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Title	ADSORPTION OF HYDROGEN AND CARBON MONOXIDE AND THEIR MIXTURES ON IRON FISCHER-TROPSCH CATALYSTS : Part 1 : Synthesis experiments and adsorption studies with hydrogen and carbon monoxide on promoted and unpromoted iron catalysts
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ADSORPTION OF HYDROGEN AND CARBON MONOXIDE AND THEIR MIXTURES ON IRON FISCHER-TROPSCH CATALYSTS

Part I: Synthesis experiments and adsorption studies with
hydrogen and carbon monoxide on promoted
and unpromoted iron catalysts

By

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Abstract

In order to gain an insight into the nature of the reactive substrate formed in FISCHER-TROPSCH synthesis and its relation with experimental parameters such as the influence of promoter, temperature, pressure, and composition of the mixture of hydrogen and carbon monoxide used, investigations were carried out on the behaviour of two iron catalysts, one of which had alkali as the promoter.

In the synthesis with $1\text{H}_2:1\text{CO}$ mixture, the catalyst with alkali (Fe 2) gave about 28 g/m^3 of liquid and solid hydrocarbons whereas the catalyst without alkali (Fe 1) gave negligible amounts of the liquid products. In the adsorption from single gases, Fe 2 adsorbed about half the volume of the gas as compared with Fe 1. This is attributed to the coverage of nearly 70% of the iron surface in Fe 2 by alkali.

Introduction

The variables of FISCHER-TROPSCH synthesis as well as the mechanism of the synthesis have been extensively investigated using different techniques. The mechanisms proposed for the synthesis have laid emphasis on the importance of chemisorption of hydrogen and carbon monoxide.

Earlier mechanisms of FISCHER and coworkers¹⁾ and CRAXFORD and RIDEAL²⁾ and MATSUMARA³⁾, postulated carbide formation as the precursor to synthesis. However, investigations carried out at the BUREAU of MINES⁴⁻⁶⁾ have established that the bulk phase carbide is not formed at any stage of the synthesis and that the carbide is neither an intermediate nor a catalytically active substrate for the reduction of carbon monoxide to hydrocarbons. These

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results were confirmed by KUMMER, DEWITT and EMMETT⁷⁾ who employed radioactive C¹⁴ as the tracer. Later, KUMMER *et al.*⁸⁾ showed that either ethyl alcohol or some other adsorption complex acts as the intermediate. These results support the views of ELVINS and NASH⁹⁾ and HAMAI¹⁰⁾, who noticed that the enolic complexes are formed first by the interaction of the adsorbed hydrogen and carbon monoxide.

The literature cited above indicates that the cobalt FISCHER-TROPSCH catalysts have been widely employed to study the mechanism of the synthesis. In recent years, however, iron catalysts have come into prominence because of their low cost and the wide range of selectivity and operating conditions. It has also been shown that the alkali added as a promoter to iron catalysts increases the activity and the average molecular weight of the hydrocarbons in the synthesis. A detailed study of the effect of alkali on the adsorption characteristics as well as the nature of products obtained in the synthesis has not been carried out so far on iron catalysts.

In the present investigations, the effect of alkali as promoter on the characteristics of the iron catalysts in the synthesis has been studied. Also, the adsorption of hydrogen and carbon monoxide from single gases on two iron catalysts (one with the alkali) at different temperatures has been studied.

Experimental

Materials: The composition of the two catalysts before reduction was as follows:

Fe 1—Fe₃O₄ (94.0%) MgO (4.6%) SiO₂ (0.7%) Cr₂O₃ (0.7%) and

Fe 2—Fe₃O₄ (93.4%) MgO (4.6%) SiO₂ (0.7%) Cr₂O₃ (0.7%) K₂CO₃ (0.8%)

The catalyst Fe 1 was prepared by the co-precipitation of ferric and chromium hydroxides by the addition of ammonia to a hot solution of 10% ferric nitrate containing the desired amount of chromium nitrate. The precipitate was washed by decantation and then thoroughly mixed with precipitated silica and magnesium oxide and washed well on a Buchner and dried at 110°C. The hard cake thus obtained was crushed to get the required size (−10+20 mesh). The second catalyst Fe 2 was prepared by the addition of the desired quantity of potassium carbonate to the wet precipitate before drying.

