[CONTRIBUTION FROM THE INDIAN INSTITUTE OF TECHNOLOGY]

On the Nature of the Active Substrate in Fischer–Tropsch Synthesis over Cobalt Catalysts[1]

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Low temperature chemisorption of carbon monoxide was utilized to determine the free cobalt on the surface of an active Fischer–Tropsch catalyst successively after it was reduced with hydrogen, used in Fischer synthesis, re-reduced with hydrogen and finally carbided. The cobalt on the the surface of the catalyst was found to be cleared to the extent of 73% by evacuation alone at the reaction temperature (200°). This indicates that under normal synthesis conditions, the carbon monoxide is held on the surface mostly as chemisorbed gas and is not appreciably "fixed" as carbide or oxide.

The theory of the Fischer–Tropsch synthesis of hydrocarbons put forward by Craxford,[2,3] depended essentially on two postulates concerning the nature of the active substrate. These were (1) the formation of the carbide of the catalytic metal as the intermediate compound in the synthesis and (2) almost complete coverage of the surface with carbide under conditions favoring oil formation. Recent researches[4–6] have, on the other hand, produced definite evidence in the case of cobalt catalysts to show that cobalt carbide is neither an intermediate nor a catalytically active substrate but acts much rather as an inhibitor for hydrocarbon formation. X-Ray analysis[4] failed to disclose any carbide in cobalt catalysts used in the normal synthesis. Tracer experiments by Kummer, *et al.*,[7] tended to revive an earlier proposal[8] that carbon–oxygen–hydrogen complexes function as the substrate intermediates in synthesis over iron and cobalt catalysts, rather than bulk or surface carbide.

At the same time certain salient features of the Fischer–Tropsch synthesis such as its slow over-all rate[9] and its high selectivity with respect to the products formed in normal synthesis,[10] indicate that only a minute fraction of the cobalt surface is covered with the synthesis-intermediate, whatever be its exact chemical nature. Most of it appears to be "poisoned" with some surface phase formed from carbon monoxide, such as carbide, oxide or even chemisorbed carbon monoxide. This implies that abundance of carbide on the catalyst surface may still be important for the formation of liquid products by inhibiting hydrogenation-cracking of the paraffin chains though it may be dismissed as an intermediate for their synthesis.

Since chemisorbed gas can ordinarily be pumped off by heating the catalyst in high vacuum, whereas the carbided or oxidized surface cannot be thus "cleared," it occurred to us that this criterion could be employed to furnish information relative to the over-all nature of the substrate formed on a Fischer–Tropsch catalyst during the steady state synthesis. The present paper sets forth such experiments on a cobalt–thoria–manganous oxide–kieselguhr catalyst. The extent of free cobalt on the surface was estimated from the chemisorption of carbon monoxide at liquid air temperature in accordance with the method given by Emmett and Brunauer.[11]

Experimental

Materials.—The catalyst studied had the composition cobalt:thoria:manganous oxide:kieselguhr as 100:6:12:200, and was prepared by adding to a boiling solution of cobalt and thorium nitrates the requisite amounts of hot potassium carbonate solution and a thin slurry containing kieselguhr and freshly prepared manganous oxide. The product was filtered, washed and dried at 110°. The kieselguhr used was an acid-washed iron-free calcined product of the British Drug Houses, Ltd., London, having a BET area of 1.44 square meters per gram.

Electrolytic hydrogen, carbon monoxide from formic acid and phosphoric acid,[12] cylinder nitrogen and helium of high purity (over 99.6%) were used after passing them through separate trains of hot copper, caustic potash pellets and granular anhydrous magnesium perchlorate.

Adsorption Studies.—The adsorption measurements were made at the temperature of fresh liquid air, 86°K., by the conventional volumetric method, employing a slight modification of Pease's apparatus.[13,14] After determining the nitrogen isotherm on the unreduced catalyst (5 g.) nitrogen and carbon monoxide isotherms were determined on the same sample after each of the following successive treatments: (1) Reduction with hydrogen at 300° for 24 hours at a space velocity of 500/hour. (2) Induction for synthesis by passing $1CO:2H_2$ mixture over the reduced catalyst at an hourly space velocity of 100 and atmospheric pressure, the temperature of the catalyst being raised from 150 to 190° in the course of four hours with "contraction schedule."[15] When the apparent contraction of gas just attained 70% and oil commenced to form at an appreciable rate, synthesis gas was shut off and pure dry nitrogen was passed over the catalyst for three hours at a space velocity of 800, keeping the catalyst at 200° to sweep away weakly sorbed gases and vapors. (3) Re-reduction with hydrogen at 200 to 300° for four hours at a space velocity of 800. Initially the outstreaming hydrogen carried with it a small amount of gaseous hydrocarbons, mostly methane. (4) Carburization with pure carbon monoxide at 200 to 250° until the exit gas bubbled through fresh baryta solution without causing

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[1] Experiments carried out by the authors at the Indian Institute of Science, Bangalore, for the A.I.I.Sc. thesis of S. R. Srinivasan.

