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Factors Influencing the Formation of Carbon on Iron Fischer-Tropsch Catalysts

I. The Influence of Promoters

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The influence of promoters on the decomposition of carbon monoxide over iron carbide at 325°C has been determined. Alkali promoters such as potassium and sodium carbonate increase the rate per cm^2 of iron area. When the alkalis are present as silicates (which are less basic) the intrinsic rates are lower than in the case of the carbonates but the overall rates are higher due to the higher surface areas of the silicate-promoted samples. Structural promoters such as Al_2O_3 while having considerable effect on the overall rate of the reaction, due to their influence on the available iron area, have little influence on the rate of deposition per cm^2 of iron surface.

INTRODUCTION

The reaction between carbon dioxide and coke at high temperatures to give carbon monoxide is very well known as the essential step in the manufacture of producer gas. The reaction is often named after Boudouard (*1*) who was the first to study the equilibrium. It was discovered by Neumann (*2*) that unless preventive measures were taken the reaction could be reversed to some extent when the gases left the fuel bed, hence lowering the heating value of the gas due to conversion of combustible carbon monoxide into the inert dioxide and finely divided carbon. This reverse reaction, referred to as the Neumann reversal (*3*) or preferably the Boudouard reaction (*4*), is of practical interest as it has a detrimental effect on brick furnace linings (*5*) while in Fischer-Tropsch synthesis over iron it results in swelling of the catalyst particles which can have serious consequences in fluidized and especially in fixed bed reactors.

The decomposition of carbon monoxide and related reactions has long been known to be catalysed by alkali (*6*). The presence of alkali, as chemical promoters, and of non-reducible oxides, as structural promoters, are vital in Fischer-Tropsch synthesis and it is therefore of importance to ascertain their relative significance in the formation of free carbon on iron catalysts.

EXPERIMENTAL

In this work fused magnetite was used as starting material throughout. The preparation of the catalysts containing the promoters MgO, Al_2O_3, CaO and SiO_2 has been described (*7*) and their distribution within the catalyst has been discussed (*8*). Alkali was added by impregnating with either carbonate or silicate (waterglass) solutions followed by drying at 120°C.

Four samples each of 5 g of magnetite (100–200 mesh) were run simultaneously in pyrex reactor tubes (see Fig. 1) contained in a solid aluminum core electrically heated furnace. Hydrogen, for reduction, was purified by passing it through a char-

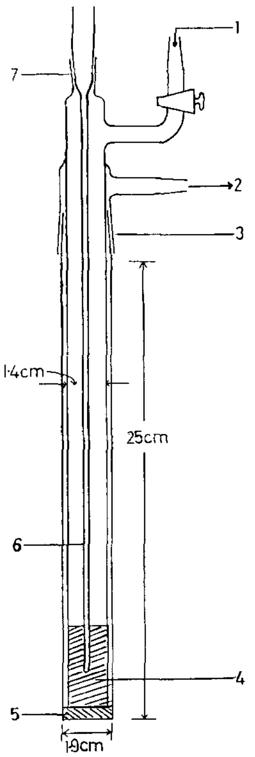

FIG. 1. Sample tube. 1-Gas-inlet; 2-Gas exit; 3-B29 ground glass joints; 4-Catalyst Sample; 5-Glass wool plug; 6-Thermocouple well; 7-B10 ground glass joints

coal trap maintained at —197°C. Carbon monoxide was purified by passing it through consecutively a liquid oxygen trap, copper turnings at ca. 340°C, a liquid oxygen trap, zinc oxide at ca. 340°C, a liquid oxygen trap and finally an ascarite trap. Using this purification system it was found, unlike previous workers (*5*), that the carbon monoxide did not affect ascarite. The amount of carbon formed on the catalyst therefore could be measured indirectly by trapping out with ascarite and weighing the amount of carbon dioxide liberated by the Boudouard reaction. Checks on the increase in the catalyst sample weight at the end of a run were, within experimental limits, the same as that calculated from the weight of the carbon dioxide released, hence confirming the reliability of the method.