Carbon monoxide was prepared by the dehydration of formic acid. The gas was analysed by the Orsat apparatus and was found to be quite pure (99.5%). Electrolytic hydrogen was purified by passing over platinised asbestos at 350°C. The gases were dried over phosphorus pentoxide and stored over

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mercury. Helium from the cylinder was purified by passing over activated charcoal cooled to -184°C .

The catalysts were thoroughly reduced at 400°C in a stream of pure hydrogen for nearly 72 hours till no more moisture was detected in the exit gas.

The adsorption of nitrogen, hydrogen and carbon monoxide was conducted on samples evacuated at 400°C under a vacuum of 10^{-5} mmHg for 8 hours. After each adsorption run, the catalyst was reduced again at 400°C for about 24 hours and evacuated at the same temperature for 8 hours for use in subsequent runs.

Adsorption apparatus: The apparatus used for adsorption was the conventional B.E.T. apparatus used by GHOSH *et al.*¹¹⁾ The system could be evacuated by an oil diffusion pump to a pressure of 10^{-5} mmHg. For maintaining the catalyst at different temperatures, acetone (53°), water (97°) and nitrobenzene (134°) were used as boiling liquid baths. For degassing the catalyst an electric furnace controlled by a Sunvic energy regulator to within $\pm 1^{\circ}$ was used.

Measurement of adsorption: The adsorption isotherms were determined in the usual manner from the volumes of gas admitted and the pressures registered on the manometer. The dead space was determined using helium.

Results and discussion

Surface areas:

The surface areas of the two samples were determined by the B.E.T. technique using nitrogen isotherms (area per molecule 17 \AA^2 at -184°C). The specific surface areas for Fe 1 and Fe 2 were $36.9 \text{ m}^2/\text{g}$ and $31.3 \text{ m}^2/\text{g}$ respectively. The introduction of 0.6% of alkali in Fe 2 did not appreciably change the specific surface area of the catalyst. As shown later, the incorporation of the alkali considerably changed the active metal centres and the adsorption characteristics of the catalyst Fe 2.

Synthesis experiments:

The two catalysts were tested for their efficiency in the synthesis with $1\text{H}_2 : 1\text{CO}$ (by volume) gas mixture, at atmospheric pressure, and at 8 atms. pressure under the static and flow conditions.

1. Atmospheric pressure synthesis:

The catalyst was well packed in a hard glass tube and maintained at 180°C , 220°C and 250°C . A mixture of H_2 and CO (1 : 1) was passed over

the catalyst for 6 hours. The effluent gas was cooled at -12°C to collect any liquid formed. A sample of the gas was then collected over mercury and analysed for carbon dioxide, unsaturated hydrocarbons, carbon monoxide, hydrogen and saturated hydrocarbons.

2. Static experiments at 8 atmospheres :

These experiments were conducted in a steel bomb with external electric heating. A $1\text{H}_2 : 1\text{CO}$ gas mixture was allowed to remain in contact with the catalyst at 180°C , 220°C and 250°C till maximum contraction was observed (40–60 mins.). The products were let out through a bubbler cooled to -12°C and the effluent gas was analysed as mentioned above.

In both the atmospheric pressure synthesis and high pressure static experiment no detectable liquid products were present in the effluent gas, due perhaps, to the small amount of the gaseous mixture (2 litres) employed. However the analysis of effluent gases revealed some important features. Results of experiments at 250°C are reported in Table 1. At lower temperatures the conversions were low and hence the results of these experiments are not reported. From Table 1, it is seen that there is a marked contrast between Fe 1 and Fe 2 in the specificity of conversion. The $\text{CH}_4/\text{C}_2\text{H}_6$ ratio for Fe 2 is smaller than that for Fe 1.

TABLE 1. Analysis of effluent gases during atmospheric and high pressure (static) syntheses

Gas	Composition of effluent gas (% by volume)			
	Temp. 250°C			
	1 atmosphere		8 atmospheres (static)	
	Fe 1	Fe 2	Fe 1	Fe 2
CO_2	36.1	24.0	38.7	7.1
Unsaturated hydrocarbons	1.0	1.1	0.9	1.8
CO	4.0	4.8	10.4	10.5
H_2	40.0	35.0	19.0	20.0
CH_4	11.4	22.2	19.7	29.8
C_2H_6	5.5	12.0	10.4	27.1

3. Flow experiments at 8 atmospheres :

In these experiments the compressed $1\text{H}_2 : 1\text{CO}$ mixture from a cylinder was passed at a space velocity of 100 hr^{-1} over the catalysts (55 g) at 220°C while the pressure was maintained at about 120 psig. At the end of 50 hrs., the catalyst Fe 1 gave negligible amounts of liquid products while Fe 2 gave about 28 g/m^3 of liquid products.

