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MIXED CATALYSTS[1]

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It has long been known that the presence of certain substances (*promoters*) in a given catalyst increases its activity. But to explain how they influence a catalyst in a given reaction presents innumerable difficulties. Unrelated facts, generally observed by accident, have trickled drop by drop into the body of this science to form the mass of data on which various people have based various explanations of this phenomenon. Most of these have been inspired by the physical changes which take place. Because the rate of chemical reaction depends on the area of the surface of the catalyst, scientists saw in the promoters a means of increasing the surface of the catalyst, and thereby either increasing the amount of active center or preventing the growth of crystals in the catalyst. No one paid much attention to the possibility of the promoters taking part with the catalyst in the rate of reaction, because it was not established that the catalyst itself could produce a definite chemical reaction with a catalyzed substance under suitable conditions (namely, such reactions as would agree with its chemical function). So, in order that one might see "chemism" in catalytic chemical reactions, and, with its help, try to understand them, it was necessary to discover a series of new reactions and their corresponding catalysts. Then by comparing the chemical properties of the catalyst and the substance on which it is to work, we can begin to understand the chemical reaction which will take place. This new knowledge will allow us soon to classify catalysts according to their catalytic actions based on their

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[1] Willard Gibbs address, given at a meeting of the Chicago Section of the American Chemical Society, May 25, 1940.

chemical properties. The last forty years have already given us such a wealth of experimental data on chemical reactions that even now we are able to make certain predictions on the choice of a catalyst for a given reaction.

There exist to-day various physical-chemical theories which try to explain catalytic processes by the aid of the electron theory, ion theory and others. I do not dispute the benefits to be derived from such investigations, but it is my contention that we chemists must first investigate the chemical properties of catalysts, both simple and mixed, in order to understand the processes occurring from the chemical point of view. This was the purpose of our last work, and I want to tell you about some of the more interesting results obtained by us.

In many cases the role of a promoter can be explained only on a chemical basis. The case of aluminum chloride, hydrogen chloride, may be cited. Pure aluminum chloride is not a catalyst for alkylation unless hydrogen chloride is present, either added as such or formed *in situ*. Working with Drs. Pines and Schmerling,[2] I have shown that this is due to the fact that the hydrogen chloride is necessary for the formation of hydrogen aluminum tetrachloride, which is the true catalyst for the reaction.

The significance of the influence of the mixed catalyst nickel oxide and alumina, which I discovered in 1910–12,[3] on the rate of catalytic hydrogenation opened a new page in the field of catalysis. The mixed catalyst nickel oxide and alumina further catalyzes the hydrogenation of camphor, fenchone, and other saturated cyclic ketones because alumina dehydrates the intermediate alcohols into unsaturated hydrocarbons which are much easier to hydrogenate than the original ketones.

The new investigations made by Drs. Corson, Kurbatov and myself[4] showed that sometimes it is necessary to add only a very small amount of one catalyst to another of the same type to increase greatly the activity of the latter. We have made a number of systematic experiments with mixed catalysts containing reduced copper and different oxides, mostly chrome oxide, studying the hydrogenation of benzene and isopentene under ordinary pressure and 225° C. Under the test conditions, both of the pure components—copper and chromium oxide—were inactive, but as chromium oxide was added to copper, the activity rose abruptly to a maximum at 5 per cent. of oxide, and then fell with continued addition. We propose to call this composition of maximum activity the *eucoactic* composition. It will be interesting in the future to study the dependence of the eucoactic composition upon the type of unsaturation and upon the operating conditions. Another problem for future study concerns poisoning and heat of deactivation as a function of chemical composition.

The subject becomes more complicated when we add a third substance, nickel, to this mixed catalyst. Our former experiments had established that nickel, with the carrier kieselguhr (70 per cent. Ni: 30 per cent. Si), can completely hydrogenate benzene at 50° C and one second contact time at ordinary pressure, and that neither copper nor chrome oxide, the components of the mixed catalyst, is able to produce this reaction even slightly. When copper and chrome oxide are mixed in proportions of 95 per cent. copper and 5 per cent. chrome oxide (eucoactic at 225° C), this mixed catalyst will hydrogenate benzene 16 per cent. in 90 seconds contact time.

Mixed copper chromium oxide catalysts are even more susceptible to activation by traces of nickel than copper alone. For instance, copper containing not more than 0.001 per cent. of nickel does not hydrogenate benzene at ordinary pressure and 225° in ninety seconds, and the presence of 0.005 per cent. of nickel raises the hydrogenation to 4 per cent. On the other hand, the hydrogenating activity of the 95 per cent. copper, 5 per cent. chromium oxide, is raised from 16 per cent. to 24 per cent. by the addition of 0.005 per cent. of nickel.

Another example of this amplifying effect is the following. The addition of 0.2 per cent. of nickel raises the hydrogenating activity of copper from 0 to 19 (per cent. hydrogenation of benzene at ordinary pressure and 225° C in a contact time of twelve seconds), whereas the same addition of nickel raises the activity of the 95 per cent. copper, 5 per cent. chromium oxide catalyst, from 2 to 62.