The samples were reduced in a hydrogen flow of 200 ml/min for sixteen hours at 400°C. The furnace was then cooled down to 190°C and the hydrogen replaced by carbon monoxide. The samples were then carbided to Hägg carbide by systematically raising the temperature from 190 to 290°C in 10°C steps at twenty minute intervals. On adding between 86–90 mgC/gFe the presence of 100% Hägg carbide Fe_5C_2 (*9*) was confirmed by X-ray analysis. At this point the samples were cooled to room temperature and the study of free carbon commenced the next day at a temperature of 325°C.

RESULTS

Table 1 summarizes the runs that were carried out to determine the effect of promoters on free carbon formation.

Runs 3, 6 and 7 are expressed graphically in Figs. 2, 3 and 4a. From these figures it can be seen that initially free carbon is deposited at a higher rate; strictly speaking the figures given in Table 1 should therefore not be directly compared between

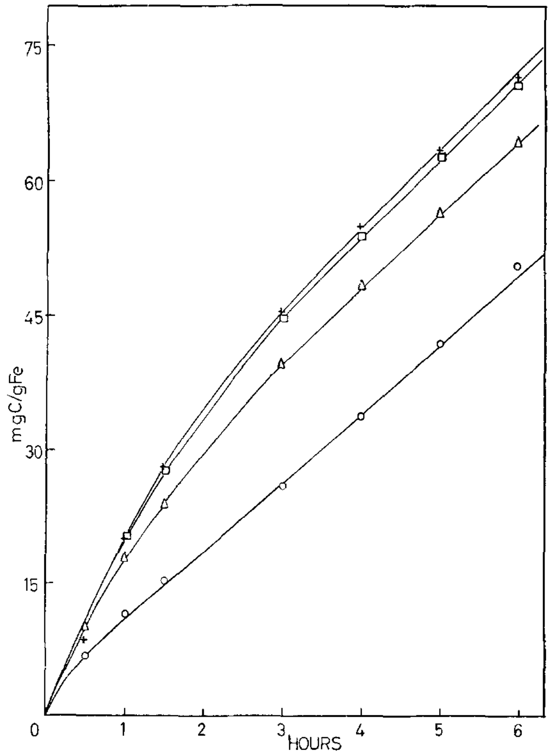

FIG. 2. The effect of potassium on free carbon formation. ○ Sample 3a-0.0 K_2O; △ Sample 3b-0.17 K_2O; □ Sample 3c-0.31 K_2O; + Sample 3d-1.19 K_2O.

TABLE 1

EFFECT OF PROMOTERS ON FREE CARBON FORMATION

Run[a]		Length of run (hr)	Promoters (expressed as g atoms promoter cation per 100 g atoms of Fe)	Rate of C formation mg C/gFe/hr
1	a	8	0.0 Na_2O	7.5
	b		0.20 Na_2O	7.5
	c		0.41 Na_2O	7.8
	d		0.81 Na_2O	8.0
2	a	4.25	0.0 Na_2O	9.4
	b		0.20 Na_2O	9.4
	c		0.41 Na_2O	9.4
	d		0.81 Na_2O	9.8
3	a	6	0.0 K_2O	8.5
	b		0.17 K_2O	10.9
	c		0.31 K_2O	12.0
	d		1.19 K_2O	12.1
4	a	5	1.41 Na_2O	10.0
	b		0.59 K_2O	12.5
5	a	12.5	1.98 Na_2O, 2.51 SiO_2	9.2
	b		1.41 Na_2O	7.3
	c		0.74 K_2O, 1.40 SiO_2	10.0
	d		0.59 K_2O	9.6
6	a	16	0.66 Na_2O, 1.05 SiO_2	8.4
	b		0.69 Na_2O	6.1
	c		0.25 K_2O, 0.48 SiO_2	8.3
	d		0.28 K_2O	7.1
7	a	13	Unpromoted	6.3
	b		2.19 Al_2O_3	18.6
	c		3.26 SiO_2	6.6
	d		1.35 CaO	4.4

[a] All the samples in runs 1 to 6 contain 2.22 MgO as well as the promoters given above.

different runs. It was also found that the results varied a little from run to run but on a comparative basis they were much the same. All the samples in runs 1 to 6 were prepared from the same batch of magnetite.

