



Title	ADSORPTION OF HYDROGEN AND CARBON MONOXIDE AND THEIR MIXTURES ON IRON FISCHER-TROPSCH CATALYSTS : Part : Adsorption from mixtures of 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 II: Adsorption from mixtures of hydrogen and carbon monoxide on promoted and unpromoted iron catalysts

By

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Abstract

Adsorption studies on the promoted and unpromoted iron catalysts were conducted with $1\text{H}_2:1\text{CO}$, $1\text{H}_2:2\text{CO}$ and $2\text{H}_2:1\text{CO}$ mixtures using a thermal conductivity meter for analysis. Kinetic studies indicated that initially adsorbed hydrogen was partly displaced by carbon monoxide below 53°C . At higher temperatures, the displacement of hydrogen did not occur. The amounts of the adsorbed hydrogen and carbon monoxide increased concomitantly, with all the three mixtures. During the equilibrium studies, it was observed that with an increase in temperature, the amount of hydrogen adsorbed increased, but the increase in the adsorption of carbon monoxide was less prominent. On the unpromoted catalyst, at 97°C , the $\text{H}_2:\text{CO}$ ratio in the adsorbed phase was $1:1.4$ with the $1\text{H}_2:1\text{CO}$ and $1\text{H}_2:2\text{CO}$ mixtures but was $2:1$ with $2\text{H}_2:1\text{CO}$ mixture. This ratio, however, decreased nearly to $1:2$ with all the mixtures on the promoted catalyst. The higher adsorption of carbon monoxide with the promoted catalyst is attributed to be responsible for the differences in the behaviour of the catalysts in Fischer-Tropsch synthesis. It is also pro-

posed that a surface complex of the type $\text{R}-\overset{\text{H}}{\underset{\text{OH}}{\text{C}}}-\text{M}$ is formed initially on both the catalysts and this complex initiates the reaction.

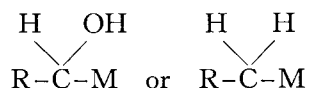
Introduction

Temperature effect on the adsorption of hydrogen and carbon monoxide with unpromoted and alkali-promoted catalysts (Fe 1 and Fe 2 respectively) has been described in Part I. When compared with the studies on the adsorption of single gases on a variety of adsorbents, the data on the adsorption of mixtures are scanty, especially in the region of chemisorption. Non-

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mutual enhancement of adsorption of hydrogen and carbon monoxide on cobalt catalysts has been reported by SASTRY *et al.*¹⁾ KINI²⁾ working on a cobalt Fischer-Tropsch catalyst suggested that an initial substrate of 1H₂ : 1CO is formed on the catalyst. Evidence suggesting the formation of a surface complex is provided by the infrared studies on the adsorption of mixtures of hydrogen and carbon monoxide on silica-supported iron³⁾. It is reported in this study that on adsorbing hydrogen and carbon monoxide, at 180°C on Cab-o-Sil supported iron, three bands at 3.3 μ corresponding to gas phase methane are obtained. The authors suggest the formation of intermediates of the type



where R is a hydrogen atom or an alkane group.

In order to augment the information about the influence of adsorption of one gas on the adsorption of the other, during simultaneous adsorption, studies were undertaken with three gaseous mixtures of composition 1H₂ : 1CO, 1H₂ : 2CO and 2H₂ : 1CO. The studies were conducted at -78°, 0°, 53° and 97 °C on the two catalysts Fe 1 and Fe 2.

Experimental

The method of preparation of the catalysts and the gases employed in the studies has been described in Part I. The apparatus employed for the studies has also been described therein.

To determine the composition of the gaseous mixture in equilibrium with the catalyst, a differential thermal conductivity meter (Katharometer) was employed. The Katharometer consisted of four matched Pirani cells, forming a Wheatstone bridge network. Two of the cells were connected to the system while the other two were sealed with a 1H₂ : 1CO mixture for reference. When the gas in the system was different in composition from the reference gas, it gave rise to an off-balance potential, which was indicated by a sensitive galvanometer. The readings of the latter were calibrated with mixtures of known composition.

The Katharometer was tested for quick response to the variation of the composition of the equilibrium mixture. In a test experiment, a known amount of hydrogen (9 c.c. NTP) was let into the evacuated system consisting of an empty catalyst tube. A known volume (8.7 c.c. NTP) of carbon monoxide was also added to the system. To ensure uniformity of gas composition throughout the system, the mixture of the gases was agitated using the

levelling bulb of the gas burette. It was found that at the end of 25 mins., the Katharometer indicated the calculated reading for the mixture of the two gases and thereafter, the reading was constant. Within ten minutes, the Katharometer reading gave 80% of the expected value. In all the experiments conducted with the mixtures, the equilibrium composition was read off after an interval of 30 mins.

After the equilibrium studies, conducted for a period of 16 hours, the gaseous phase was removed using a Töpler pump and analysed for carbon dioxide, unsaturated hydrocarbons, carbon monoxide, hydrogen and saturated hydrocarbons. Below 97°C, the desorbed gas consisted of only hydrogen and carbon monoxide showing the absence of any chemical reaction between the two gases. At 97°C, however, the analysis indicated that the reaction had set in to an extent of about 8% of the total gas. The results reported for 97°C are not hence strictly quantitative. However, they provide a qualitative treatment of the nature of adsorption. Studies were restricted to a maximum temperature of 97°C.

Results

Kinetics of adsorption from mixtures

The kinetics of adsorption from mixtures at -78° , 0° , 53° and 97°C were carried out to assess the composition of the adsorbed phase at various intervals of contact with the catalyst. Mixtures (10 cc NTP) of known composition ($1\text{H}_2 : 1\text{CO}$, $1\text{H}_2 : 2\text{CO}$ and $2\text{H}_2 : 1\text{CO}$) were allowed into the catalyst tube containing 5.4 g. of the adsorbent. The Katharometer readings were recorded at 15 minute intervals to begin with and then the interval was increased to 60 mins. The readings were taken for about 10 hours when equilibrium was attained. Since the volume, pressure and the composition of the gaseous phase at various intervals were known, the amounts of hydrogen and carbon monoxide taken up by the catalyst could be calculated.