[2] S. R. Craxford, *Trans. Faraday Soc.*, **35**, 946 (1939); **42**, 576 (1946).

[3] S. R. Craxford and E. K. Rideal, *J. Chem. Soc.*, 1604 (1939).

[4] S. W. Weller, L. J. E. Hofer and R. B. Anderson, THIS JOURNAL, **70**, 799 (1948).

[5] R. B. Anderson, W. K. Hall, A. Krieg and B. Seligman, *ibid.*, **71**, 183 (1949).

[6] J. T. Kummer, T. W. DeWitt and P. H. Emmett, *ibid.*, **70**, 3632 (1948).

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

[8] O. C. Elvins and A. W. Nash, *Nature*, **118**, 158 (1926).

[9] H. H. Storch, N. Golumbic and R. B. Anderson, "The Fischer–Tropsch and Related Syntheses," John Wiley and Sons, Inc., New York, N. Y., 1951, p. 528.

[10] H. H. Storch, *et al.*, *ibid.*, pp. 14 to 20.

[11] P. H. Emmett and S. Brunauer, THIS JOURNAL, **59**, 310, 1553 (1937).

[12] Thompson, *Ind. Eng. Chem.*, **21**, 389 (1929).

[13] R. N. Pease, THIS JOURNAL, **45**, 1196 (1923).

[14] M. V. C. Sastri and K. V. Ramanathan, *J. Phys. Chem.*, **56**, 220 (1952).

[15] H. H. Storch, *et al.*, "Synthetic Liquid Fuels from Hydrogenation of Carbon Monoxide. Part I, "Technical Paper No. 709, pp. 89 and 90, Pittsburgh, U. S. Bureau of Mines, 1948.

turbidity, indicating nearly complete carbiding. This took about 32 hours.

Before each adsorption measurement the catalyst was "degassed" by heating in high vacuum ($< 10^{-4}$ mm.) for eight hours. The temperature of evacuation was 300° in all cases *except* after the induction treatment (2) when the temperature was kept at 200° to avoid the possibility of decomposition of carbide, if any were formed at all.

A modified form of the adsorption tube described by Anderson[16] enabled the determination of carbon monoxide and nitrogen isotherms to be made as well as gas flow to take place over the same sample of the catalyst. Constant temperatures above 150° were attained in a small resistance furnace controlled by means of a "Sunvic Energy Regulator." The dead space values, measured by helium, were corrected for the non-ideal behavior of nitrogen and carbon monoxide at low temperature. Each adsorption measurement was repeated to check reproducibility. All the isotherms presented in Fig. 1 were found to be accurately reproducible.