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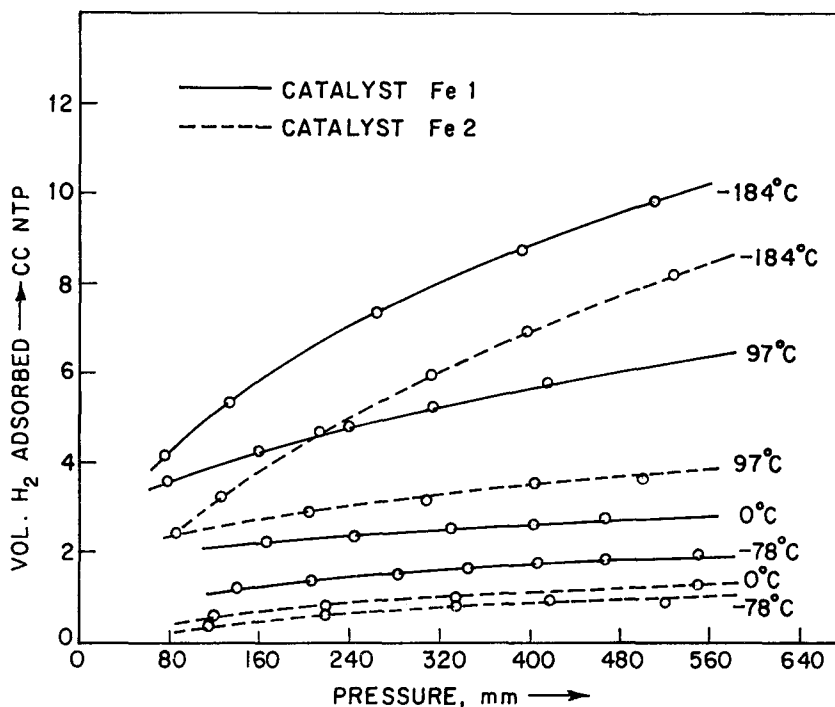


Fig. 1. Adsorption isotherms of hydrogen on Fe 1 and Fe 2.

The results of the above experiments show that Fe 1 gives mainly hydrocarbons of low average molecular weight while Fe 2 gives hydrocarbons of high average molecular weight. This prompted the authors to investigate the adsorption characteristics of the two catalysts which were expected to throw light on the mechanism of the synthesis and the effect of alkali as promoter.

Adsorption of hydrogen and carbon monoxide on Fe 1 and Fe 2:

Adsorption of hydrogen and carbon monoxide on the catalysts was carried out at temperatures ranging from -184°C to 134°C . Prior to every adsorption run, the catalyst (5.4 g) was degassed at 400°C at a pressure of 10^{-5} mm Hg for 8 hours. After the determination of the isotherm, the catalyst was maintained at the temperature of the experiment and the gas in the free space and the gas that could be desorbed from the catalyst were collected using a Töpler pump to determine the volume of the gas retained at the solid surface. In the case of CO adsorption, the gas thus collected was analysed to find out the extent of any chemical reaction.