The volumes of hydrogen and carbon monoxide adsorbed from 15 cc NTP of the mixture were plotted as a function of time. Kinetic plots are given in Fig. 1, for the adsorption from different mixtures at 0°C on Fe 1. The following general conclusions can be drawn from the data. (a) The extrapolated values for the adsorption of hydrogen and carbon monoxide at zero time are nearly the same as the composition of the mixture admitted. (b) With the progress of time, there is a gradual diminution in the adsorption of hydrogen and an increase in the adsorption of carbon monoxide. It can be inferred that carbon monoxide displaces hydrogen from the surface for about 6 hours. (c) Beyond 6 hours, there is a slight increase in the adsorption

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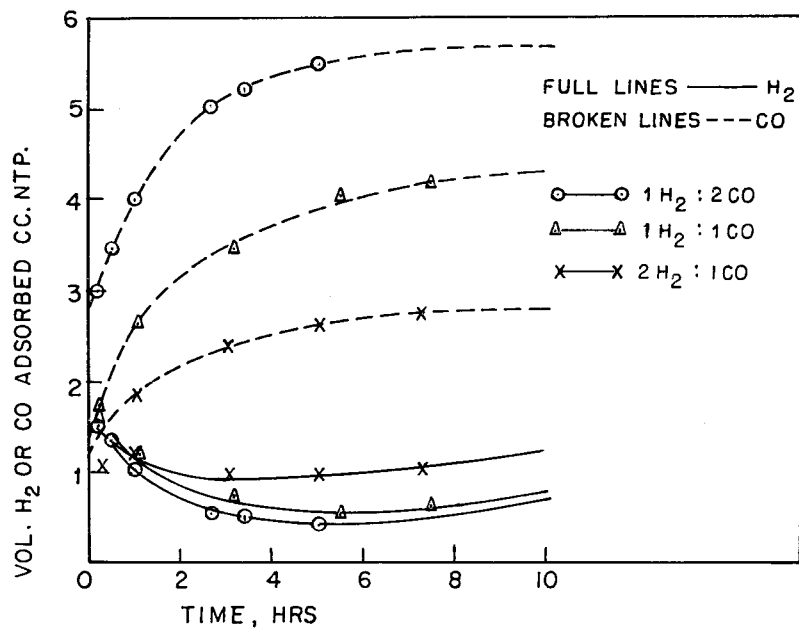


Fig. 1. Kinetics of adsorption of hydrogen and carbon monoxide on Fe 1 at 0° from different mixtures.

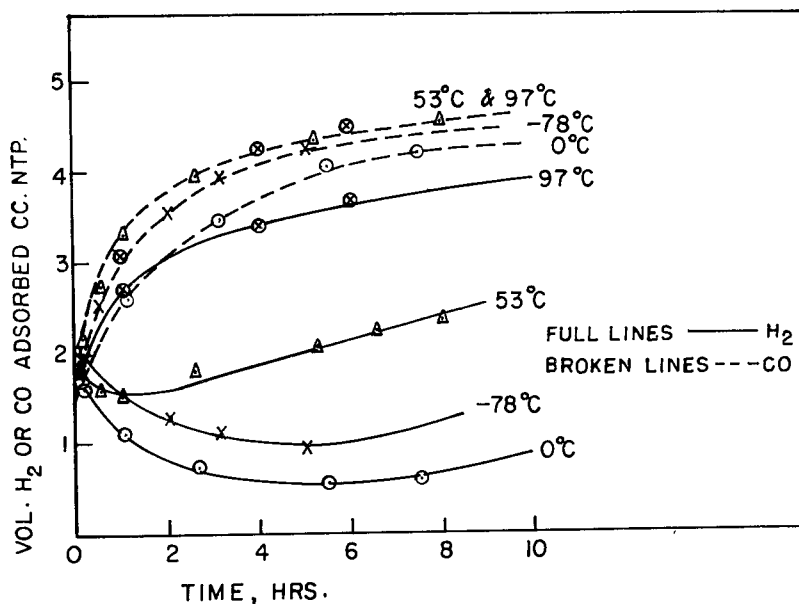


Fig. 2. Kinetics of adsorption of hydrogen and carbon monoxide on Fe 1 at different temperatures from $1 H_2 : 1 CO$ mixture.

of hydrogen. In general, the amount of carbon monoxide adsorbed, is far greater than that of hydrogen.

The effect of temperature on the adsorption of hydrogen and carbon monoxide from $1\text{H}_2 : 1\text{CO}$ mixture is illustrated by Fig. 2. From the figure, the following conclusions can be arrived at: (a) As the temperature is increased from 0° , there is a pronounced increase in the adsorption of hydrogen and only a slight increase in the adsorption of carbon monoxide. However, the adsorption of hydrogen is lower than that of carbon monoxide. (b) At 97° , there is no substitution of the initially adsorbed hydrogen and the adsorptions of hydrogen and carbon monoxide increase concomitantly. The results obtained at -78° , however, cannot be easily interpreted because of the possibility of chemisorption and physical adsorption of the gases occurring simultaneously.

The kinetic curves for the adsorption of hydrogen and carbon monoxide at 0°C from the three mixtures for the catalyst Fe 2 are given by Fig. 3. The kinetic curves for Fe 2 are similar to those obtained for Fe 1 (Fig. 1).

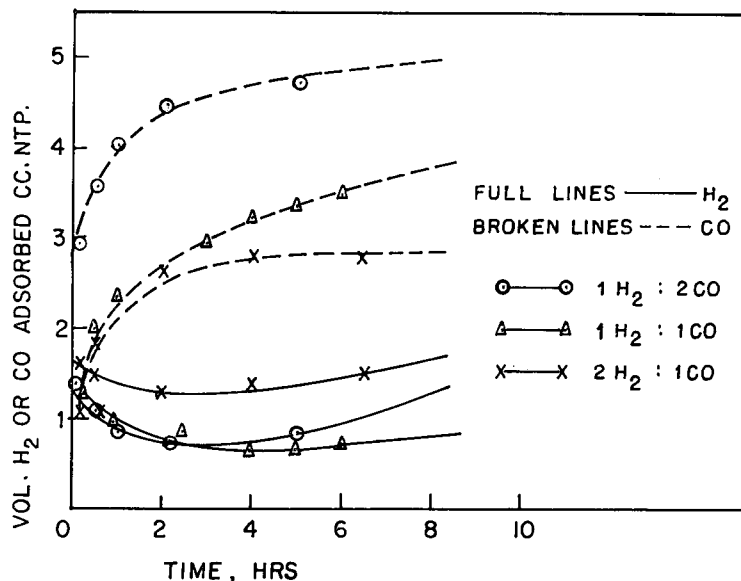


Fig. 3. Kinetics of adsorption of hydrogen and carbon monoxide on Fe 2 at 0° from different mixtures.