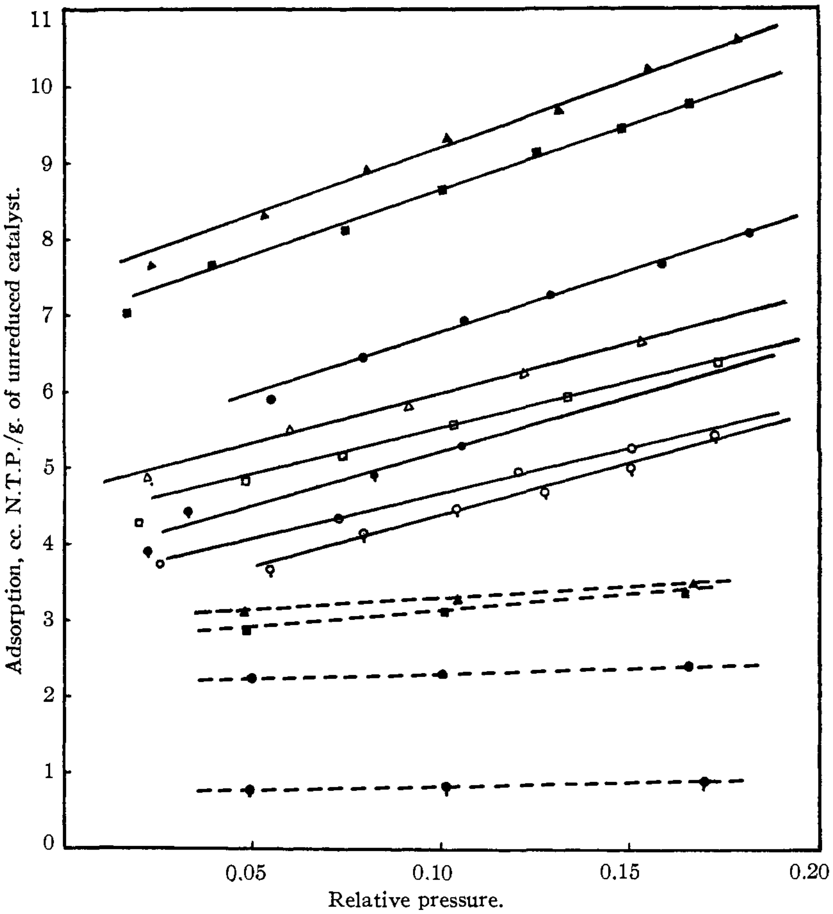

Fig. 1.—Carbon monoxide and nitrogen isotherms at 86°K. Solid points refer to CO adsorption and open points to N_2 adsorption; broken lines represent vol. CO chemisorbed; (i) Δ, reduced catalyst; (ii) O, after active synthesis; (iii) □, after reactivation; (iv) ♀, after carburization.

Results

The adsorption data presented in Fig. 1 and Table I are expressed in terms of ml. (N.T.P.) of gas adsorbed per gram of the original unreduced catalyst. In Fig. 1 the adsorptions of nitrogen and carbon monoxide are plotted against the relative pressure, and the volume of chemisorbed carbon monoxide was reckoned from the difference between the nitrogen and carbon monoxide adsorptions at equal relative pressures. As these differences increased slightly with pressure, probably due to a weaker pressure-dependent chemisorption of carbon monoxide on the non-metallic part of the catalyst surface (*cf.*, Joy and Dorling[17]), the extrapolated values of chemisorbed carbon monoxide at $p/p_0 = 0$ (Table I, V_{CO}) were taken as representing the extent of free cobalt on the surface. The surface areas were calculated from the nitrogen isotherms by the BET method.[18] The ratio of chemisorbed carbon monoxide to nitrogen in the saturated monolayer V_{CO}/V_m given in the last column of Table I indicates roughly the fraction of the surface covered by free cobalt atoms.

TABLE I

ADSORPTION DATA[a] FOR THE CATALYST UNDER VARIOUS CONDITIONS OF PRETREATMENT

Pretreatment, see Fig. 1	Evacuation temp., °C.	B.E.T. surface area sq. m./g.	V_m,[b] ml./g.	V_{CO},[c] ml./g.	V_{CO}/V_m
Original catalyst	300	81.4	18.1	..	..
(i) Above, reduced at 300°	300	24.5	5.45	3.00	0.55
(ii) Above, used for synthesis	200	15.0	3.35	2.20	0.66
(iii) Above, reactivated with hydrogen	300	24.0	5.35	2.75	0.52
(iv) Above, carburized with carbon monoxide	300	18.8	4.19	0.70	0.17

[a] Per gram of the original unreduced catalyst. [b] Constant in B.E.T. equation = volume of nitrogen, ml. N.T.P. in saturated physical monolayer at 86°K. [c] Volume of carbon monoxide chemisorbed at 86°K., ml. N.T.P., at $p/p_0 = 0$.

TABLE II

SYNTHESIS DATA ON THE REDUCED CATALYST

Weight of the unreduced catalyst, 18.9 g., bulk volume of the unreduced catalyst, 60 ml., temperature of steady-state operation, 190°; composition of the synthesis gas used, CO 30.4%, H_2 64.8%, CO_2 0.4%, O_2 nil.

		Product distribution, grams per normal cubic meter of synthesis gas passed						
				Hydrocarbons				
SVH[a]	contraction,[b] %	H_2O	CO_2	C_1–C_2	C_3–C_4	Liquid and solid	Unsaturated	Total[c]
44	60.6	168	8.4	15.8	36.5	85.1	11.8	149.2
83	65.6	157	15.3	20.7	35.2	109.8	17.2	182.9
108	76.9	180	10.4	11.9	23.0	119.4	18.6	172.9
120	64.2	136	11.3	12.3	14.9	90.7	19.7	137.6
149	60.6	231	19.4	9.0	11.4	57.3	9.9	87.6

[a] Volume of gas passed (N.T.P.) per unit volume of catalyst per hour. [b] Apparent carbon dioxide free contraction of gas. [c] Sum of preceding four values.

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(16) R. B. Anderson, *Ind. Eng. Chem., Anal. Ed.*, **18**, 156 (1946).