The values of adsorption of hydrogen and carbon monoxide at various

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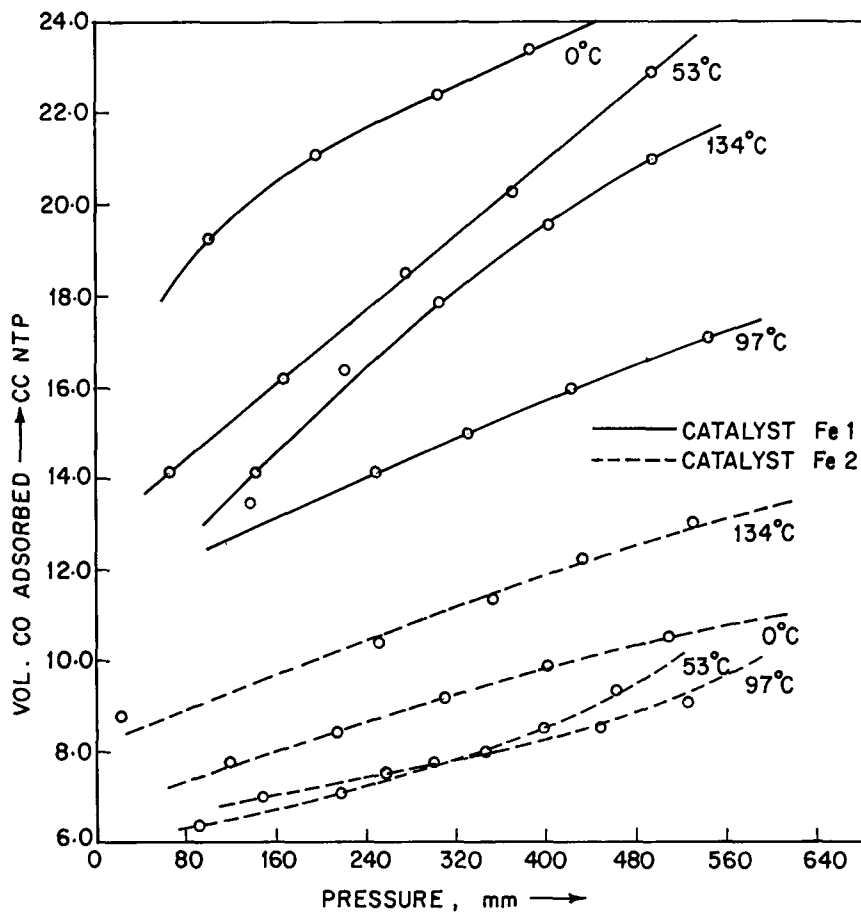


Fig. 2. Adsorption isotherms of carbon monoxide on Fe 1 and Fe 2.

TABLE 2. Retention of hydrogen and carbon monoxide by Fe 1 and Fe 2

(Expressed as c c NTP for 5.4 g catalyst)

Temp. °C	A. Hydrogen		B. Carbon monoxide	
	Fe 1	Fe 2	Fe 1	Fe 2
- 184	nil	nil	26.0	20.0
- 78	0.9	0.2	—	—
0	1.0	0.2	20.0	9.1
53	2.9	1.8	14.3	9.3
97	3.4	2.0	10.1	7.7
134	3.0	1.8	7.4	7.3

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temperatures on Fe 1 and Fe 2 are presented in Figs 1 and 2 respectively.

The adsorption of H₂ at -184°C is purely physical since all the gas could be desorbed by the Töpler pump. At temperatures of -78°C and above, some of the gas adsorbed could not be removed by the Töpler pump showing that chemisorption had set in. The amounts of gases retained on desorption are given by Table 2.

The results indicate that the retention of hydrogen with both the catalysts increases with an increase in temperature. The amount is always higher for Fe 1 than for Fe 2. The amount of carbon monoxide retained is quite high as compared with that of hydrogen. At elevated temperatures the desorbed gas contained carbon dioxide obtained by disproportionation of carbon monoxide into carbon and carbon dioxide (2% at 97°C for both Fe 1 and Fe 2 and 15% for Fe 1 and 6% for Fe 2 respectively at 134°C).

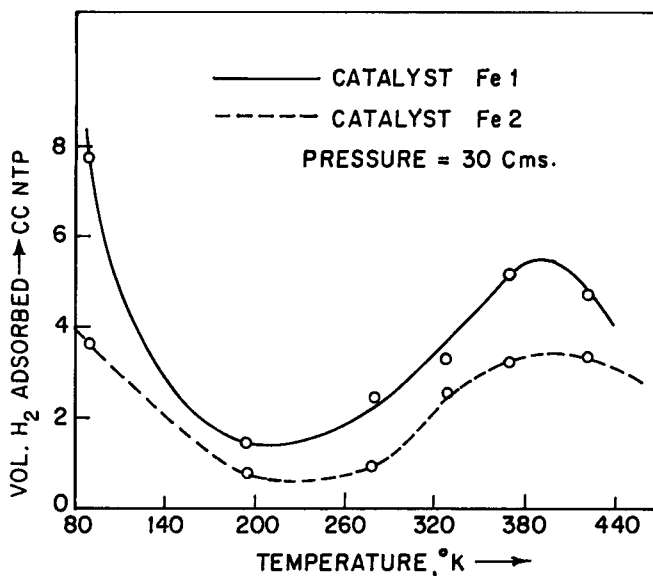


Fig. 3. Adsorption isobars of hydrogen on Fe 1 and Fe 2.