The effect of temperature on the adsorption from the $1\text{H}_2 : 1\text{CO}$ mixture at various temperatures is illustrated in Fig. 4. As in the case of Fe 1 (Fig. 2), an increase in temperature from 0°C enhances the adsorption of the gases.

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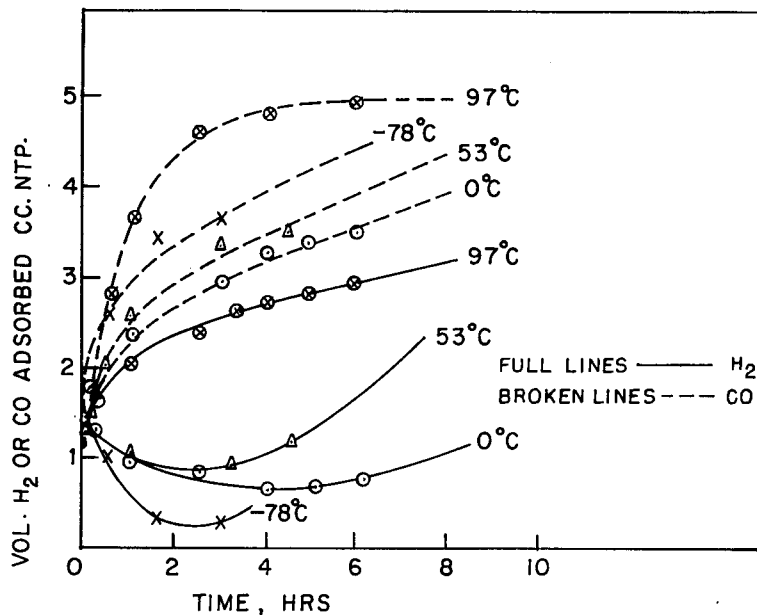


Fig. 4. Kinetics of adsorption of hydrogen and carbon monoxide on Fe 2 at different temperatures from 1H₂:1CO mixture.

At elevated temperatures, it is noticed that the CO/H₂ ratio in the adsorbed phase is higher for Fe 2 than for Fe 1.

Effect of pressure on the composition of the adsorbed phase at equilibrium

After the completion of the kinetic studies (8 hrs.), a further quantity of the same mixture was added to the system and the gas phase was agitated as described earlier. The equilibrium was attained, in general, within two hours, after which the Katharometer reading was noted. The amounts of hydrogen and carbon monoxide adsorbed at the end of this period were calculated. The procedure was repeated with additional quantities of the mixture, until the total pressure was about 55 cms. The volumes of the gases adsorbed were plotted against the respective partial pressures at equilibrium. Three mixtures of composition 1H₂:1CO, 1H₂:2CO and 2H₂:1CO were used at each of the temperatures, -78°, 0°, 53° and 97°C. Studies were not conducted above 97°C for reasons enumerated already.

Results obtained with catalyst Fe 1

The results of the equilibrium studies at the four temperatures and with the three mixtures for 5.4g of the catalyst Fe 1 are presented in Figs. 5, 6, 7 and 8. Fig. 6 gives the amounts of adsorption of hydrogen and carbon

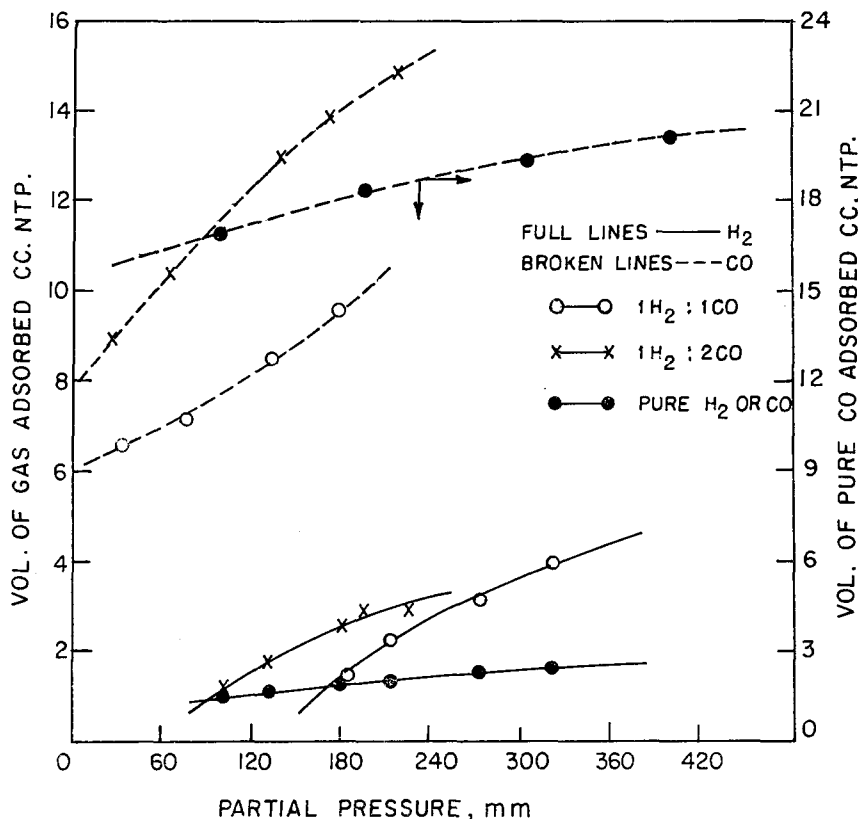


Fig. 5. Adsorption isotherms of hydrogen and carbon monoxide from mixtures on Fe 1 at -78° .

monoxide plotted against the partial pressures, at $0^\circ C$. The adsorption of carbon monoxide at $0^\circ C$ is far greater than that of hydrogen. However, the adsorption of hydrogen as well as carbon monoxide is less than that from the single gases at a given partial pressure. It is also clear from the figure that the adsorption of a small quantity of hydrogen brings down the adsorption of carbon monoxide. At a pressure of 15 cms., for example, 0.8 cc NTP of hydrogen is adsorbed from $1H_2 : 1CO$ mixture, the value for carbon monoxide being 7.8 cc NTP. If carbon monoxide were adsorbed alone, the value would be 20.2 cc NTP.

