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ADSORPTION AND CATALYSIS IN CARBON MONOXIDE OXIDATION

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Although it has long been known that good adsorbents are not necessarily efficient catalysts, some sort of connection between the two properties has often been assumed. Recent experiments[2] on the adsorption of gases by certain oxide catalysts had for their primary object the determination of whether or not such a relation exists in the case of catalysts for the oxidation of carbon monoxide.

These experiments showed that gases are adsorbed by these oxides in two distinct ways, which were designated as "primary" and "secondary" adsorption, to indicate the kind of valence forces involved. The latter is the more familiar type which occurs with inactive adsorbents and is not specific, but parallels the melting or boiling points of the adsorbents and adsorbed substances. Primary adsorption is apparently determined by chemical affinity in its usual sense, and is therefore highly specific. Here the extent of adsorption is much less dependent on temperature and pressure than in the secondary type. Other investigators[3] have observed two such types of adsorption by metals.

Under the conditions of the present experiments a complication entered, in that occasionally both types of adsorption took place simultaneously, so that a method had to be devised for differentiating between them. The adsorption of carbon dioxide, oxygen and nitrogen, and of carbon monoxide and hydrogen at low temperatures, was found to be mainly of the secondary type, while of the more chemically active oxides at higher temperatures carbon monoxide and hydrogen were adsorbed largely by primary valence. The order of decreasing secondary adsorption, per gram of oxide, was as follows: silica, ferric oxide, manganese dioxide, cobalt sesquioxide, Hopcalite,[4] cupric oxide, vanadium pentoxide. The order of decreasing primary adsorption of carbon monoxide was found to be Hopcalite, cupric oxide, manganese dioxide, ferric oxide, vanadium pentoxide, silica.

The extent of adsorption, whether primary or secondary, must depend, for a given adsorbing substance, on the extent and condition of its surface.

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[1] National Research Fellow in Chemistry.

[2] See the preceding paper.

[3] (a) von Hemptinne, *Z. physik. Chem.*, **27**, 429 (1898). (b) Langmuir, THIS JOURNAL, **38**, 2221 (1916); (c) **40**, 1361 (1918). (d) Taylor and Burns, *ibid.*, **43**, 1273 (1921).

[4] A mixture of 60% of manganese dioxide and 40% of cupric oxide.

Consequently it would not be justifiable to compare adsorptions per gram of material with other properties of the oxides, such as melting point, which do not depend on these factors, unless it could be shown that the extent and condition of the surfaces were nearly the same for all the oxides. That this was probably true in these experiments may be inferred from the fact that analogous methods, as nearly as practicable, of preparation, washing and drying were used for all. Catalytic activity is a property which does depend, for a given substance, on the extent and condition of the surface. In order to compare adsorption and catalytic activity, therefore, it is necessary only that the materials used for measurements of the latter should be prepared in the same way as those used in determining the adsorption. These remarks apply equally to comparisons of chemical reactivity (rate of reduction, etc.) with adsorption and catalytic activity.

Relation between Extent of Adsorption and Catalytic Activity.—The catalytic behavior of these oxides in the combination of carbon monoxide and oxygen has been investigated[5] by the Chemical Warfare Service, and also to some extent by the Munitions Inventions Department in England. The order of catalytic activity was found to be Hopcalite, cobalt sesquioxide, cupric oxide, manganese dioxide, ferric oxide. Vanadium pentoxide was not investigated and therefore cannot be placed with certainty, but it is known[6] that silica comes at the end of the list. All the oxides whose adsorptive capacities were measured were prepared and dried by the same processes as those used for the samples whose catalytic activity had been determined, except in the case of Hopcalite. Hopcalite similar to that used for the adsorption experiments was found[7] to be less than 100% efficient at temperatures below 40°, so that this mixture must be put in second place, after cobalt sesquioxide, in the activity series. For convenience of comparison, these facts are collected in Table I, together with the results of the adsorption measurements. In the table the properties in question decrease from left to right.

