

THE ADSORPTION OF SYNTHESIS GAS AND ITS COMPONENTS ON FISCHER-TROPSCH CATALYSTS

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THE Fischer-Tropsch Process for the commercial synthesis of liquid hydrocarbons from modified water-gas is, perhaps, one instance of a technical chemical process in which interest in the reaction mechanism went almost *pari passu* with its industrial development. Ever since its discovery in 1926, the mechanism of the reaction, with special reference to the function of the catalyst, has been the subject of considerable controversy.

In the reaction mechanism originally proposed by Fischer and his co-workers¹ and later extended by Rideal² and Craxford,³ it was postulated that metallic carbides were formed as intermediate products out of the chemisorbed carbon monoxide and that these were reduced by the gaseous hydrogen present to form methylene groups which in turn link up to form the paraffin chains. Matsumura⁴ slightly modified this hypothesis by suggesting that chemisorbed hydrogen was required to reduce the carbide to methylene radicals.

On the other hand, Elvins and Nash⁵ proposed that carbon-hydrogen-oxygen complexes were more probable than carbides as intermediates in the Fischer-Tropsch synthesis, since oxygenated compounds were always found in the final products along with the hydrocarbons. Hamai⁶ suggested a similar mechanism according to which enolic complexes were formed on the surface by the interaction of adsorbed carbon monoxide with adsorbed hydrogen.

Investigations carried out during the past three years in the United States of America⁷ have produced a considerable volume of evidence to disprove the carbide hypothesis and all its affiliations. Instead, the alternative proposal of an adsorbed reaction complex of carbon monoxide and hydrogen seems to be gaining support.

Both schools of thought, however, accept the importance of the adsorption, or rather the chemisorption, of the reactant gases as a vital step in the formation of the active substrate. The controversy arises mainly with regard to the subsequent transformation of this substrate under synthesis conditions: whether it enters into a reaction with the catalyst metal and thus gets fixed as carbide, or whether the adsorbed molecules interact with each other so as to form

C-O-H complexes chemisorbed on the surface. It is evident that a considerable knowledge on this aspect of the controversy could be derived from a systematic study of the adsorption of the reactant gases, more especially from their mixtures, on the catalysts, at temperatures progressively approaching, without yet reaching, the minimum temperature of appreciable reaction.

Such studies were initiated in the General Chemistry Laboratories of the Indian Institute of Science, Bangalore, in 1945 and the results so far obtained with cobalt catalysts are indeed interesting and informative. The first two catalysts studied had the compositions: (A) Co 34%, Cu 4%, ThO₂ 2.33%, Ce₂O₃ 0.24% and the rest kieselguhr, and (B) Co, Cu, ThO₂ and Ce₂O₃ same as in (A) plus 4% Cr₂O₃ and the rest kieselguhr. Brief reports of these investigations have appeared in this journal and elsewhere⁸ and a more detailed account was presented before the Division of Fuel, Gas and Petroleum, of the XIIth International Congress of Pure and Applied Chemistry held at New York in September last.

On these catalysts, the individual adsorptions of carbon monoxide and hydrogen were studied at a series of temperatures not only from the pure gases but also from 1 CO : 1 H₂* and 1 CO : 2 H₂* mixtures at temperatures ranging from 25 to 97° C. The adsorption studies from the mixtures were made with the aid of a thermal conductivity meter, specially designed for quick response and small dead space. The thermal conductivity measurements were also unaffected by pressure variations between 10 and 80 cm. At the maximum temperature at which measurements were made of mixed adsorption, namely, 97° C., it was verified by thermal conductivity reading as well as by independent chemical analysis, that the gas pumped out of the adsorption tube was free from traces of hydrocarbons, water and carbon dioxide. In general, the results appeared to be the net resultant of two opposing effects, namely, (1) a mutual suppression of the adsorption of each gas as would normally be expected from the Langmuir Theory⁹ and (2) an enhancement of the adsorp-

* These denote the initial compositions of the gas admitted.

tion of either constituent due, in all probability, to interaction and complex formation in the substrate.

It is quite possible for the two effects to take place simultaneously on different parts of the surface. Since chemical complex formation would require an activation energy, there would be negligible complex formation at low temperatures and the net result would be a suppression of the adsorption of one gas in the presence of the other. As the temperature increases, however, substrate-interaction or surface complex formation takes place to an increasing extent with the result that at a certain temperature (still below the reaction temperature) the adsorption from mixtures surpasses that determined at the same temperature and at equivalent pressures from the pure gas. This has been found to be the case with the adsorption of carbon monoxide on catalyst A and of hydrogen on catalyst B. In either case, the adsorption from the mixtures up to 76° C. was lower than that from the respective pure gases, while at the higher temperature, 97° C., there was a pronounced increase in the adsorption of either gas, relative to the pure gas isotherms. The adsorption of hydrogen from mixtures on catalyst A was found to be markedly higher than the pure gas isotherms, even at the lowest temperature studied, namely, 25° C., indicating that at a still lower temperature the suppression effect would have become evident.

On both catalysts it has been observed that the adsorption of each constituent commenced to increase with temperature at much lower temperatures than in the absence of the latter. In other words, when compared with the adsorption isobars of the pure gases, the positions of minimum adsorption of the same gases from the mixtures were, as a rule, shifted substantially to lower temperatures. For instance, the isobars for the adsorption of pure carbon monoxide passed through a minimum at ca 90° C.; this minimum was shifted to ca. 50° C. when the adsorption of carbon monoxide took place from 1 : 1 mixture.

