[Contribution from the Indian Institute of Technology]

Adsorption of Carbon Monoxide and Hydrogen on Cobalt: Presorption Experiments[1]

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The effect of the prior adsorption of carbon monoxide on the subsequent adsorption of hydrogen and *vice-versa* was studied on a cobalt Fischer–Tropsch catalyst at temperatures below that of detectable reaction on the catalyst surface. The results indicate the formation of carbon–oxygen–hydrogen complexes on the surface as reaction temperature is approached and these presumably act as intermediates in the Fischer–Tropsch synthesis.

Theories of heterogeneous catalytic reactions invariably stress the importance of the adsorption of reactant gases on the catalyst surface as a preliminary step, which is followed by interaction between the adsorbed species resulting finally in the reaction product. A study of such interaction between the chemisorbed molecules, in addition to information concerning the adsorptive properties of the catalyst for the individual gases, is useful in the elucidation of reaction mechanisms.

The presorption method of Griffin, wherein is noted the effect of the prior adsorption of one gas on the subsequent adsorption of another, is of interest in this connection. Griffin[2] found that on an unsupported copper catalyst, minute amounts of presorbed carbon monoxide increased the adsorption of hydrogen at low pressures. To account for this increase Griffin suggested that each of the carbon monoxide molecules adsorbed on centers of the highest activity was able to link to itself several hydrogen molecules. In the absence of carbon monoxide, only one hydrogen "molecule" would have been adsorbed on each such site. Similar observations with slight variations, on the effect of presorbed carbon monoxide on hydrogen adsorption, were made by White and Benton[3] in the case of massive nickel and by Griffin[4,5] in the case of supported copper and nickel catalysts.

A somewhat analogous method was employed by Brunauer and Emmett[6] in their survey of the various adsorptive sites on iron catalysts by studying the chemisorptions of carbon monoxide, oxygen, nitrogen and hydrogen and the effect of the prior adsorption of one gas on the subsequent adsorption of the others. Though in most cases the gas admitted first had merely the effect of suppressing by an equivalent amount the adsorption of the second gas by a process of exclusion, it was found on a singly promoted iron catalyst, on which the activated adsorption of nitrogen had taken place, the activated adsorption of hydrogen was enhanced. This was interpreted by them as arising from a strong interaction between the chemisorbed atoms leading to the formation of $-NH$ and $-NH_2$ complexes on the surface.

In view of the interest in the mechanism of the Fischer–Tropsch synthesis, it was decided to study by this method the interaction between carbon monoxide and hydrogen on Fischer–Tropsch catalysts. Previous work in the field of adsorptive interaction is essentially that of Ghosh, Sastri and Kini[7] who investigated the adsorption of mixtures of carbon monoxide and hydrogen on two complex cobalt catalysts. They noticed that the adsorption of each gas was very significantly modified by the presence of the other and that interactive association between the two gases seemed to occur with the formation of carbon–oxygen–hydrogen complexes as reaction temperature was approached. Agliardi[8] studied the velocities of the adsorption of hydrogen at different temperatures on unsupported cobalt, as well as the metal pretreated with carbon monoxide, but the velocity observed might have been complicated by the occurrence of reduction of cobalt carbide which must have been formed at the temperatures employed.

The present study on the influence of small amounts of presorbed carbon monoxide on the adsorption of hydrogen and conversely the effect of small amounts of presorbed hydrogen on the adsorption of carbon monoxide was undertaken on a cobalt–thoria–kieselguhr catalyst. These experiments were performed at temperatures progressively approaching, without quite reaching, that at which detectable reaction occurs on the catalyst surface.

Experimental

The catalyst had the composition cobalt:thoria:kieselguhr as 100:18:200 parts by weight and was prepared by adding simultaneously potassium carbonate and kieselguhr to the mixed nitrates. The precipitate was washed, dried and broken up in the usual way.

A rapid stream of pure dry hydrogen was passed over the catalyst which was gradually heated in stages up to the final reduction temperature of 350°. Reduction was continued at this temperature till no more moisture could be detected in the exit gas by a liquid air trap as described by Kummer and Emmett.[9] This took nearly 36 hours. The same sample of the catalyst was used for surface area, carbon monoxide chemisorption at liquid air temperature and the presorption experiments.