The most obvious conclusion to be drawn from Table I is that *no connection whatever exists between the extent of secondary adsorption and catalytic activity for carbon monoxide oxidation. The primary adsorption of carbon monoxide, however, is in exactly the same order as the catalytic activity.*

This means that if the *total* adsorptions as measured are compared with the catalytic activity, no relation will appear, because the adsorption consists in general of two different phenomena, only one of which has a bearing on the activity. The powerful force fields at the surface of silica, indicated

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[5] Rideal and Taylor, *Analyst*, **44**, 89 (1919). Rideal, *J. Chem. Soc.*, **115**, 993 (1919). Lamb, Bray and Frazer, *J. Ind. Eng. Chem.*, **12**, 213 (1920). Merrill and Scalione, THIS JOURNAL, **43**, 1982 (1921).

[6] Bodenstein and Ohlmer, *Z. physik. Chem.*, **53**, 166 (1905). This statement is supported by new experiments with precipitated silica.

[7] In an experiment by H. S. Taylor.

by its high melting point, produce a comparatively high adsorption of all gases, but it is a secondary valence adsorption and consequently leads only to weak, if any, catalytic effects. Charcoal, probably the best adsorbent known, catalyzes few reactions, because the adsorptions in question are largely secondary. Charcoal does catalyze the chlorination of natural gas as well as a number of oxidation reactions, but the adsorption of oxygen certainly[9] is of the primary valence type, as is probably also that of chlorine. Secondary adsorption appears to produce, at the most, only a comparatively slight activation of the adsorbed molecules.

TABLE I

COMPARISON OF CATALYTIC ACTIVITY AND ADSORPTION

Catalytic activity	Co_2O_3, Hopcalite, CuO, MnO_2, Fe_2O_3, V_2O_5(?), SiO_2
Secondary adsorption	SiO_2, Fe_2O_3, MnO_2, Co_2O_3, Hopcalite, CuO, V_2O_5
Primary adsorption of CO	Co_2O_3,[8] Hopcalite, CuO, MnO_2, Fe_2O_3, V_2O_5. SiO_2.

Adsorption and Promoter Action.—Hopcalite is a more active catalyst than either of its constituents, and therefore this mixture exhibits promoter action. In Table II are given the results of adsorption measurements for these three catalysts at 0°, together with the values calculated for Hopcalite according to the mixture law.

TABLE II

VOLUMES ADSORBED BY ONE GRAM OF ADSORBENT AT 0°

Adsorbent		O_2	CO_2	CO
CuO		0.128	4.53	1.66
MnO_2		0.34	8.66	1.90
Mixture	calc.	0.26	7.01	1.80
	obs.	0.247	6.18	4.42

Since carbon monoxide is held on all 3 of these catalysts at 0° almost entirely by primary adsorption, the result of admixture may conveniently be summed up in the statement that thereby the secondary adsorption of all gases is slightly diminished, but the primary adsorption of carbon monoxide is greatly increased. Consequently in this case, at least, it is not necessary to seek any special mechanism for promoter action beyond that which accounts for the catalysis itself, but the reason for the increased chemical reactivity of the mixture has not been satisfactorily explained. The observed decrease in secondary adsorption points to a reduction in surface area, or it may be thought of as due to the fact that the mixture must have a lower melting point than the weighted mean of its components.

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[8] Carbon monoxide reacted so rapidly with cobalt sesquioxide at 0° that the adsorption measurement was uncertain. But this high reaction rate, taken together with the observation that primary adsorption parallels chemical reactivity, justifies the position assigned to this oxide.

[9] Compare Rhead and Wheeler, *J. Chem. Soc.*, **103**, 461 (1913). Lowry and Hulett, THIS JOURNAL, **42**, 14 (1920).

Adsorption and Heterogeneous Reaction.—In many cases, as for example carbon monoxide on platinum,[3c] the interaction of the gas and the adsorbent ceases at the stage of primary adsorption. But if the conditions were such that the surface compound could become isolated, as in the formation of carbonyls, then the primary adsorption would be only an intermediate step in the heterogeneous reaction. This is the case when carbon monoxide acts on active oxides, at least at comparatively low temperatures.