(17) A. S. Joy and T. A. Dorling, *Nature*, **168**, 433 (1951).

(18) S. Brunauer, P. H. Emmett and E. Teller, THIS JOURNAL, **60**, 309 (1938).

Table II illustrates the catalytic activity and synthesis characteristics of the cobalt–thoria–manganous oxide–kieselguhr catalyst on which adsorption measurements were carried out. The data refer to runs at atmospheric pressure and at the optimum temperature of 190° under which conditions the activity of the catalyst was nearly constant for two months.

The catalyst after being thoroughly carbided with carbon monoxide at 200° was found to have the same characteristics as previously reported for similar carburized catalysts,[4,5] yielding with synthesis gas an apparent contraction of only 7.3% at the temperature of 190°.

Discussion

Carbiding of the catalyst results in only a slight reduction of the surface area but reduces the volume of chemisorbed carbon monoxide to about a fourth of the value found prior to carbiding. This experiment also establishes that carbided cobalt is not appreciably "cleared" by heating at 300° for several hours in high vacuum.

The amount of carbon monoxide chemisorbed by the reduced catalyst after use in synthesis is 73% of the value obtained with the original reduced catalyst. Nearly three-fourths of the cobalt atoms on the surface could thus be "cleared" by evacuation alone at 200° and hence the inference can be drawn that during active synthesis the catalyst does *not* contain appreciable amounts of either bulk or even surface carbide. If either had been present, the surface could not have been cleared by evacuation alone. The temperature of evacuation in this step was kept low enough to avoid cracking the carbide, if it were formed at all, or the hydrocarbon product. The reason for stopping the synthesis run almost immediately after the induction period was to avoid excessive deposition of oil and wax on the catalyst which would be difficult to remove by evacuation.

The 40% decrease in the surface area of the reduced catalyst after its brief use in synthesis indicates the blocking up of a portion of the surface by tenaciously held products of the synthesis. It is interesting to note that on using the sample for synthesis the surface area decreases relatively more than the carbon monoxide chemisorption. This may be due to the presence of narrow pores which were too remote to be covered with cobalt during the impregnation of kieselguhr and which were later filled with oil during synthesis.

Craxford and Rideal put forward the view that during the induction period a steady accumulation of surface carbide took place, and when thereafter the initial methane formation gave place to synthesis of higher hydrocarbons the surface was almost entirely covered with carbide. The experiments reported in the present paper show that appreciable amounts of carbide are not formed under synthesis conditions either as an active intermediate or as a poison to hydrogenation-cracking. It is concluded therefore that carbon monoxide is held on the surface mostly in the chemisorbed state and is not appreciably converted into any "fixed" phase such as carbide or oxide on the surface during the steady state synthesis.

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Molecular Complexes Involving Iodine[1]

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Absorption bands have been found in the ultraviolet spectra of solutions of iodine in a number of "inert" solvents such as saturated hydrocarbons and alkyl halides which are not found in the spectra of either iodine or the solvents alone. These bands are attributed to molecular complexes between iodine and the solvents such as have been previously reported for solutions of iodine in aromatic and olefinic hydrocarbons. It is shown that a relationship exists between the frequencies of the absorption bands of all the iodine complexes and the ionization potentials of the corresponding bases (solvents). This work has led to a simple extension of Mulliken's theory of molecular complexes to the prediction of the frequencies of the absorption bands of the complexes. It is shown that $h\nu = I_B - D + 2\beta^2/(I_B - D)$, where $h\nu$ is the absorption frequency of the iodine complex; I_B is the ionization potential of the base; $D = E_A + e^2/r - C_{AB}$; E_A is the electron affinity of the acid; e^2/r is a coulomb attraction term; C_{AB} is the sum of all other energy terms; and β is an approximately constant term arising out of the quantum mechanical treatment. A discussion is given of the observed frequency-ionization potential relationship in light of the equation.

Introduction

A considerable amount of interest has been shown in the fact that iodine in solution in various solvents exhibits different colors. Originally these solvents were divided into two classes, those which caused a violet color (inert) and those which caused a brown color (active). The original assumption that solvates were formed only in the case of the so-called "brown" solvents had to be modified later when a number of workers showed that the visible absorption band of iodine shifted gradually to the blue in a series of solvents.[2]

A number of significant developments in the study of iodine solutions have occurred in the last few years. Benesi and Hildebrand[2] have found a new absorption band in the ultraviolet spectra of

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(1) Presented at the Symposium on Molecular Structure and Molecular Spectroscopy, Ohio State University, June 9–13, 1952.

(2) H. A. Benesi and J. H. Hildebrand, THIS JOURNAL, **71**, 2703 (1949).