Preparation of Gases.—Carbon monoxide was prepared by the dehydration of formic acid,[10] and hydrogen by the electrolysis of 15% potassium hydroxide. These, as well as tank helium and tank nitrogen of high purity (better than 99.5%) were freed from traces of oxygen and water vapor by passage through separate trains of hot copper and anhydrous magnesium perchlorate. The carbon monoxide was in addition passed through a bed of caustic potash pellets to remove traces of carbon dioxide.

The adsorption apparatus into which was incorporated a

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[1] Experiments carried out by the authors at the Indian Institute of Science, Bangalore, for the M.Sc. thesis of T. S. Viswanathan accepted by the Madras University in 1952.

[2] C. W. Griffin, This Journal, **42**, 2136 (1927).

[3] (a) T. A. White and A. F. Benton, *J. Phys. Chem.*, **35**, 1784 (1931); (b) A. F. Benton and T. A. White, This Journal, **53**, 3301 (1931).

[4] C. W. Griffin, *ibid.*, **57**, 1206 (1935).

[5] C. W. Griffin, *ibid.*, **59**, 2431 (1937).

[6] S. Brunauer and P. H. Emmett, *ibid.*, **62**, 1732 (1940).

[7] J. C. Ghosh, M. V. C. Sastri and K. A. Kini, *Ind. Eng. Chem.*, **44**, 2463 (1952).

[8] N. Agliardi and S. Marelli, *Gazz. chim. ital.*, **78**, 707 (1948).

[9] J. T. Kummer and P. H. Emmett, *J. Phys. Colloid Chem.*, **55**, 337 (1951).

[10] J. G. Thompson, *Ind. Eng. Chem.*, **21**, 389 (1929).

thermal conductivity meter for gas analysis has been described previously.[7] Isothermal temperatures were maintained in jacketed tubes containing condensing vapors of suitable liquids in the annular space. Higher temperatures needed during evacuation were maintained to ±2° by an electrically heated tube furnace controlled by a Sunvic Energy Regulator type TYB.

Seelig[11] has reported the formation of carbonyl when iron is exposed to carbon monoxide at temperatures ranging from 0 to 108°. It was therefore essential to verify that, at the highest temperature at which adsorption measurements were carried out in the present experiments (97°), the results were not vitiated by the formation of cobalt carbonyl from carbon monoxide and cobalt, or the occurrence of traces of reaction between the gases on the catalyst surface leading to water or hydrocarbons. Accordingly, a mixture of 1CO: $2H_2$ gas was kept in contact with the catalyst at 97° for 24 hours. The gas was then withdrawn slowly through a trap cooled in liquid air and finally the catalyst, maintained at 97°, was pumped down to high vacuum through this trap. After isolating the trap and allowing it to warm up to 100° no pressure could be detected in the attached manometer. This test indicated that no water vapor, cobalt carbonyl or hydrocarbons were formed when the catalyst was exposed to a mixture of hydrogen and carbon monoxide at 97°. Synthesis gas kept in equilibrium with the catalyst at 97° failed to indicate the presence of carbon dioxide or hydrocarbons when analyzed by semi-micro Bone and Wheeler method.

In the presorption runs, the gas to be presorbed was introduced to the catalyst kept at the isothermal temperature, an hour before the start of the isotherm. In all the cases, the gas so admitted was found to be taken up completely and very rapidly by the catalyst without leaving any residual pressure in the system. Purity of the gas added subsequently, verified by thermal conductivity meter reading, showed that during the course of the run the presorbed gas was not displaced from the surface by the gas admitted later.

Preparation of the Catalyst Surface for Adsorption.—After the reduction of the catalyst, the catalyst tube was attached to the adsorption apparatus. The catalyst was alternately treated with hydrogen at 350° and evacuated at the same temperature. The reproducibility of the uptake of hydrogen by the catalyst at this temperature indicated that no further reduction of the catalyst could occur at 350° or below.

The degassing schedule was as follows. After every hydrogen isotherm the catalyst was evacuated at 350° for eight hours. After each carbon monoxide isotherm the catalyst was evacuated at 100° for two hours to remove most of the carbon monoxide. The temperature was then slowly raised to 350° and kept there for eight hours, continuing the evacuation throughout. When very occasionally lowering of adsorptive capacity was noted, due probably to the formation of traces of carbide, the catalyst was treated repeatedly with hydrogen at 350° and evacuated. This brought the adsorption invariably to the original value.