In order to ascertain the effect of area on free carbon formation the total surface area and the iron area were determined on the reduced samples used in runs 6 and 7. The total area was measured by nitrogen adsorption at —197°C and the iron area by irreversible carbon monoxide chemisorption at —80°C (*7*). Using the values of iron area together with the measured rates of free carbon deposition (column 4, Table 1) the intrinsic deposition rates (i.e., $mgC/m^2Fe/hr$) were calculated. The results are given in Table 2.

DISCUSSION

The results of runs 1 to 4 in Table 1 indicate that sodium has a relatively small promotional effect on the overall rate of carbon deposition. The influence of potassium is more marked and clearly the rate of carbon formation is enhanced by the addition of this alkali. It is well established (*11*, *12*) that promotion of iron catalysts with either potassium or sodium salts results in a pronounced loss of both total and iron surface area. Bearing this in mind the influence of sodium is then not as small as the results in Table 1 would appear to indicate. While an increase in the sodium promoter content must result in a lower surface area, the overall rate of carbon deposition remains much the same

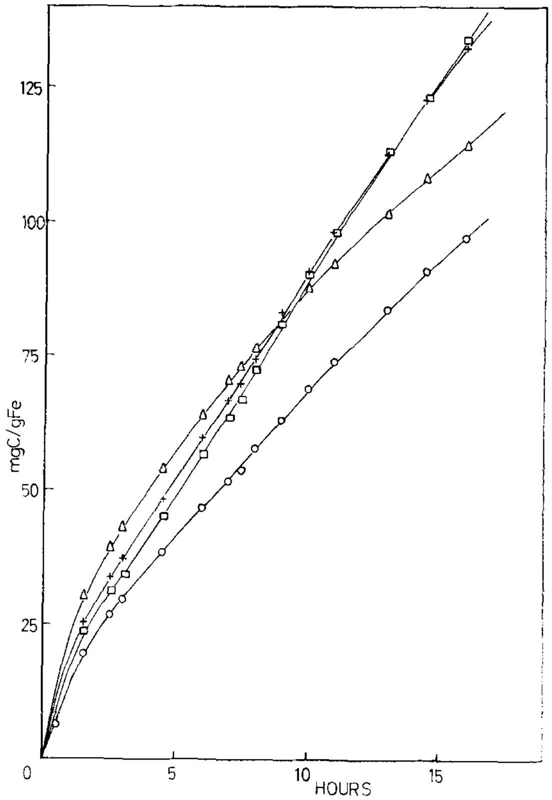

FIG. 3. The effect of alkali and alkaline silicates on free carbon formation. □ Sample 6a-0.66 Na_2O, 1.05 SiO_2; ○ Sample 6b-0.69 Na_2O; + Sample 6c-0.25 K_2O, 0.48 SiO_2; △ Sample 6d-0.28 K_2O.

which must mean that the intrinsic rate, i.e., the rate per unit area, increases with sodium content. Recent calorimetric studies (*10*) carried out in this laboratory showed that alkali promotion increased the heat of chemisorption of carbon monoxide on reduced iron catalysts. It was postulated that the effect was due to the ability of the alkali to donate electrons to neighboring surface iron atoms. It seems reasonable to suggest that by strengthening the adsorption of carbon monoxide on the iron surface its decomposition to carbon is more likely to occur, thus explaining the observed promotional effect of alkali. As potassium is a stronger base and hence a better electron donor than sodium, it could be expected that potassium would have a greater effect than sodium on the rate of carbon monoxide decomposition, this was in fact found to be the case.

The effect of area on alkali-promoted samples is well illustrated by runs 5 and 6 (Table 1) in which it is seen that those samples promoted with both alkali and silica deposited free carbon at a higher rate than those promoted with alkali only. From Table 2, however, it is shown that silica prevents the loss in iron area that would otherwise have been caused by the presence of alkali alone. Therefore while the overall effect of silica is to increase free carbon formation it actually lowers free carbon formation on a unit iron area basis (see Table 2). This is to be expected because the presence of silica serves to reduce the basic nature of the alkali promoter hence reducing its electron donating potential.