A further interesting observation was made with catalyst B. When the simultaneous adsorptions of the constituent gases were plotted against each other, the 'isotherms' so obtained tended to become linear especially at the higher temperatures. At 97° C., after an initial equimolecular adsorption of either gas, the respective adsorptions increased further in the proportion of 2 CO : 1 H₂, even from mixtures con-

taining 3 to 10 times as much hydrogen as carbon monoxide at equilibrium.

These observations, taken together, point to the possibility of a progressive formation of CO-H complexes on the surface of the cobalt catalysts, under conditions approaching those required for the synthesis of hydrocarbons. Furthermore, observation of the kinetics of mixed adsorption, facilitated by the use of the thermal conductivity meter, indicated a progressive replacement of part of the initially adsorbed hydrogen by carbon monoxide in the course of the formation of these CO-H complexes.

Independent corroboration of the results of mixed adsorption on catalyst B was received from experiments¹⁰ in which the effect of the prior-adsorption, or 'pre-sorption', of each gas on the adsorption isotherms of the other was determined at 52°, 76° and 97° C., employing the technique of Griffin.¹¹ While small amounts of hydrogen presorbed on the catalyst led to a marked enhancement of the adsorption of carbon monoxide at all the temperatures, the effect of a pre-sorption of carbon monoxide was to lower the hydrogen adsorption. As a rule, the adsorption of each gas on the catalyst, pre-treated with a given (small) dose of the other, increased with temperature, so that it could reasonably be expected that the adsorption of hydrogen on the "poisoned" surface would, at a few degrees above 97° C., exceed the value found on the clear surface.

Some interesting experiments have just been carried out¹² which indicate the absence of any extensive amounts of carbide on the surface of a cobalt catalyst under synthesis conditions. In these studies, synthesis and carburization runs alternated with measurements of the surface area and CO-chemisorption at low temperature. The latter is generally considered to represent a measure of the free, exposed, cobalt on the surface.¹³ Synthesis gas was passed over an active cobalt catalyst, while the temperature was gradually raised from 150° C. to 190° C. As soon as the volumetric contraction reached 70%, the catalyst was flushed with nitrogen at 200° C. to remove physically sorbed vapours and further degassed by evacuation at the same temperature. The value of the CO-chemisorption obtained for the catalyst after this treatment was 75% of the value found for the fresh catalyst after reduction and prolonged evacuation at 300° C. This clearly demonstrates that at least 75% of the substrate in synthesis could be 'cleared' by evacuation at the reaction temperature. That this could not have happened had

there been any extensive carbiding of the catalyst, was shown by another experiment in which the catalyst was deliberately carburized by passing carbon monoxide for nearly 32 hours at 200° to 250° C. Evacuation at 300° C., after this treatment, did not restore more than 25% of the original value for the chemisorption of carbon monoxide. The carbided catalyst was also found to be almost inactive in hydrocarbon synthesis. Only a little methane, but no higher hydrocarbons, was produced, possibly by the slow reduction of the carbide by the hydrogen present.

These researches, concerning the nature of the active substrate in the Fischer-Tropsch reaction lead to the conclusion that a chemisorbed complex of the reactants, such as CO-H, rather than a metal carbide, is the intermediate precursor to -CH₂- groups. This view places us in agreement with the results of two recent investigations reported from the U.S.A. Employing the 'tracer' technique, Kummer, et al.,¹⁴ have shown that "either ethyl alcohol or some surface complex formed by the adsorption of ethyl alcohol behaves as an intermediate in hydrocarbon synthesis over iron Fischer Tropsch cata-

lysts and that at least the first of the added carbon atoms attaches itself principally to the α -carbon atom of the surface complex". Drawing a parallel between the formation of branched chain hydrocarbons and that of branched chain alcohols in an operating Fischer Tropsch unit, Weitkamp¹⁵ concludes that the same mechanism operates in both cases.

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OIL REFINERY TO BE ESTABLISHED IN BOMBAY*

DURING his recent visit to the U.S.A. and U.K., Dr. Bhatnagar, who was entrusted with the task of exploring the oil refinery problem, held discussions with the Standard Vacuum Oil Company and Caltex in New York, and with the Burmah Shell and B.O.C. in London. These companies showed their willingness to start oil refineries in India and discussions were continued in India after his return. The proposal which has now been accepted by the Government of India is the result of this discussion. According to the agreement signed on November 30, the Standard Vacuum Oil Company of New York will instal a million ton oil refinery at Trombay, near Bombay.

To facilitate the project, the Government of India have given certain assurances to Standard Vacuum, including exemption from compulsory acquisition for a period of 25 years and exemption from certain provisions of the Industries (Development and Regulation) Act. Standard-

Vacuum on their part have assured Government that the refinery would be completed as early as possible, that an adequate number of Indian personnel will be trained in refinery operations for employment in the refinery and that byproducts of the refinery will be made available for subsidiary Indian industries.

The Company has already brought out to India a group of marine engineers and refinery experts who will collaborate with the Government of Bombay and the Bombay Port Trust officials for the necessary improvements in the dock and harbour facilities near the site where the refinery would be set up, and for the solution of other preliminary technical problems. The company hopes to bring the refinery into actual production within four years.

This is the first instance in which large-scale foreign investment is coming to India with a view to setting up a vital, new and complicated industry. Discussions are at the moment proceeding with other oil companies which may lead to additional refineries being established.

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