Pure gas isotherms were determined in between presorption runs. The reproducibility of these indicated that no gaseous component was progressively accumulating on the surface in a series of runs.

Results and Discussion

The weight of the catalyst sample was 4.66 g. when unreduced and 3.73 g. when reduced. All adsorption values reported in this paper represent results obtained with this weight of the catalyst. The adsorption values were reproducible to ±0.05 ml.

The nitrogen monolayer volume for the catalyst was 80.91 ml. and the chemisorption of carbon monoxide at liquid air temperature 25.4 ml. This works out to 21.69 and 6.81 ml. per gram of the reduced catalyst. The chemisorption value was determined by taking the difference between carbon monoxide and nitrogen isotherms obtained on the catalyst at liquid air temperature, following Anderson's procedure.[12] The assumptions involved in this procedure and their validity have been discussed elsewhere.[13]

Figure 1 represents the adsorption of hydrogen at 53° on the cleared catalyst as well as the catalyst having various small amounts of carbon monoxide ranging from 0.04 to 1.00 ml. Figures 2 and 3 give similar isotherms of hydrogen at 76 and 97°, respectively. Table I shows the change in hydrogen adsorption under various conditions, caused by the presorption of carbon monoxide.

TABLE I

EFFECT OF PRESORBED CARBON MONOXIDE ON THE ADSORPTION OF HYDROGEN

Vol. of CO presorbed, ml. N.T.P.	ΔV_1,[a] ml. N.T.P.					
	Pressure 30 cm.			Pressure 60 cm.		
	53°	76°	97°	53°	76°	97°
0.04	0.03	0.07	..	0.07	0.07	..
.08	..	.07	..	..	.17	..
.20	.29	..	0.70	.56	..	..
.50	.42	.37	.94	.77	.62	1.35
1.00	.56	1.03	1.31	1.22	1.36	..
2.00	..	1.23	..	..	1.73	..

[a] ΔV_1 is volume of hydrogen adsorbed on the surface with presorbed CO *minus* the volume of hydrogen adsorbed on the cleared surface under the same conditions.

It is seen that the adsorption of hydrogen is enhanced under all conditions studied by the presorption of carbon monoxide. Three general trends are clearly in evidence. Firstly, at any temperature, the enhancement is larger, the higher the amount of presorbed carbon monoxide. For a particular amount of carbon monoxide, the enhancement effect is larger the higher the temperature. The enhancement caused, calculated per unit volume of presorbed gas, is larger the smaller the volume of gas presorbed; *i.e.*, the first portions of the presorbed gas are much more effective in causing enhancement of hydrogen adsorption than are later portions.

These results indicate that some process is occurring on the surface of the catalyst other than the simple blocking up of a part of it by the presorbed carbon monoxide. The first small portions of carbon monoxide added may be expected to be taken up on the most active sites on the surface. The enhancement in hydrogen adsorption caused by these molecules is analogous to that reported by Griffin in the case of copper and nickel. It is seen that at 53°, 0.20 ml. of presorbed carbon monoxide causes an enhancement of hydrogen adsorption of 0.35 ml. at a hydrogen pressure of 40 cm.; *i.e.*, each presorbed carbon monoxide molecule causes on the average an *extra* 3.5 atoms of hydrogen to be adsorbed on the surface. If one atom of hydrogen is adsorbed on top of each presorbed carbon monoxide molecule, the adsorption of hydrogen on the surface previously covered with carbon monoxide would be the same as on the bare surface. The observed enhancement of 0.35 ml. shows that each carbon monoxide molecule is associated with four or more hydrogen

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[11] R. E. Probst, S. Meyerson and H. S. Seelig, THIS JOURNAL, **74**, 2115 (1952).

[12] R. B. Anderson, W. K. Hall and L. J. E. Hofer, *ibid.*, **70**, 2465 (1948).

[13] M. V. C. Sastri and V. Srinivasan, *Current Science* (*India*), **23**, 154 (1954).

