

well as many memorable works by I. LANGMUIR and his collaborators. During the same period innumerable catalytic reactions have been discovered, among which are to be specially noted those achieved by REPPE or ZIEGLER.

When we turn to the theory of heterogeneous catalysis, however, a serious question remains to be explained: Has any single remarkable reaction ever been predicted by the current theory of heterogeneous catalysis? Has any theory been developed taking practical problems fully into account, such as the search for new catalysts or the preparative techniques of practical solid catalysts? In this sense the current theory of solid catalysts based on the adsorption mechanism is open to criticism. The authors would like to find the reason for this in the following fundamental postulate, which is still widely prevalent among scientists on catalysis: "the working field of solid catalysts is the two-dimensional, unchangeable surface".

Apart from the many evidences to be given in the succeeding paragraphs, the above assumptions should be denied purely from logical reasons, as stated below:

1) Any solid catalyst is exposed to the attack of reactants, having equal chances of participating in the reaction as the reactants outside. When the catalysts suffer no change, there should be some special reason, unless the catalysts are too inactive. The authors would like to find the very features of catalysis in this special reason.

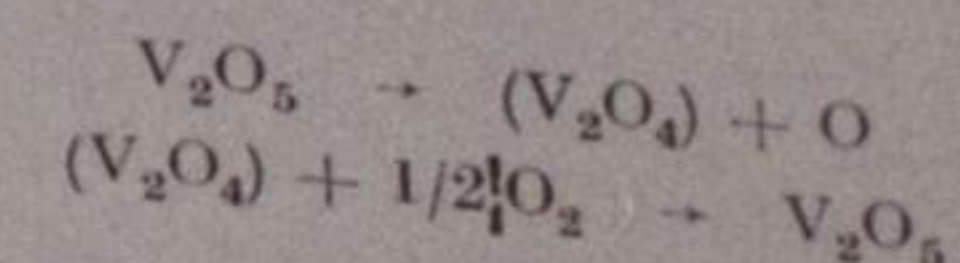
2) There should be some common factor between homogeneous and heterogeneous catalysts, when considered as equally "catalytic". We would like to find this factor in the fact that the catalysts are reactive in general but, nevertheless, apparently unchangeable.

3) The true mechanism of solid catalysts should, however complicated it might be, not be outside the scope of chemical reaction mechanism. Then there should exist some way of predicting the adaptability or activity of solid catalysts. This, to some extent, is actually the case with homogeneous catalysts.

4) Solid catalysts are, as is well known, extremely sensitive to defect structure. This suggests the important role of the defect solid states. The current theory, however, takes these factors only poorly into consideration. The only exception is the semiconductor theory of solid catalysts. Even in this case the motions of atoms or ions are neglected, only the behavior of electrons being considered. A new approach is desirable from the solid side, using the modern theory of defect solid states and solid phase reactions.

5) It is thought to be very difficult for the time being to find every detail of the structures and processes in the adsorption layer of catalysts,

because the mechanism is not yet completely known even in the oldest and most familiar reactions, such as the combustion of hydrogen and hydrocarbons. On the other hand we should pay attention to the following facts in attacking the problem of solid catalysts. Vanadium pentoxide is a universally effective catalyst for the oxidation of inorganic and organic substances, such as  $\text{SO}_2$ , naphthalene, etc. This fact suggests that no special steric relations are required between  $\text{V}_2\text{O}_5$  and oxidizable substances. Further, naphthalene is oxidized to phthalic acid also in the liquid phase by various homogeneous oxidants, such as chromic acid or conc.  $\text{H}_2\text{SO}_4$  containing mercury. This fact suggests again that any substance (naphthalene in this case) requires, in general, no special steric relations to its oxidants. In a word, the oxidation takes place actually in any combination of oxidants and reductants, provided that an oxidant has a sufficient potential both in the thermodynamic and in the kinetic sense. Fine structures of the reaction, including the steric relations between the reactants and catalysts, come into question only when we treat the higher order characters, such as the selectivity of catalysts. In this example, therefore, it will suffice to show that the essential cause of catalytic activity of  $\text{V}_2\text{O}_5$  lies in its capacity to activate molecular oxygen, and not in how  $\text{SO}_2$  or naphthalene adsorbs on  $\text{V}_2\text{O}_5$  catalyst. A way to show the adaptability of  $\text{V}_2\text{O}_5$  for activating molecular oxygen is to show the ease of the following two reactions:



In this expression  $(\text{V}_2\text{O}_4)$  means  $\text{V}_2\text{O}_5$  containing oxygen ion vacancies. The authors would, therefore, like to search for an alternative to the current way of attack based on the adsorption mechanism. A new postulate is made here, where the solid catalysts are treated as solid reactants, through which it has become possible to predict the adaptability in some simpler cases.

## II. TWO FACTORS OF CATALYTIC ACTIVITY

As is well known, we do not use silica as the catalyst for hydrogenation, nor  $\text{CaF}_2$  for the oxidation of  $\text{SO}_2$  or  $\text{CO}$ . The answer to this is not necessarily self-evident, but our chemical common sense suggests that these catalysts are lacking in "adaptability" for the respective reactions. We should, thus, first consider the "adaptability" of the catalyst. When the adaptability of a catalyst is very great, it is intrinsically suited to that reaction. We shall call this kind of catalytic activity "the material factor" of the catalytic activity. We have, however, another factor for the catalytic