Dr. Corson and I[5] also studied the performance of fourteen series of mixed copper catalysts containing different metal oxides. These catalysts were carefully made from reagent chemicals, and several compositions in each series were determined by spectrum analysis. Evidently there are many substances which, although catalytically inactive alone, possess the property of activating copper for the hydrogenation of benzene. Our experimental data show that one of the most important is that in studying catalytic reactions from a physical-chemical point of view, it is necessary to pay special attention to the purity of the catalyst. Pure copper, containing 0.001 per cent. nickel as determined by spectro-analysis, is not able to hydrogenate benzene at all under the conditions of 225° and ordinary pressure and a great contact time.

Our calculations show that when copper contains 0.001 per cent. nickel, one atom of nickel is surrounded

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[2] Ipatieff, Pines and Schmerling, *Jour. Org. Chem.*, 5: 253, 1940.

[3] Ipatieff and Matov, *Ber.*, 45: 3205, 1912.

[4] Ipatieff, Corson and Kurbatov, *Jour. Phys. Chem.*, 43: 589, 1939; 44: 670, 1940.

[5] Corson and Ipatieff. (In publication.)

by 90,000 atoms of copper, and benzene can not be hydrogenated under ordinary pressure. If we increase the nickel content to 0.002 per cent., where one atom of nickel is surrounded by 45,000 atoms of copper, we can detect a slight addition of hydrogen to benzene. With the nickel content 0.02 per cent., the proportion of copper to nickel atoms being 4,500 to one, benzene is hydrogenated 2.5 per cent. In the same contact time, if nickel is increased to .1 per cent., corresponding to 900 atoms of copper to one of nickel, the hydrogenation of benzene reaches 10 per cent.

In our experiments on the hydrogenation of benzene in the presence of reduced copper, we used Dr. Hahn's method of emanation for the study of the dependence of the activity of a catalyst on its surface area. The data without doubt are very interesting, but we consider them only as preliminary experiments, and can draw from them only limited conclusions. It was established that the addition of alumina or chromium oxide to copper brought about a considerable increase in emanating ability and, therefore, a considerable increase in surface. In order that a catalytic process would go like any other chemical process, it is necessary that the energy given out be able to prepare the neighboring molecules to go into the reaction and that this repeat itself indefinitely; then the catalyst will fulfill the role of *multi-actor*. The activating energy of a catalyst can be very great, but it will not be able to work if conditions will not be suitable for its action.

On the other hand, a catalyst with not much activating energy will be able to produce a desired reaction if the external energy be transformed into chemical energy which has a sufficient factor of tension. It is also necessary that this energy does not disperse but is handed on to the neighboring molecules with a sufficient factor of tension so that the reaction will continue.

THE POISONS OF CATALYSTS

Chemical literature contains many articles concerning the deactivation of catalysts from which we can draw one indisputable conclusion. The amount of a substance which can poison a catalyst can be so small that a molecular film will not cover the catalyst completely. A hypothesis was made on the basis of these data that only the active centers of the catalyst are poisoned, and this explanation, in turn, was used to confirm the existence of such centers in the catalyst. I do not intend here to criticize this hypothesis, nor the necessity of introducing such a term for the explanation of catalytic reactions, but I, nevertheless, believe that molecules of different chemical constitution will always be found in a catalyst. If the catalyst is a reduced metal, it will also contain the metal oxides (as shown by many analyses); if the catalyst contains metal oxides, then some of its molecules will be metal hydrate oxides, etc. On the basis of my theory of catalytic processes, these molecules having a definite composition will serve as initiators of definite chemical reactions if the conditions will be suitable for this process. For example, only the presence of definite amounts of a particular hydrate of alumina oxide in an alumina catalyst will give this catalyst the ability to take water from alcohols with the theoretical yield at low temperatures. The same thing can be said about the presence of metal oxides in reduced metals and their hydrogenating activity.

A catalyst poisoner being introduced in negligible amounts can stop the action of a catalyst by weakening or paralyzing the action of the molecules producing a given process, in consequence of which the neighboring molecules will not receive a sufficient amount of energy and the process will choke.

We saw earlier that the addition of a minute amount of nickel to the mixed catalyst copper chromium oxide greatly increased its activity. But this mixed catalyst can lose its activity in part or completely, if we add to it a small amount of other substances such as lead, cadmium, bismuth, certain salts, etc. Dr. Corson and I studied the poisoning effect of several metals and salts on two mixed catalysts: copper-nickel and copper-chromium-oxide, under ordinary and high pressure. We took two catalysts for our study in order to show that a mixed catalyst activated by the addition of chromium oxide is better able to resist the action of poisons.

We took the hydrogenation of benzene as the reaction for our study of the poisoning of catalysts. The following table shows our results using 99.8 per cent. copper and 0.2 per cent. nickel as the catalyst, and bismuth, cadmium and lead as poisons.