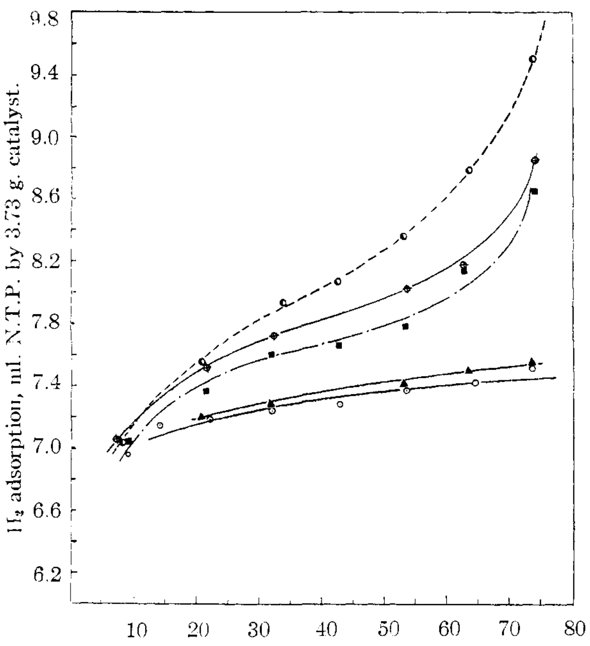

Fig. 1.—Effect of presorbed carbon monoxide on adsorption of hydrogen at 53°: O, on cleared surface; ▲, with 0.04 ml. CO; ■, with 0.20 ml. CO; ⊗, with 0.50 ml. CO; ◐, (top curve) with 1.00 ml. CO.

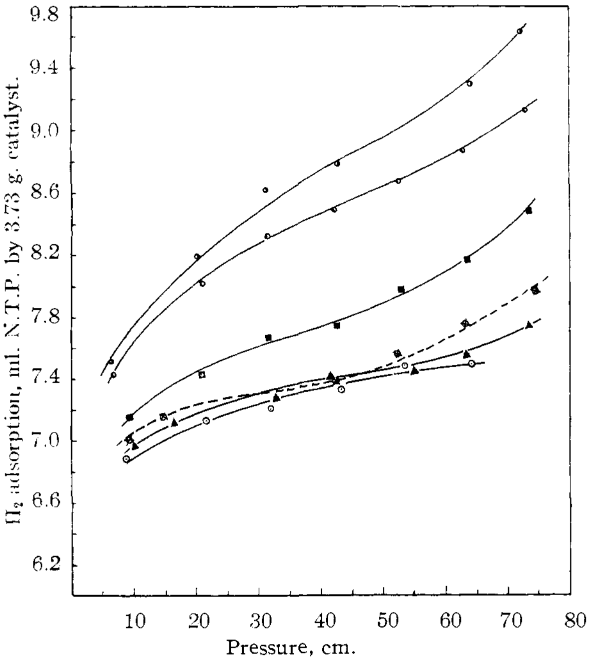

Fig. 2.—Effect of presorbed carbon monoxide on adsorption of hydrogen at 76°: O, on cleared surface; ▲, with 0.04 ml. CO; (broken line) ⊗,with 0.08 ml. CO; ■, with 0.50 ml. CO; (second from top) ◐, 1.00 ml. CO; (top curve) ◑, with 2.00 ml. CO.

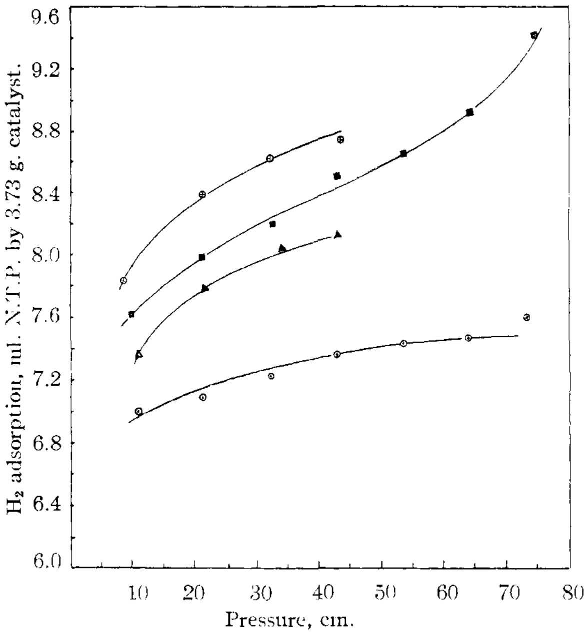

Fig. 3.—Effect of presorbed carbon monoxide on adsorption of hydrogen at 97°: O, on cleared surface; ▲, with 0.20 ml. CO; ■, with 0.50 ml. CO; (top curve) ⊗, with 1.00 ml. CO.

