JOURNAL OF SOLID STATE CHEMISTRY 12, 282 (1975)

Infrared Studies of the Surface Chemistry of Oxides*

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Received July 3, 1974

Many of the striking advances in structural chemistry since 1900 have been achieved by the use of spectroscopic techniques. Early in the century, the discovery of X-rays enabled the first detailed study to be made of crystals at an atomic level.

Infrared and Raman spectroscopy, from initially being entirely in the domain of the physicist, came to be used in the decade 1930–1940, by chemists for structural determination of a very wide range of molecules, both inorganic and organic. These techniques had the singular advantage that they could be used to study matter in all phases (gas, liquid, and solid), without restrictions as to degree of order or size. Also in this period, some application of electron diffraction was made to chemical and surface problems, but this technique suffers, in general, from the double disadvantage that in addition to similar degrees of order being needed as in X-ray work, the sample has to be studied under vacuum conditions.

Extensive development in high frequency radio techniques took place under the pressure of radar development during World War II. These techniques became of chemical interest when physicists studying the nuclear magnetic resonance (NMR) of certain nuclei (e.g., H_2, Al, Si, P, etc.) found that these resonances were affected by the electronic structure of the molecule surrounding the resonating nucleus, and dubbed these changes the "chemical shift." The discovery of this small frequency shift has given birth to an extensive development of NMR as applied to chemistry, initially restricted to the protons in organic compounds, but later, other nuclei were studied. Electron spin resonance (ESR) has a certain similarity in experimental techniques to NMR, and is much more sensitive, but is restricted to situations where unpaired electrons occur in the molecule.

Of all these techniques, that of ir spectroscopy has been found to have the widest application to surface phenomena at oxide interfaces. It is one of the most direct means of detecting and defining the interactions and perturbations that occur at the surface of the solid during the adsorption process. In addition, it can determine the structure, chemical nature, and physical state (e.g., rotational freedom) of the adsorbed phase for a very wide range of molecules.

Experimental techniques involved the application of ir spectroscopy to the surface chemistry of oxides will be discussed.

Examples will be given of the type of information that can be obtained about the surfaces of finely divided oxides such as silica, alumina, titania, and crystalline aluminosilicates (zeolites).

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* Invited paper.

Printed in Great Britain