The isobars of adsorption of hydrogen and carbon monoxide on Fe 1 and Fe 2 are given in Figs. 3 and 4 respectively, for a pressure of 30 cms. In the case of hydrogen, an increase in temperature from -184°C to -78°C shows a marked fall in adsorption. Further increase in temperature enhances the adsorption, indicating chemisorption of hydrogen at elevated temperatures. A maximum is observed at 100°C . EMMETT and HARKNESS¹²⁾ also observed similar hydrogen isobars with iron catalysts and explained the nature of the

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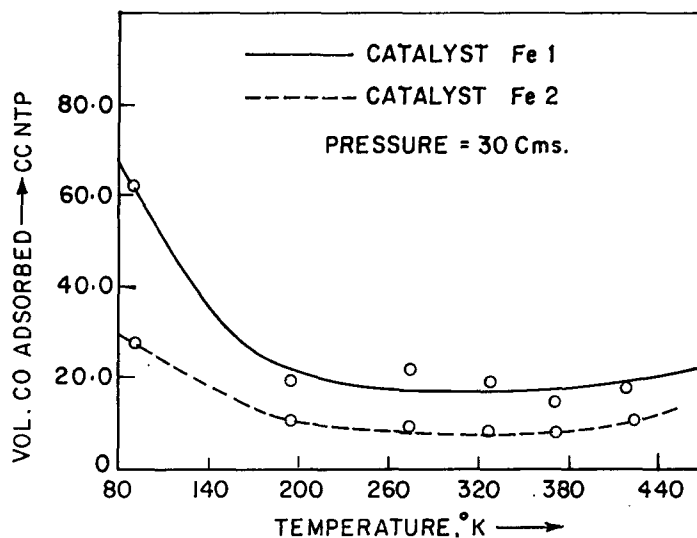


Fig. 4. Adsorption isobars of carbon monoxide on Fe 1 and Fe 2.

isobar on the basis of different types (type A and type B) of chemisorption occurring on the catalyst surface.

In the case of carbon monoxide, however, the adsorption decreases upto about 195°K (−78°C) and then remains practically constant for both the catalysts at higher temperatures.

In order to explain the difference in the adsorptive properties of Fe 1 and Fe 2, the extent of the free metallic surface was determined. ANDERSON'S method¹³⁾ was used for purposes of comparison of the surface properties of Fe 1 and Fe 2. Using this method, the fraction of the metallic surface, $\frac{V_{CO} - V_{N_2}}{V_m(N_2)}$ that is active in chemisorbing carbon monoxide on Fe 1 has been found to be 0.43 and that on Fe 2 to be 0.16. It is thus evident that introduction of 0.6% of alkali in Fe 2 has diminished the active metallic area from 43% (in Fe 1) to 16% (in Fe 2) of the total surface.

The adsorption of hydrogen is very much less in the case of Fe 2 than in the case of Fe 1 (Fig. 1). The difference between the two values is marked at lower temperatures. The difference in the values of adsorption of hydrogen and carbon monoxide between promoted and unpromoted catalysts has also been reported by BRUNAUER and EMMETT¹⁴⁾ who explain that inclusion of about 1% of alkali would curtail chemisorption of carbon monoxide which occurs only on metallic sites. It is reported that the alkali covers as much as 50% of the metallic surface. The higher adsorption on Fe 1 can

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be attributed to the higher metallic surface (43% of the total area) as compared with Fe 2 (16% of the total area).

In spite of the lowering of the metallic surface area, it is interesting to note that Fe 2 shows enhanced catalytic conversion of hydrogen and carbon monoxide into hydrocarbons of higher molecular weight. NIELSEN¹⁵ has also noticed similar non-parallelism between 'metallic surface areas' and catalytic activities on singly and doubly promoted as well as unpromoted catalysts.

Alkali has a profound influence on the characteristics of the catalysts and is responsible for Fe 2 giving hydrocarbons of higher molecular weight. The change in the catalytic activity may be due to a change in the composition of the adsorbed layer when it is in equilibrium with a mixture of hydrogen and carbon monoxide in the gaseous phase. This aspect is presented in detail in Part II.

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