Fig. 7 gives the isotherms for the adsorption of hydrogen and carbon monoxide from the mixtures at $53^\circ C$. The nature of adsorption at $53^\circ C$ is similar to that observed at $0^\circ C$. The percentage hydrogen in the adsorbed phase is, however, greater at $53^\circ C$ than at $0^\circ C$ at a given partial pressure.

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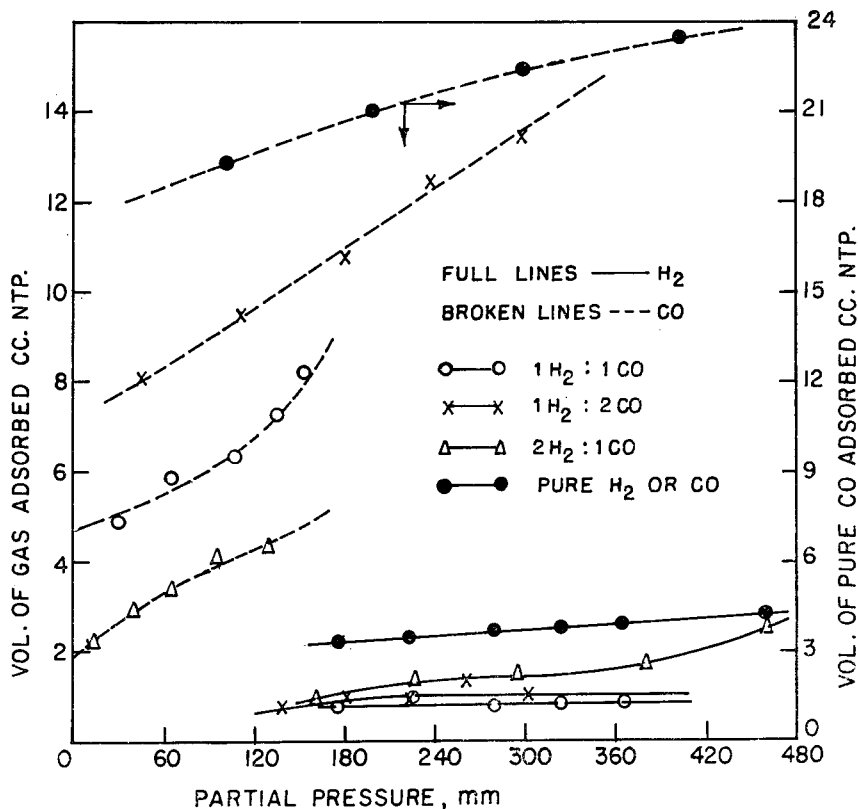


Fig. 6. Adsorption isotherms of hydrogen and carbon monoxide from mixtures on Fe 1 at 0°.

When the temperature is increased to 97°C (Fig. 8), there is a pronounced increase in the adsorption of hydrogen. As against the adsorption at 0°C or 53°C, the adsorption of hydrogen from mixtures at 97°C far exceeds that from single gas. The increase is greatest in the case of $2H_2 : 1CO$ mixture. This adsorption is also greater than the adsorption of carbon monoxide from the same mixture.

Table 1 gives the overall picture of the effect of temperature on the composition of the adsorbed phase and the total adsorption ($H_2 + CO$) with Fe 1, at the end of 16 hours of contact with the catalyst. The total adsorption is recorded as the value based on 40 cc NTP of the gas mixture admitted, for 5.4 g of the catalyst.

It is evident from Table 1 that at a given temperature, an increase in the partial pressure of hydrogen in the mixture greatly enhances the percentage

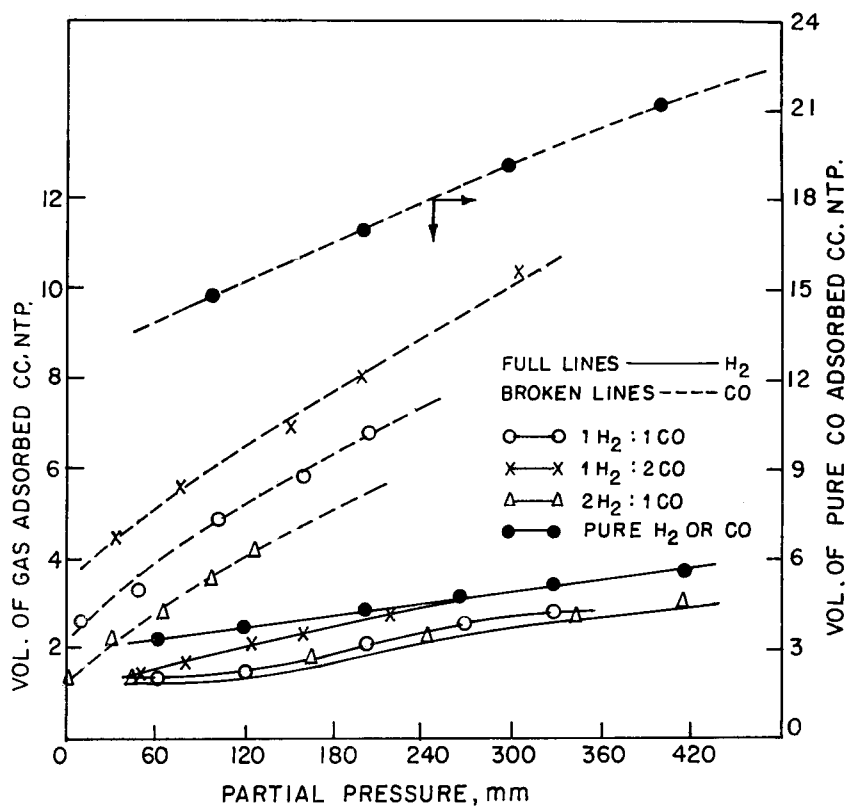


Fig. 7. Adsorption isotherms of hydrogen and carbon monoxide from mixtures on Fe 1 at 53°.

