DETERMINATION OF THE ACIDITY
OF CATALYSTS BY THERMOADSORPTION WITH
A CYCLIC TEMPERATURE PROGRAM

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A novel method is described, consisting in the determination of admolecules which are the most loosely bonded on the surface. This permits a better characterization of active centers on catalysts.

Surface acidity, understood as the ability of the surface to carry out a catalytic process selectively, seems to be a complex function of chemical composition and electronic structure. Such parameters as proton and OH-group concentration, adsorption, heat of adsorption, free electron number or surface inner-shell electron binding energy are measured instead of acidity. This is the reason for the great variety of methods in the field and usually the poor consistence of results.

There are also other factors causing discrepancies of results, such as e.g., changes in chemical composition followed by the standardization. Moreover, a shift of defect equilibrium and a departure from stoichiometry are sometimes present in oxides. These parameters can hardly be controlled, giving various states of the surface to be examined. Owing to the factors mentioned, neither the concentration nor the energy distribution of active centers can be determined precisely. The acidity, taken as

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the result of an experiment, does not characterize unequivocally the surface and therefore it cannot be the measure of catalytic activity, but can be correlated with it. Catalytic activity, as we believe, does not depend on the presence of all adsorption sites but only on a selected set of them. Each member of this set has a definite composition of neighbors, with which it may form a surface complex.

The distinct feature of the method presented is its ability to determine, not all admolecules, but only a definite group of them, which in the given conditions interact dynamically with the catalyst surface.

EXPERIMENTAL

The experiments were performed in a standard vacuum system (Fig. 1). Finely ground samples of catalysts with a total surface area of 1 m² were spread on the reactor walls in the form of a thin layer. They were then subjected to thermal and vacuum treatment according to a program and depending on their chemical properties. After standardization, a program of periodical temperature changes was switched on with a frequency chosen in the 6–10 cycle/h range, and a definite amount of ammonia was admitted to the measuring chamber. The initial pressure of NH₃ was usually about 10⁻² Torr. Periodical changes of pressure following the programmed temperature changes were then recorded (Fig. 2).

Resulting from the measurement, the number of NH₃ moles interacting with 1 m² surface is proportional to the number of acidic centers active in catalysis. With regard for present terminology and for the sake of convenience, the value thus determined will be called "acidity" in the text to follow.

According to our expectation, it has been found that the acidity (pressure amplitude) depends on the average total pressure chosen for the experiment, decreasing with the increase of total pressure. For this reason, all experiments were performed in a pressure range with only a slight dependence on the total pressure. The acidity appeared to be independent of the frequency.