The association theory[10] of chemical reactions postulates that reaction occurs in three stages: (1) direct addition of the reactants to form a new molecule held together by residual affinity; (2) intramolecular change; (3) breaking up of the complex molecule into the reaction products. In heterogeneous reactions the corresponding steps may be described as: (1) secondary adsorption; (2) rearrangement of the surface complex; (3) evaporation of the reaction product from the surface. Thus in the reduction of a metallic oxide by carbon monoxide, the conditions at the oxide surface, neglecting side reactions,[11] may be represented as follows.

$$>MO + CO\uparrow \rightleftharpoons >MO{\cdot}CO \rightleftharpoons >M{\cdot}OCO \rightleftharpoons >M + CO_2\uparrow \qquad (1)$$

Here $>MO$ and $>M$ represent a section of the oxide and metal surfaces, respectively, and the metal atom, M, is chemically combined to the rest of the solid throughout the process. The electron shift involved in the intermediate stage must be thought of as taking place as follows:

$$>MO{\cdot}CO \rightleftharpoons >MOCO \rightleftharpoons >M{\cdot}OCO \qquad (2)$$

This is necessitated by the observations that carbon monoxide or carbon dioxide held on oxides by secondary adsorption, or carbon dioxide on metals, can readily be pumped off, but carbon monoxide held on oxides by primary adsorption can be pumped off only with the greatest difficulty. Under the conditions of the measurements, therefore, the intermediate compound, $>MOCO$, represents a relatively stable stage in the process, namely, the primary adsorption. Since adsorption equilibria appear to be established with great rapidity, the measured initial rate of reduction will ordinarily be determined by the velocity of the intramolecular change represented by Equation 2.

As Langmuir[12] has shown, heterogeneous reactions are either interfacial or non-interfacial, according to whether or not the transformation of one group on the surface facilitates that of adjacent groups. In the former type separate solid phases are produced, while in the latter solid solutions may be formed. The local temperature rise resulting from an exothermic

[10] Compare Mellor, "Chemical Statics and Dynamics," Longmans Green and Co., **1914**, p. 316.

[11] Such as possible carbonate formation or adsorption of carbon monoxide by the reduced metal.

[12] Ref. 3b, p. 2263.

reaction tends to make it interfacial; but if there is a large primary adsorption, the interfacial nature of the process may be masked because the reaction spreads over the surface much more rapidly than within the mass. Thus the velocity curves for the reduction of copper oxide[13] by hydrogen show the characteristics of interfacial reactions to a higher degree than the curves for carbon monoxide.

Mechanism of Carbon Monoxide Oxidation in Contact with Active Oxide Catalysts.—There appear to be four ways in which this reaction might occur: (1) by interaction of carbon monoxide and oxygen adsorbed in adjacent positions; (2) by carbon monoxide striking adsorbed oxygen; (3) by oxygen striking adsorbed carbon monoxide; (4) by decomposition of the surface complex with carbon monoxide into carbon dioxide and reduced oxide, the latter being then reoxidized by oxygen. The adsorption measurements show that these oxide catalysts adsorb much more carbon monoxide than oxygen, and further that the difference is greater the more active the catalyst, so that (1) and (2) probably do not play any considerable part in the catalytic process, especially since the adsorption of oxygen was mainly of the secondary type. Mechanism 3 is not at variance with the observation that the primary adsorption of carbon monoxide by different oxides is in the same order as their catalytic activity, but is nevertheless very improbable, since it seems necessary to assume that the adsorbed carbon monoxide molecules are oriented with the oxygen atoms toward the gas phase. Mechanism 4 is free from all these objections, and receives strong support from the fact that the primary adsorption of carbon monoxide by different oxide catalysts is in the same order as the rates of reduction by carbon monoxide.