TABLE 1. Effect of temperature on the composition of the adsorbed phase and total adsorption (H_2+CO) for Fe 1

Composition of mixture	-78°C		0°C		53°C		97°C	
	% H_2 in adsd phase	Total adsn.	% H_2 in adsd phase	Total adsn.	% H_2 in adsd phase	Total adsn.	% H_2 in adsd phase	Total adsn.
$1H_2:2CO$	15.3	13.5	8.4	14.4	23.0	12.3	36.0	18.1
$1H_2:1CO$	24.8	17.9	11.0	9.1	30.0	9.6	45.0	15.5
$2H_2:1CO$	—	—	31.0	6.8	44.3	7.1	69.8	22.4

hydrogen in the adsorbed phase. In general, the total amount adsorbed decreases with an increase in the partial pressure of hydrogen except at 97°C.

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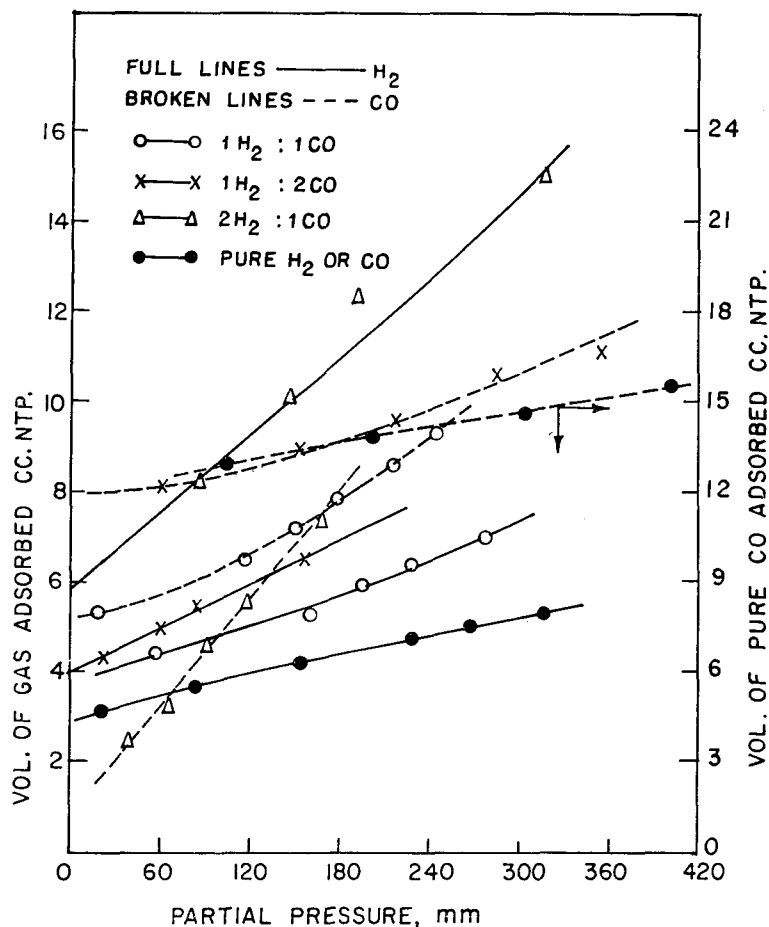


Fig. 8. Adsorption isotherms of hydrogen and carbon monoxide from mixtures on Fe 1 at 97°.

For a given mixture, an increase in temperature above 0°C enhances the percentage hydrogen in the adsorbed phase. The total adsorption is greatly enhanced at 97°C as compared with that at 0°C or 53°C.

However, a close comparison of the adsorptive behaviour of the two catalysts can be made when the equilibrium partial pressure for each of the component gases is fixed at a particular value. For this purpose, a reference partial pressure of 120 mm Hg has been selected. The values of adsorption at this pressure for the three mixtures at different temperatures taken from Figs. 5, 6, 7 and 8 are presented in Table 2.

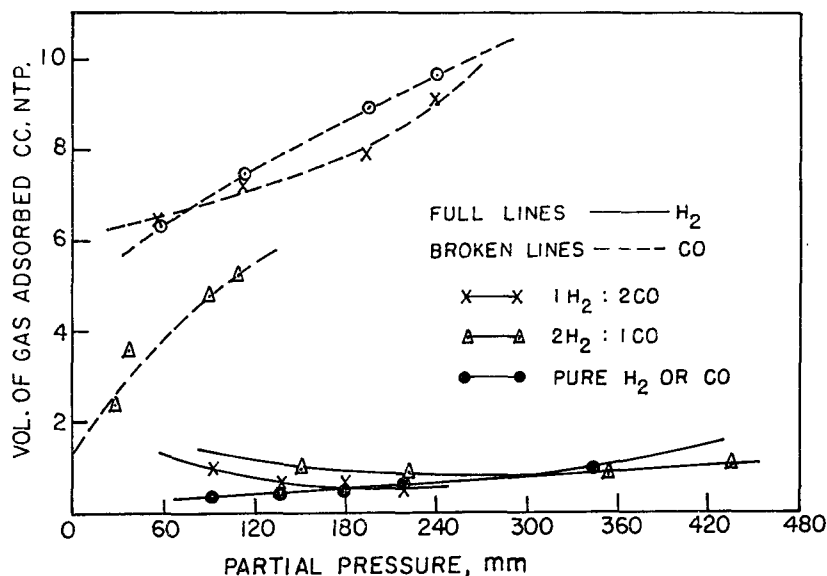
The results of Table 2 indicate that the total adsorption diminishes in

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TABLE 2. Adsorption of hydrogen and carbon monoxide (CC NTP) from different mixtures by catalyst Fe 1 (Wt.=5.4 g)

Original composition of gas mixture	Temp. -78°C		Temp. 0°C		Temp. 53°C		Temp. 97°C	
	H_2	CO	H_2	CO	H_2	CO	H_2	CO
$1\text{H}_2 : 2\text{CO}$	1.60	12.35	0.60	9.70	1.95	6.30	6.00	8.60
Ratio $\text{H}_2 : \text{CO}$	1 : 8		1 : 16		1 : 3.2		1 : 1.4	
$1\text{H}_2 : 1\text{CO}$	0.50	8.20	0.60	6.80	1.45	5.05	5.00	6.60
Ratio $\text{H}_2 : \text{CO}$	1 : 16		1 : 11		1 : 3.2		1 : 1.4	
$2\text{H}_2 : 1\text{CO}$			0.60	4.20	1.30	4.00	9.20	5.70
Ratio $\text{H}_2 : \text{CO}$			1 : 7		1 : 3.1		1 : 0.6	
Adsorption from single gas	1.12	17.00	2.00	19.65	2.40	15.20	3.95	13.23

the order $1\text{H}_2 : 2\text{CO} > 1\text{H}_2 : 1\text{CO} > 2\text{H}_2 : 1\text{CO}$. At temperatures below 97°C , the adsorption of hydrogen and carbon monoxide from the mixtures is less than that from the single gases. At 97°C , the hydrogen adsorption from mixtures far exceeds that from single gas. The adsorption of carbon monoxide, however, is less than that from single gas.