atoms. It is difficult to visualize on valence considerations how each adsorbed carbon monoxide molecule could link to itself so many hydrogen atoms by primary valence forces. For small amounts of presorbed carbon monoxide, therefore, some sort of activation of the surface by the presorbed gas must be invoked in addition to complex formation. Modern ideas about the electronic structure of catalysts offer a clue to the nature of the activation. Boudart[14] has suggested a mechanism by which traces of an adsorbed impurity can greatly modify the adsorptive properties of the solid by altering its electron work function. It is found that with 1.0 ml. presorbed carbon monoxide, the adsorption of hydrogen at 53° and 30 cm. pressure is enhanced by 0.56 ml. In this case as well as for larger amounts of presorbed carbon monoxide, the whole of the enhancement in hydrogen adsorption can be accounted for on the basis of the formation of complexes on the surface between the two gases.

The larger enhancement effect at the higher temperatures suggests the occurrence to a greater extent of carbon monoxide–hydrogen complexes, the formation of which may be associated with an activation energy. These complexes may well be the intermediates from which methylene groups are ultimately derived. These results are in conformity with the views of Anderson[15] and Emmett[16,17] who postulate the occurrence of oxygenated intermediates in the course of the synthesis.

It was decided to verify whether the enhancement effect was observable on areas other than the most active ones. Accordingly, after all other experiments were completed, the catalyst was sintered at 425° till the adsorption of hydrogen was reduced to about 3.5 ml., that is, nearly half the original value. Presorption of 0.20 ml. of carbon mon-

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[14] M. Boudart, THIS JOURNAL, **74**, 3556 (1952).

[15] H. H. Storch, N. Golumbic and R. B. Anderson, "Fischer-Tropsch and Related Syntheses," John Wiley and Sons, Inc., New York, N. Y., 1951, p. 592.

[16] J. T. Kummer, W. B. Spencer, H. H. Podgurski and P. H. Emmett, THIS JOURNAL, **73**, 564 (1951).

[17] J. T. Kummer and P. H. Emmett, *ibid.*, **75**, 5177 (1953).

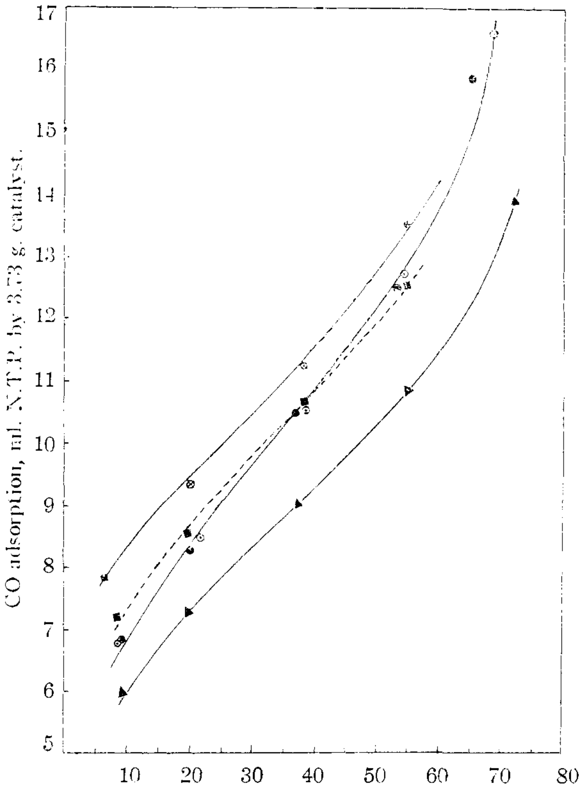

Fig. 4.—Effect of presorbed hydrogen on adsorption of carbon monoxide at 53°: O, on cleared surface; ▲, with 0.20 ml. H_2; ■, with 0.50 ml. H_2; (top curve) ⊗, with 1.00 ml. H_2; ●, repeat value for cleared surface after run ⊗.

oxide on this sample was found to enhance the adsorption of hydrogen at 53° as well as 97° over that on the cleared surface, though the enhancement observed was about half that noted on the original unsintered catalyst under the same conditions. This indicates that the ability to form carbon monoxide–hydrogen complexes is not confined only to the most active areas on the surface.