TABLE 2

COMPARISON BETWEEN ABSOLUTE AND INTRINSIC FREE CARBON DEPOSITION RATES

Sample[a]	Promoters	Total area (m^2/gFe)	Iron area (m^2/gFe)	Absolute rate (mgC/gFe/hr)	Intrinsic rate (mgC/m^2Fe/hr)
6a	0.66 Na_2O 1.05 SiO_2	12.6	9.5	8.4	0.88
6b	0.69 Na_2O	8.9	4.0	6.1	1.52
6c	0.25 K_2O 0.48 SiO_2	9.4	7.5	8.3	1.10
6d	0.28 K_2O	7.6	5.4	7.1	1.32
7a	—	5.7	3.2	6.3	1.97
7b	2.19 Al_2O_3	24.4	9.6	18.6	1.94
7c	3.26 SiO_2	6.1	3.0	6.6	2.22
7d	1.35 CaO	6.7	1.7	4.4	2.38

[a] The samples in run 6 are of a different magnetite base stock to those in run 7.

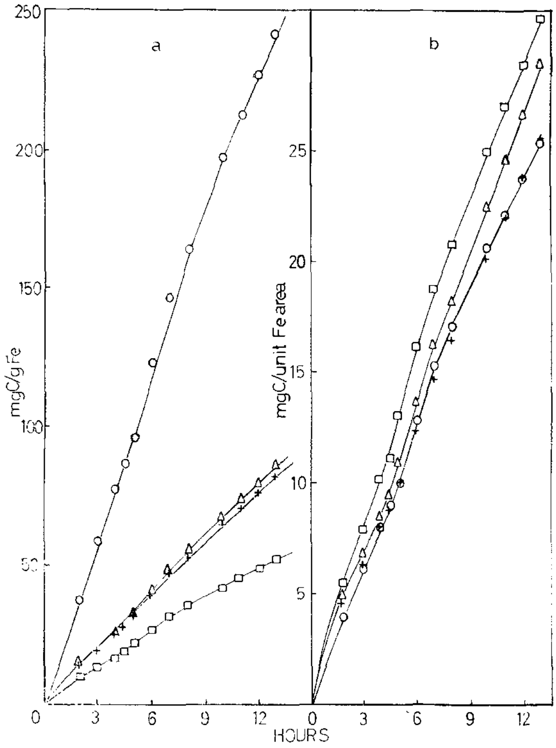

FIG. 4. The effect of structural promoters on free carbon formation. *4a* Absolute depositions *4b* Intrinsic depositions + Sample 6a-unpromoted; ○ Sample 6b-2.19 Al_2O_3; △ Sample 6c-3.26 SiO_2; □ Sample 6d-1.35 CaO.

The effect of iron area on free carbon deposition is highlighted by run 7. Figure 4a shows that the alumina-promoted sample deposited free carbon at three to five times the rate of the other samples. From Table 2, however, it can be seen that the iron area of the alumina sample is greater than that of the other samples by a similar margin. From Table 2 and Fig. 4b the effect of alumina on an area basis is approximately the same as the other samples.

In the light of the above it is interesting to consider the work of Brill (*13*) on ammonia synthesis. He found that the activation energies for the synthesis were the same for iron catalysts with and without alumina. The rate of ammonia production per cm² of iron surface was the same for both samples. The alumina, he concluded, was therefore neither an activator nor a promoter for the synthesis but only a stabilizer. From our results on the Boudouard reaction we can similarly say that Al_2O_3, CaO and SiO_2 have no chemical promotional effects on the reaction but act only as stabilizers or structural promoters. Recent work by Rozovskii and Savel'ev (*14*) on carbidization on iron catalysts confirms this in that alumina-promoted samples had only a slight effect on the activation energy of the reaction.

CONCLUSIONS

When considering the decomposition of carbon monoxide over iron catalysts two important parameters are the available iron area and the basicity of the catalyst sites. Structural promoters, while increasing the overall rate of decomposition by enhancing the total iron area, have no effect on the rate of decomposition per cm² of iron surface. Additives which are strong bases, on the other hand, increase the intrinsic rate.

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