Fig. 9. Adsorption isotherms of hydrogen and carbon monoxide from mixtures on Fe 2 at -78° .

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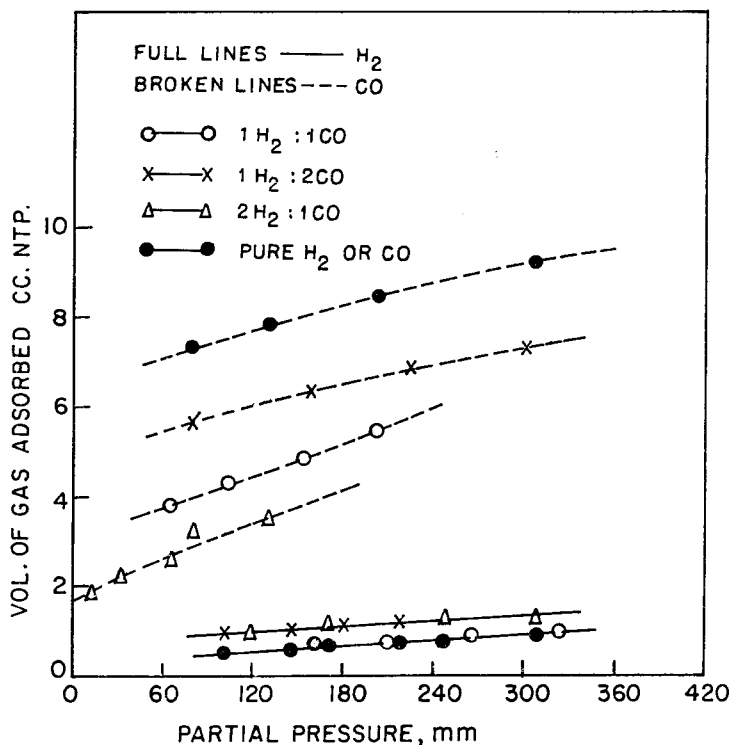


Fig. 10. Adsorption isotherms of hydrogen and carbon monoxide from mixtures on Fe 2 at 0°.

The CO/H₂ ratio for a given mixture diminishes, in general, with an increase in the temperature as can be inferred from Tables 1 and 2. The results obtained at -78°C cannot be easily explained since both physical adsorption and chemisorption might occur simultaneously at this temperature.

Catalyst Fe 2

Fig. 10 indicates the adsorption of hydrogen and carbon monoxide from mixtures at different partial pressures at 0°C for the catalyst Fe 2. As for Fe 1 (Fig. 6), the adsorption of carbon monoxide is far greater than that of hydrogen at a given partial pressure. The adsorption of hydrogen from the mixtures is either equal to or slightly greater than that for the single gas. The adsorption of carbon monoxide, however, is far less than that from the single gas.

Fig. 11 indicates that, at 53°C, the adsorption of both hydrogen and carbon monoxide is less than that from the single gases. However, the percentage hydrogen in the adsorbed phase is greater with all the mixtures

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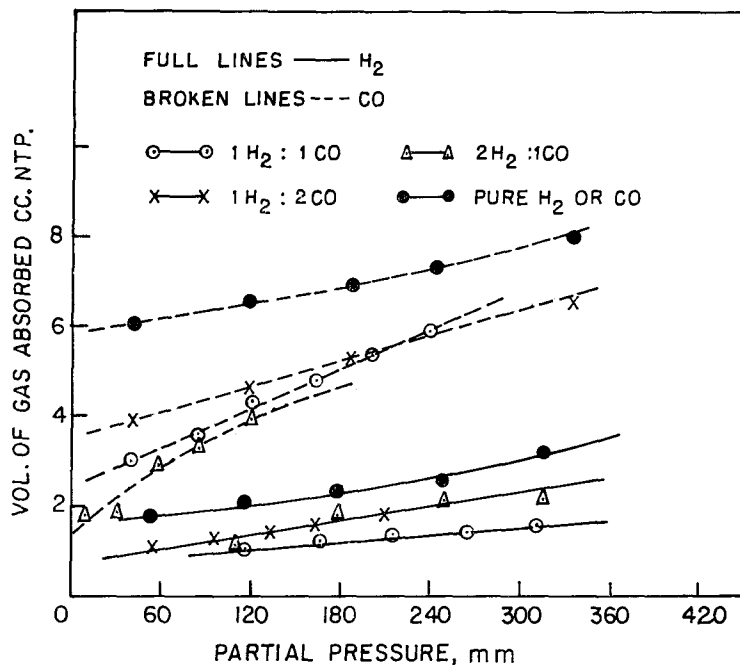


Fig. 11. Adsorption isotherms of hydrogen and carbon monoxide from mixtures on Fe 2 at 53°.

at 53°C than at 0°C (Fig. 10).

At 97°C, the catalyst Fe 2 exhibits exceptional behaviour (Fig. 12) as compared with Fe 1 (Fig. 8). With Fe 1, the adsorption of carbon monoxide from mixtures is lower than that from the single gas. The reverse is true in the case of Fe 2. Though the adsorption of hydrogen is greater with the mixture than with single gas, the adsorption on Fe 2 is greatest with 1H₂:2CO mixture, whereas this occurs with 2H₂:1CO mixture on Fe 1. Table

TABLE 3. Effect of temperature on the composition of the adsorbed phase and total adsorption (H₂+CO) for Fe 2

Composition of mixture	% H ₂ in adsd phase	Total adsn	% H ₂ in adsd phase	Total adsn	% H ₂ in adsd phase	Total adsn	% H ₂ in adsd phase	Total adsn
1H ₂ :2CO	8.10	9.67	14.30	8.52	21.50	8.27	32.70	25.84
1H ₂ :1CO	—	—	15.70	6.46	23.90	6.82	38.30	19.86
2H ₂ :1CO	19.40	6.27	32.40	5.08	41.50	6.48	49.90	12.42