Presorbed Hydrogen.—Figures 4, 5 and 6 indicate the adsorption of carbon monoxide at 53, 76 and 97°, respectively, on the catalyst having various small amounts of presorbed hydrogen up to 1.50 ml. Table II gives the change in carbon monoxide adsorption under various conditions caused by the presorption of hydrogen.

Table II

Effect of Presorbed Hydrogen on the Adsorption of Carbon Monoxide

Vol. of H_2 presorbed, ml. N.T.P.	ΔV_2[a] at a pressure of 20 cm., ml. N.T.P. 53°	76°	97°
0.04	....	....	−0.30
.20	−1.00	−0.25	− .65
.50	+0.35	− .45	− .85
1.00	+1.40	0	−1.00
1.50	....	0	−1.10

[a] ΔV_2 is the volume of carbon monoxide adsorbed on the surface with presorbed hydrogen *minus* the volume of carbon monoxide adsorbed on the cleared surface under the same conditions.

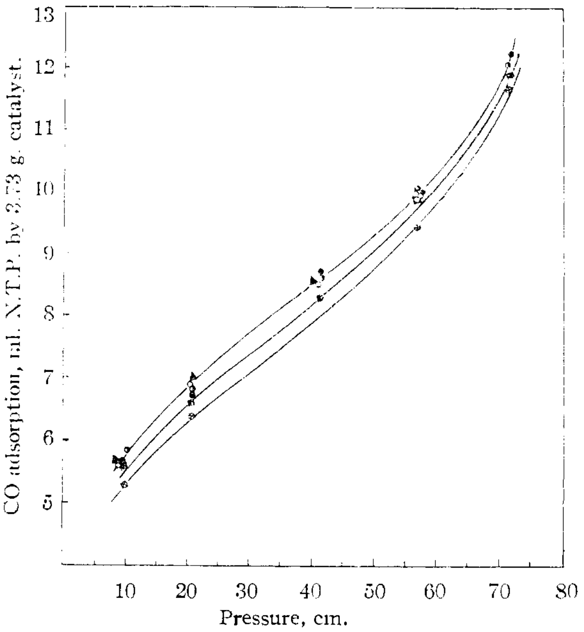

Fig. 5.—Effect of presorbed hydrogen on adsorption of carbon monoxide at 76°: (top curve) O, on cleared surface; ■, with 0.20 ml. H_2; (lowest curve) ⊗, with 0.50 ml. H_2; (top curve) ◑, with 1.00 ml. H_2; (top curve) ▲, with 1.50 ml. H_2; (top curve) ●, repeat value for cleared surface obtained between runs ⊗ and ◑.

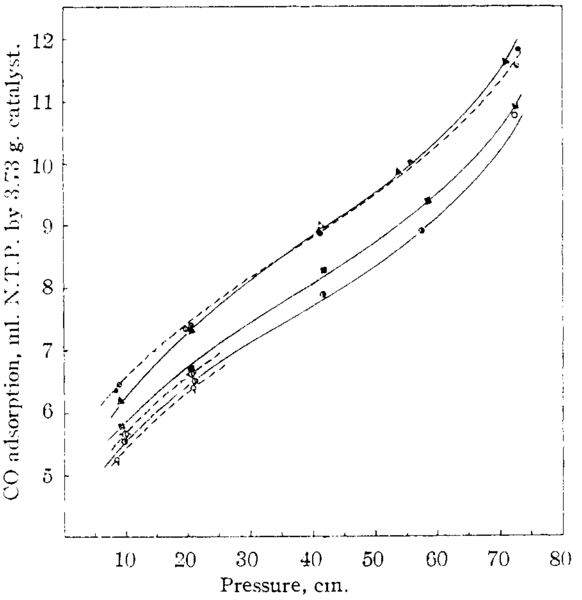

Fig. 6.—Effect of presorbed hydrogen on adsorption of carbon monoxide at 97°: (top broken curve) O, on cleared surface; ▲, with 0.04 ml. H_2; ■, with 0.20 ml. H_2; (middle broken curve) ⊗, with 0.50 ml. H_2; (lowest solid curve) ◑, with 1.00 ml. H_2; (lowest broken curve) ♀, with 1.50 ml. H_2; (top broken curve) ●, repeat value for cleared surface obtained between runs ⊗ and ◑.