TABLE 1

POISONING EFFECT OF BISMUTH, CADMIUM AND LEAD ON COPPER AND NICKEL CATALYSTS

Poison wt. per cent.	Hydrogenation of benzene wt. per cent.		
	Bismuth	Cadmium	Lead
0.0	19	19	19
0.00001	16	20	28
0.0001	15	20	27
0.001	17	18	24
0.01	10	13	16
0.1	3	3	2
0.2	0	0	0
1.0	0	0	0

Conditions: T. 225°; C.T. 12 sec.; H_2/C_6H_6 7 Pressure: Atmospheric

At ordinary pressure, 0.1 to 0.2 per cent. of bismuth, cadmium or lead deactivates 99.8 per cent. copper and 0.2 per cent. nickel almost completely. Below 0.1 per cent. concentration, bismuth and cadmium have no effect, whereas lead functions as a weak promoter. This interesting behavior of lead was checked several times with different catalyst preparations so as to make sure of the facts.

An alternative method is to study the poisoning effect under more severe conditions of time, temperature and pressure, choosing such conditions that pure copper may show sufficient activity to allow evaluation of the poisoning effect. The results are shown in Table 2.

TABLE 2

CATALYST COPPER POISONING BY BISMUTH, CADMIUM AND LEAD

Poison wt. per cent.	Hydrogenation of benzene		
	Bismuth	Cadmium	Lead
0.000	33	33	33
0.005	21	6	5
0.05	6	1	1
0.5	2	0	0
1.0	0	0	0

Conditions: T. 350°; reaction time: 12 hours; charge 50 cc of benzene, 5 gr catalyst, 100 atms of hydrogen; Apparatus: 850 cc Ipatieff rotating bomb with glass liner.

As may be observed, we obtained the same picture with poisoned copper at superatmospheric pressure as at ordinary pressure with poisoned 99.8 per cent. copper and 0.2 per cent. nickel.

We previously reported that nickel is more effective in the activation of 95 per cent. copper, 5 per cent. chromium oxide, than of pure copper. Table 3 shows the effect of lead on the activity of this catalyst.

A comparison of the data of Tables 1 and 3 shows us that 0.1 per cent. of lead lowers the activity of the nickel-promoted 95 per cent. copper, 5 per cent. chromium oxide, from sixty-two to twenty-three (63 per cent. drop) and that of nickel-promoted copper from 19 per cent. to 2 per cent. (90 per cent. drop).

TABLE 3

POISONING OF COPPER CHROMIUM OXIDE NICKEL BY LEAD

	Hydrogenation of benzene wt. per cent.
Copper	0
" – 5 per cent. Cr_2O_3	2
" – 5 " " Cr_2O_3 – 0.2 per cent. Ni	62
" – 5 " " Cr_2O_3 – 0.2% Ni	62
" – 5 " " Cr_2O_3 – 0.2% Ni – 0.1% Pb	23

Conditions: T. 225°; C.T. 12 sec. H_2/C_6H_6 7 Pressure: Atms.

As a result of these investigations with mixed catalysts containing activating and poisoning substances, we can make the following remarks. Our preliminary survey emphasizes the extreme delicacy of catalytic processes and the necessity of careful definition of purity before drawing conclusions as to the catalytic properties of any particular element of a catalyst. The sensitivity of the system benzene-hydrogen-copper competes with the spectroscope in the detection of traces of nickel, bismuth and cadmium, and it goes beyond the range of the spectroscope in its sensitivity to traces of lead. Therefore in the case of lead, at least, spectroscopic purity is no guarantee of catalytic purity, which means that in order to introduce into the catalyst traces of different promoters or poisons, it is necessary to prepare the catalyst by a special method to be sure of its composition.

In conclusion, I wish to state that for a thorough investigation of the mechanism of catalytic reaction it will be necessary to apply all the chemical and physical tools at our disposal.

VIRUSES AND THEIR PART IN DISEASE

By Professor W. G. MACCALLUM

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WHILE we are very familiar with the details of the lives of animal parasites, fungi and bacteria which invade and live and develop in the tissues of other animals and plants, producing diseases and stirring defensive reactions, all consistent with their living activities and with those of the invaded hosts, there are many other diseases, both of animals and plants, in which the invading agencies have only recently been recognized. This is because they are so minute as to escape all our ordinary means of making such things visible or evident through most of our usual methods of study, but recently new methods have been devised which afford enough information to reveal a whole world of extraordinary active contenders for propagation at the expense of the living creatures with which we have been familiar. These are the viruses, so-called because of their harmful effects, but not yet sharply classified into groups since they vary so much in character, such as size and life history, that these subdivisions have not been completed. Some, such as those which cause typhus fever and related Rickettsia infections or those found in smallpox and vaccinia, are distinctly visible as very minute granules and can be traced in their relationship with the cells of the infected tissues, so that there is some question as to whether their nature may not be closer to that of the bacteria than is the case with other viruses which are so minute that they can never be seen.

But the matter of size, which in most cases is such as to allow the viruses to pass through a filter which has pores so small that no bacteria can pass and which has given rise to the name filterable viruses, is obvi-