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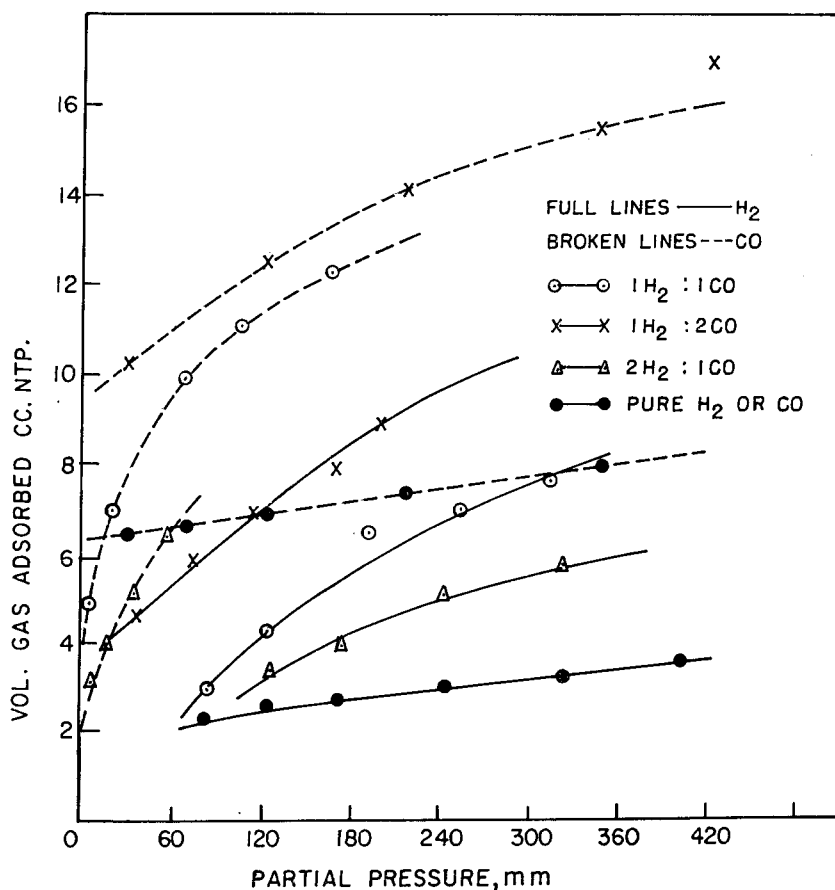


Fig. 12. Adsorption isotherms of hydrogen and carbon monoxide from mixtures on Fe 2 at 97°.

3 gives the overall picture of the effect of temperature on the composition of the adsorbed phase and the total adsorption ($H_2 + CO$) on Fe 2 at the end of 16 hours of contact with the catalyst. The total adsorption is calculated on the basis of 40 cc NTP of the gas mixture admitted, for 5.4 g of the catalyst.

The results of Table 3 indicate that, for a given mixture, the percentage hydrogen in the adsorbed phase increases with increasing temperature as in the case of Fe 1. The amount of mixture adsorbed does not vary much between -78°C and 53°C but is enormously increased at 97°C . The composition of the adsorbed phase (% H_2) remains almost the same for $1H_2 : 2CO$ and $1H_2 : 1CO$ mixtures. The composition is very different, however, in the

case of $2\text{H}_2 : 1\text{CO}$ mixture. The total adsorption decreases with an increase in the partial pressure of hydrogen in the mixture.

Values of adsorption (cc NTP) at a reference partial pressure of 120 mm of Hg for both hydrogen and carbon monoxide are taken from the isotherms (Figs. 9, 10, 11 and 12) and are presented in Table 4, for purposes of comparison with results for Fe 1.

TABLE 4. Adsorption of hydrogen and carbon monoxide from different mixtures by Fe 2 (Wt. 5.4 g)

Original Composition	Temp. -78°C		Temp. 0°C		Temp. 53°C		Temp. 97°C	
	H_2	CO	H_2	CO	H_2	CO	H_2	CO
$1\text{H}_2 : 2\text{CO}$	0.70	7.35	1.05	6.05	1.35	4.65	6.95	12.30
Ratio $\text{H}_2 : \text{CO}$	1 : 10.5		1 : 5.7		1 : 3.5		1 : 1.8	
$1\text{H}_2 : 1\text{CO}$	—		0.55	4.50	1.00	4.20	4.10	11.30
Ratio $\text{H}_2 : \text{CO}$			1 : 8.2		1 : 4.2		1 : 2.9	
$2\text{H}_2 : 1\text{CO}$	1.05	5.45	1.05	3.45	1.35	3.95	3.05	8.60
Ratio $\text{H}_2 : \text{CO}$	1 : 5.2		1 : 3.9		1 : 2.9		1 : 2.8	
Adsorption from single gas	0.35	7.70	0.55	7.60	1.95	6.50	2.45	6.80

Table 4 indicates that as in the case of Fe 1 (Table 2), the total amount of gases adsorbed generally diminishes in the order $1\text{H}_2 : 2\text{CO} > 1\text{H}_2 : 1\text{CO} > 2\text{H}_2 : 1\text{CO}$. At a given temperature, the total adsorption from mixtures is less than that calculated on the single gas basis, except at 97°C . At 97°C , the total adsorption as also the adsorption of the individual gases from mixtures, are greater than the adsorption calculated on the single gas basis. This is in marked contrast to the behaviour of Fe 1. The adsorption is highest with $1\text{H}_2 : 2\text{CO}$ mixture as against with $2\text{H}_2 : 1\text{CO}$ mixture in the case of Fe 1. The CO/H_2 ratio in the adsorbed phase decreases, in general, with an increase in the temperature.

Retention observations with Fe 1 and Fe 2

After the equilibrium studies, the gaseous mixture was desorbed at the same temperature and analysed for the constituents. The hydrogen and carbon monoxide retained on the catalyst were computed from the difference between the amounts admitted and the amounts desorbed. The temperature of the catalyst was then raised to 97°C and the gaseous phase that could be desorbed further was analysed. The amounts of hydrogen and carbon monoxide retained on the surface were calculated. The results of these studies are given in Table 5 (A and B) for the two catalysts.