At 53°, 0.20 ml. of presorbed hydrogen causes a suppression of carbon monoxide adsorption, persumably by occupying active adsorptive sites to the exclusion of carbon monoxide. The decrease in carbon monoxide adsorption in this case (1.0

ml.) is, however, more than can be accounted for on the basis of exclusion of an equivalent amount of carbon monoxide. When 0.50 ml. of hydrogen is presorbed, the carbon monoxide adsorption at 53° is nearly the same as that on the cleared catalyst, while with 1.0 ml. of presorbed hydrogen, the adsorption of carbon monoxide is distinctly higher than on the cleared surface. This difference in behavior shows that the latter amounts of hydrogen are adsorbed on sites which are qualitatively different from those on which the first portions of hydrogen are adsorbed. Hydrogen at higher coverages, *i.e.*, when adsorbed on sites other than the most active, seems to cause an enhancement in the adsorption of carbon monoxide.

At 76°, quantities of presorbed hydrogen up to 0.50 ml. cause a suppression of carbon monoxide adsorption, while 1.0 and 1.5 ml. of presorbed hydrogen bring up the adsorption of carbon monoxide to the value found on the cleared catalyst. At 97° all doses of presorbed hydrogen up to 1.5 ml. cause a suppression of carbon monoxide adsorption. It is seen, however, that the first portions of hydrogen have a distinctly higher suppression effect than subsequent portions per unit volume of presorbed gas. In fact it has been found that when much higher amounts of hydrogen are present on the surface, as in the case when both hydrogen and carbon monoxide are adsorbed simultaneously from mixtures on this catalyst, the adsorption of carbon monoxide is higher than that from the pure gas at the same partial pressure at 97° as well as at lower temperatures.[18] In these presorption experiments, however, the gas phase contained one component only and the amount of hydrogen presorbed was at no time more than 1.5 ml., since higher amounts gave rise to detectable amounts of hydrogen in the gas phase during the adsorption measurement.

The enhancement in the adsorption of one gas caused by the presence of the other may be attributed to the formation of complexes between the two on the catalyst surface. While apparently complex formation is taking place at 97° when the surface is previously treated with carbon monoxide, it may appear strange that complexes are not formed when the surface is first treated with hydrogen. This may be explained plausibly if we assume that when a carbon–oxygen–hydrogen complex is to be formed, the hydrogen atom adsorbed on the surface has to switch over from a surface atom to the adsorbed carbon monoxide molecule. This shift will be more difficult, the stronger the binding between the surface and hydrogen, *i.e.*, when the adsorption heat is high, as when the first portions of hydrogen are adsorbed on the most active areas on the bare surface. Increase of temperature seems to affect the adsorption of hydrogen in such a way that a great number of adsorbed hydrogen atoms are very strongly bound to the surface, when the surface is first treated with hydrogen. It may be noted that this restriction does not hold when the surface is first covered with carbon monoxide.

On the basis of the above experiments as well as those on the simultaneous adsorption of hydrogen and carbon monoxide on the same catalyst, complex formation seems to be taking place indubitably on the major part of the surface. It may be recalled that sites which are very active for adsorption would be more or less "poisoned" by tenaciously held reactant or product and that the main burden of the catalytic reaction is carried by sites on which the heat of adsorption is neither too high nor too low.[19]

The following picture emerges from the above discussion. On the most active sites on the surface, (a) presorbed carbon monoxide causes an enhancement of hydrogen adsorption and (b) presorbed hydrogen causes a suppression of carbon monoxide adsorption. On the slightly less active but more numerous sites on the surface, there is a mutual enhancement of the adsorption of each gas by the presence of the other indicating a considerable amount of interaction between the two chemisorbed species. Carbon–oxygen–hydrogen complexes are formed on the surface and these are presumably the precursors of methylene groups formed on the surface during the synthesis.

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[18] M. V. C. Sastri and T. S. Viswanathan, *J. Sci. Ind. Research (India)*, **13B**, 590 (1954).

[19] G. D. Halsey, Jr., *J. Chem. Phys.*, **17**, 758 (1949).