Bone and Wheeler,[14] after an extended investigation of the catalytic combination of hydrogen and oxygen, concluded that this process does not depend on alternate oxidation and reduction. If this were true it would seem unlikely that carbon monoxide oxidation was determined by these factors. These authors base their conclusion mainly on measurements of the relative rates of water formation when the mixtures, $2\ H_2 + O_2$, and $2\ H_2 + N_2$, respectively, were passed over oxide catalysts. Using nickel oxide and ignited spathic iron ore the rate of water formation was much greater with the former mixture than with the latter, that is, the catalysis far exceeded the rate of reduction. With copper oxide, on the other hand, the reduction was much more rapid than the catalysis. It is to be noted that all these oxides were strongly ignited and consequently were relatively inactive catalysts compared with the precipitated oxides with which the present paper is more particularly concerned. It is conceivable then that Bone and Wheeler's oxides actually functioned, like silica and porcelain,

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[13] Wright, Luff and Rennie, *J. Chem. Soc.*, **35**, 475 (1879).

[14] Bone and Wheeler, *Phil. Trans.*, **206A**, 1 (1906).

as inert catalysts and brought about reaction by one of the first three processes mentioned in the preceding paragraph. In this case it would still seem necessary to seek another explanation for the much greater catalytic activity of the active oxides here considered, because of all the adsorbents tested precipitated silica was found to give the highest secondary adsorptions.

Bone and Wheeler's conclusions are, however, open to objection. Pease and Taylor[15] have recently shown that oxygen in the hydrogen decreases the rate of reduction of copper oxide and, therefore, the rate of reduction *in the catalytic process* is not necessarily greater than the observed rate of catalysis. Furthermore, Bone and Wheeler compared the average reduction rate, taken over a considerable period, with the rate of the catalytic process. But it is plain that in the latter, reduction cannot have extended much below the surface, so that this comparison is legitimate only in case the reduction rate is a constant. In their experiments with nickel oxide and spathic iron ore, the rate of reduction appears to have been a maximum at the beginning. Consequently, alternate oxidation and reduction is not only a possible mechanism for these reactions but, in so far as reduction actually occurs, it is to that extent a necessary mechanism.[16]

The really striking thing about Bone and Wheeler's results in this connection is not that the rates of reduction failed to agree with the rates of catalysis, but that in some cases the latter were the greater, while with copper oxide the reverse occurred. This suggests that there is something fundamentally different about the reductions in the two cases. The reduction of copper oxide by hydrogen has been shown by Pease and Taylor to be an interfacial reaction; the reductions of ferric oxide and mangano-manganic oxide (and hence probably of spathic iron ore) are not.[17] With copper oxide, the presence of oxygen in the hydrogen decreases the rate of reduction because the oxygen rapidly reacts with the exposed copper atoms on the surface, thus decreasing the extent of the available interface between the solid phases. At sufficiently low temperatures the whole surface is thus reoxidized, and the reduction ceases entirely. On the other hand, in non-interfacial reductions, such a re-oxidation must obviously tend to keep the reduction up to its maximum initial rate. Bone and Wheeler's results are therefore in complete qualitative agreement with the requirements of the theory that in such cases the mechanism of the catalysis depends on alternate reduction and re-oxidation.

When the catalysis reaches a steady state, the rates of reduction and re-oxidation must be equal. If the reduction is interfacial, it would seem that

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[15] Pease and Taylor, THIS JOURNAL, **43**, 2179 (1921).

[16] Pease and Taylor, *ibid.*, **44**, 1640 (1922).

[17] Wright, Rennie and Menke, *J. Chem. Soc.*, **37**, 757 (1880). Fe_2O_3 and Fe_3O_4 form solid solutions over nearly the whole range. Compare Sosman and Hostetter, THIS JOURNAL, **38**, 807 (1916).

only a relatively small fraction of the hydrogen which strikes the surface can react with it, and any excess above this quantity can take no part in the catalysis. The rate of reoxidation, which appears to be non-interfacial[18] will, however, be proportional to the oxygen concentration. If the reduction is non-interfacial, its velocity will depend on the rate at which the hydrogen comes in contact with the surface. Hence, with copper oxide the combination of hydrogen and oxygen should be proportional to the pressure of the oxygen and independent, within certain limits, of that of the hydrogen. With nickel oxide and spathic iron ore, on the other hand, the reaction velocity should be proportional to the hydrogen pressure. Bone and Wheeler's results completely confirm these consequences of the theory of alternate reduction and reoxidation.