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TABLE 5. Retention of hydrogen and carbon monoxide
on desorption (CC NTP/5.4 g catalyst)

A Catalyst Fe 1

Gas retained	Composition of mixture	Temp. of desorption					
		−78°C	97°C	0°C	97°C	53°C	97°C
Hydrogen	1H ₂ : 2CO	1.04	0.59	1.39	1.09	1.95	1.95
	1H ₂ : 1CO	1.12	0.66	—	—	1.86	1.86
	2H ₂ : 1CO	—	—	0.95	0.95	2.06	2.06
Carbon monoxide	1H ₂ : 2CO	13.45	3.62	9.34	2.09	6.54	4.10
	1H ₂ : 1CO	11.10	2.45	5.93	1.36	4.91	3.81
	2H ₂ : 1CO	—	—	3.83	1.16	3.47	2.82

B Catalyst Fe 2

Gas retained	Composition of mixture	Temp. of desorption					
		−78°C	97°C	0°C	97°C	53°C	97°C
Hydrogen	1H ₂ : 2CO	1.12	0.50	1.06	0.69	1.05	1.00
	1H ₂ : 1CO	—	—	1.25	0.60	1.37	1.25
	2H ₂ : 1CO	1.19	0.55	1.32	0.56	—	—
Carbon Monoxide	1H ₂ : 2CO	6.53	1.26	6.24	4.78	5.71	5.16
	1H ₂ : 1CO	—	—	4.72	3.18	4.58	4.17
	2H ₂ : 1CO	3.35	1.26	3.13	2.45	—	—

It is evident from Table 5 that on both the catalysts, about 40% of the hydrogen retained at the temperature of the experiment (−78°C or 0°C) can be desorbed on raising the temperature to 97°C. When the temperature of desorption is raised from 53°C to 97°C, however, almost all the gas remains on the surface for both Fe 1 and Fe 2. Contrary to these observations, Fe 1 and Fe 2 exhibit a pronounced difference with regard to retention of carbon monoxide. About 75% of the carbon monoxide retained at −78°C or 0°C and about 35% of the gas retained at 53°C can be removed by desorption at 97°C in the case of Fe 1. The corresponding figures for the catalyst Fe 2 are only 25% and 10%. Also, the ratio CO/H₂ of the gases retained on the surface of Fe 2 in the range 53°C to 97°C is higher as compared with the catalyst Fe 1 (Tables 2 and 4).

These facts clearly indicate that inspite of the lower metallic area, Fe 2 retains more carbon monoxide on the surface than Fe 1.

Discussion

Comparison of results obtained with Fe 1 and Fe 2

From Tables 2 and 4, it can be inferred that carbon monoxide is adsorbed to a great extent in preference to hydrogen on both the catalysts. However, this preferential adsorption is greater with Fe 2 than with Fe 1. At 0°C, the CO/H₂ ratio is quite high with Fe 1 as compared with Fe 2. At 53°C, the ratios are nearly the same. At 97°C, the CO/H₂ ratio is greater with Fe 2 than with Fe 1. With Fe 1, at 97°C, there is a great enhancement in the adsorption of hydrogen compared with single gas adsorption and diminution of adsorption of carbon monoxide. With Fe 2, on the other hand, the adsorption of both hydrogen and carbon monoxide is greater than the amounts calculated on single gas basis. The total adsorption at 97°C is greatest with a mixture richest in hydrogen (2H₂ : 1CO) in the case of Fe 1. On the contrary, a mixture richest in carbon monoxide (1H₂ : 2CO) gives rise to the maximum total adsorption in the case of Fe 2.

It has also been noted (cf. retention studies) that the catalyst Fe 2 retains more carbon monoxide than Fe 1 and that the CO/H₂ ratio is higher for Fe 2. These factors support the finding that, in synthesis, (cf. Part I of this paper) Fe 1 produces hydrocarbons of low molecular weight, the yield being more if a 2H₂ : 1CO mixture is employed. Similarly, Fe 2 produces hydrocarbons of high molecular weight, the extent of reaction being highest with 1H₂ : 2CO mixture. The analysis of the gases desorbed after the equilibrium studies has shown that the greatest amount of reaction occurs with 2H₂ : 1CO on Fe 1, whereas, this occurs with 1H₂ : 2CO on Fe 2.

The retention studies suggest that Fe 1 contains two types of active sites. The gas desorbed after raising the temperature of experiment to 97°C is perhaps adsorbed on the less active sites and the gas held adsorbed on the more active sites. In the case of Fe 2, only one type of sites could be envisaged, because almost all gas adsorbed at the lower temperature is retained at 97°C. These sites may be uniformly active.

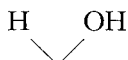
General Conclusions

Alkali addition has been found to alter the characteristics of the catalysts to a large extent (Part I of this paper). The addition reduces the metal surface active in chemisorption though there is no change in the total surface area. This reduction in metal area reduces the adsorption of the gases. When mixtures of the two gases are adsorbed, the CO/H₂ ratio in the adsorbed phase is found to be higher (about 3) for Fe 2 than for Fe 1 (about

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1) (Ref. Tables 2 and 4, 97°C). The higher CO/H₂ ratio results in polymerization of the —CH₂ radical and a consequent increase in the molecular weight of the products in synthesis. Similar results have been obtained by GHOSH *et al.*⁴⁾ who employed cobalt catalysts for their studies. On alkali promoted catalysts, STORCH *et al.*⁵⁾ found that in synthesis at 195°C the usage ratio H₂/CO, with 1H₂ : 2CO mixture, is 1H₂ : 1.5CO. The ratio H₂/CO in the adsorbed phase at 97°C on Fe 1 in the present studies is found to be almost the same (1 : 1.4).

Alkali is reported⁶⁾ to increase the chain growth and the rate of chain initiation. It is also reported to poison sites for methane formation⁷⁾. The present studies lend credence to these observations. Furthermore, BLYHOLDER *et al.*³⁾ have concluded from their infra-red studies that a surface complex of



the type R—C—M is perhaps formed when carbon monoxide and hydrogen are adsorbed from mixtures on silica-supported iron. The catalyst used by these authors is similar to those used in the present studies. The present



studies support the contention that an intermediate complex of type R—C—M is being formed on the surface and acts as a precursor to synthesis. In conclusion it can be said that alkali plays an important role in determining the selectivity of catalysts in Fischer-Tropsch synthesis.

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