Adsorption Measurements during Surface Catalysis

By Kenzi TAMARU

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It is one of the most fundamental problems in the field of surface catalysis to estimate the area of active part on catalyst surface. Since Taylor suggested his "active center theory" in 1925, many discussions have been presented from various view-points on the problem. Taylor emphasized that certain centers on the catalyst surface were responsible for most of the catalytic activity. These centers were tentatively identified as the corners and edges of the crystals in the surface. Other interpretations associated them with the existence of a number of different crystalline faces on the catalyst, each face having its own specific catalytic activity. The area of these active regions should accordingly be all extremes between the case in which all the atoms on the surface are active and that in which relatively few are active.

This short note is to emphasize a new approach to elucidate the mechanism of the catalytic reaction as well as the number of active atoms on the catalyst surface, measuring the adsorption during surface catalysis.

Recently it has been shown[1-4] that during the catalytic decomposition of germane (GeH_4) on germanium surface, which is a zero order reaction, the germanium surface is mostly saturated with chemisorbed hydrogen atoms. On the other hand it was also shown that the adsorption of hydrogen on germanium is an activated, reversible, dissociative and immobile adsorption, and also that if the chemisorbed hydrogen is supplied from the ambient hydrogen gas, the coverage of the surface in the adsorption equilibrium should be less than 0.6 under the experimental condition of the decomposition. From other data such as, for instance, obtained with deuterium and germanium deuteride, it was concluded that the desorption of chemisorbed hydrogen from the germanium surface is a rate-determining step of the overall decomposition reaction. All the evidence[1,3,5] seemed to indicate that the clean surface of germanium laid down by the decomposition of the hydride appeared to behave homogeneously energetic as to sites in the decomposition of the hydride, the major part of the germanium atoms on the surface participating in the catalysis.

It was thus suggested that the adsorption measurements during catalytic reaction would associate not only with the elucidation of the reaction mechanism, but also with the approximate estimation of active area of the catalyst surface, especially in the case of immobile adsorption.

When we study the kinetics of gas reaction on a solid catalyst, we elucidate the reaction mechanism, in most cases, on the basis of Langmuir-Hinshelwood, or sometimes, of Eley-Rideal mechanism, tacitly assuming that the elementary steps other than the rate-determining steps are all in equilibrium. The coverage of the surface to be guessed from the kinetics is that on the active part of the catalyst surface where the catalysis is actually taking place, and these coverages are not always the same with those derived from the adsorption equilibrium with the ambient gases, but are dependent upon the mechanism of the reaction, or the rate-determining step of the reaction, because of the free energy change accompanied by the reaction. This is the reason why the germanium surface is saturated with the chemisorbed hydrogen during the decomposition reaction, while the hydrogen adsorption equilibrium only covers less than sixty per-cent of the surface under the pressure.

If the adsorption on catalyst surface could be measured during reaction and the results were far from that on the active part which have been guessed from the kinetics, then we might consider that the active part on the catalyst surface which participates in the catalysis is a minor part of the surface. For instance, if a reaction is exactly zero order, it suggests that the active part of the catalyst surface is saturated with such things as reactants, products or intermediate compounds, the adsorption being independent of the ambient gas pressures. When the adsorption measurements during the reac-

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[1] K. Tamaru, M. Boudart and Hugh Taylor, *J. Phys. Chem.*, **59**, 801 (1955).

[2] P. J. Fensham, K. Tamaru, M. Boudart and Hugh Taylor, ibid. 806 (1955).

[3] K. Tamaru and M. Boudart, "Advances in Catalysis," Vol. IX Academic Press Inc., N.Y., p. 699 (1957).

[4] K. Tamaru, *J. Phys. Chem.*, **61**, 647 (1957).

[5] K. Tamaru, ibid., **60**, 612 (1956).

tion, however, would show the adsorption appreciably dependent upon the ambient gas pressure, it suggests that the active region is a minor part of the surface, and from the pressure-independent adsorption we could not only guess the area which participates in the catalysis, but also determine what actually saturates the active part, which suggests the rate-determining step of the overall reaction. On the other hand, if the adsorption is immobile and all the surface is saturated throughout the reaction, it suggests that all the surface is taking part in the catalysis, when the saturation does not result from the adsorption equilibrium of any of the ambient gases, as in the case of germane decomposition.

If the chemisorption of A in the catalytic reaction, $A+B\rightarrow C$, is rate-determining, the adsorption of A will not be observed during the reaction except the physical adsorption and the back-adsorption from C such as $C\rightleftarrows B(\text{ads.})+A(\text{ads.})$. The ammonia synthesis would be an example of this kind, as the chemisorption of nitrogen on the synthesis catalyst is generally accepted to be rate-determining.

Thus the new approach to measure the adsorption during catalytic reaction in addition to the separate measurements of each gas might enable us to attain a much better understanding of the mechanism of catalytic reaction as well as the nature of the catalyst surface. In most discussions of surfact catalysis it is tacitly assumed that the equilibrium case applies except the rate-determining step. We can also find with this new approach whether it is the case.

The adsorption measurements during reaction can be carried out in a closed circulating system in a similar way to those of the mixed adsorption. From the amount of the reactant introduced in the system and the pressure and the composition of the circulating gas, we can calculate the adsorbed amount of gases on the catalyst surface. The amount of catalyst is preferably large for accurate measurements and the adsorption should be measured under such conditions that the reaction takes place very slowly; otherwise the composition of the circulating gas will not be practically the same throughout the system and it might be affected by the heat of the reaction in the reactor.

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Department of Chemical Industry
Facluty of Engineering
Yokohama National University
Minami-ku, Yokohama