In carbon monoxide oxidation, in the presence of various oxide catalysts, similar relations are to be anticipated; but here the large primary adsorption of carbon monoxide would tend to make the velocity in all cases less dependent on the pressure of this gas. The results of Lamb, Scalione and Edgar,[19] though not conclusive on these points, seem to indicate that with Hopcalite the velocity of the reaction is dependent on the oxygen concentration, but independent of that of the carbon monoxide.

Summary

In the preceding paper describing measurements of the adsorption of gases by a number of oxide catalysts, the necessity of distinguishing between two different types of adsorption was emphasized, and the terms, "primary" and "secondary" adsorption, were suggested, to indicate the kind of valence forces involved. The former type is specific, and results in the formation of more or less stable surface complexes; the latter is the type observed with inactive adsorbents, and is not specific. The present paper deals mainly with the significance of these adsorption measurements in the catalytic oxidation of carbon monoxide.

Neither the secondary adsorptions nor the total adsorptions by different oxide catalysts bear any relation to their relative catalytic activities. The primary adsorption of carbon monoxide is, however, in exactly the same order as the catalytic activity.

The mechanism of reduction of an oxide by a reducing gas is discussed as a 3-stage process involving (1) adsorption, (2) isomeric change, (3) evaporation of product from surface.

Several possible ways are discussed in which the catalytic oxidation of carbon monoxide in contact with active metallic oxides might occur, and it is shown that only the mechanism based on alternate reduction and reoxidation is in satisfactory agreement with the adsorption data. Bone and

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[18] Wright and Menke, *J. Chem. Soc.*, **37**, 785 (1880).

[19] Lamb, Scalione and Edgar, THIS JOURNAL, **44**, 738 (1922).

Wheeler's experiments on the catalytic combination of hydrogen and oxygen in presence of metallic oxides, from which they drew the conclusion that this process does not depend on alternate reduction and reoxidation, are considered from the standpoint of the previous paragraph, and are shown to favor strongly, rather than discredit, this view of the mechanism.

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OBSERVATIONS ON THE RARE EARTHS. XIII. STUDIES IN THE ABSORPTION SPECTRA

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Introduction and Procedure

The data hitherto available on the absorption spectra of the rare earths are, for the most part, the products of various investigators using different methods and different conditions of experiment. In only a few instances have the absorption curves been plotted. The present investigation was undertaken to secure data obtained under uniform conditions, with the object of eliminating as many factors as possible that might affect the bands.

The solutions, slightly acid chlorides, were contained in a Baly absorption tube and a nitrogen-filled tungsten lamp was used as a source of light. The light was very satisfactory, being extremely constant in intensity and furnishing a continuous spectrum. If it should be desired to extend the investigation into the ultraviolet, it is practicable to insert a quartz window into the side of the bulb and refill with nitrogen. A commercial autocollimating quartz-prism spectrograph was used.

The first photograph of a series for an element was taken through a 10-cm. layer of solution and then, as the depth of solution was decreased by steps, 7 photographs were usually taken between 10 and 1 cm., the distances chosen being in a reverse geometric ratio, in order that the logarithms of the distances might be equally spaced on the graphs. At 1 cm. the solution was diluted to $^1/_{10}$ its strength and another series of photographs were taken. The dilution was continued until all bands had disappeared. It was assumed that Beer's law holds true.

All exposures were made for 5 minutes on "Spectrum Process Plates." The iron arc was used as standard of reference.[2] The wave lengths tabulated below are in International Ångstrom units.

The accompanying graphs represent the edges of absorption bands, the wave lengths plotted as abscissas and the logarithms of the equivalent

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[2] Kayser, "Handbuch der Spectroscopie," S. Hirzel, Liepzig, **1912**, vol. 6.