clear distinction should be drawn between Lewis acid–Lewis base reactions (adsorbed species remains spin-paired) and processes involving one-electron transfers, which are essentially redox reactions. A similar point was made by Professor Szabó (*6*) in a discussion at the Amsterdam Conference on Catalysis, but it seems to have escaped attention.

Adsorption of perylene on a partially dehydrated alumina surface, in the presence of molecular oxygen, gives rise to a strong partially resolved ESR signal, attributable to the perylenium cation (*4*). After a short period the original hydrocarbon cannot be desorbed from the surface. The oxidation process, which involves a one-electron transfer to the surface, is followed by chemical interaction between the adsorbate and oxygen and this leads to oxygenated species. On the other hand, adsorption of tetracyanoethylene or trinitrobenzene on an alumina surface produces electron transfer in the opposite direction, radical anions being obtained (*7*). Oxidation-reduction reactions also occur on the surface of a silica-alumina catalyst (*3*, *5*), and from infrared studies there is evidence that chemisorption of strong bases, such as ammonia, can occur through coordination of the molecules with Lewis acid sites (*8*). On the mixed oxide surface Bronsted acid–Bronsted base reactions are, of course, well known. Polymerization, alkylation, and cracking reactions catalyzed by silica-alumina all involve proton transfer (*9*).

In the field of catalysis the use of the Lewis and Bronsted concepts of acids and bases is usually unambiguous. The confusion that has arisen between Lewis acid–Lewis base reactions and redox processes probably stems from the tendency to refer to Lewis acids as electron acceptors and Lewis bases as electron donors. This is entirely correct provided it is clearly understood that a partial two-electron transfer is involved. Whether the same surface site is involved in both the Lewis acid–Lewis base reactions and the one-electron redox processes or whether different surface sites are responsible remains uncertain.

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Mossbauer Effect Spectra of a Supported Iron Catalyst*

The Mossbauer effect spectra of silica gel and alumina impregnated with iron and calcined in air have been reported by several authors (*1–3*). These samples were studied "as prepared" without any control of the environment. We wish to report some initial work on the application of the Mossbauer effect to the study of the structure of an iron-on-silica-gel catalyst in both the oxidized and reduced state.

A catalyst was prepared by impregnating Davison 923 silica gel with sufficient ferric nitrate solution enriched in iron-57 to produce a 3 wt % iron-on-silica-gel sample. This catalyst was placed in a thin-window glass cell and calcined in oxygen at 500°C for 16 hr. The Mossbauer effect spectrum after outgassing the calcined sample is shown in Fig. 1. It is similar to spectra reported by others, except for an unusually large quadrupole splitting of 1.87 mm/sec. Kündig *et al.* (*3*) prepared a series of iron-on-silica-gel samples in a manner similar to ours, but varied the crystallite size of the ferric oxide on the surface by varying the concentration of the impregnating solution. They found that the quadrupole splitting increased from 0.44 mm/sec for α-Fe_2O_3 crystallites with an average diameter of 180 Å to 0.57 mm/sec for those with an average diameter of 135 Å. A rough extrapolation of their data suggests that the α-Fe_2O_3 crystallites are about 20 Å in diameter in this sample. However, the electric field gradient responsible for the quadrupole splitting is sensitive to the geometrical and defect structure of the crys-

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