

THE BEHAVIOUR OF HYDROGEN AND CARBON MONOXIDE WITH GRAPHITE FERRIC CHLORIDE

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Intercalation in graphite appears to modify the chemical or catalytic activity of certain substances. The modification, however, may result from one or more possibilities. Thus the new activity may be caused by some substance produced by a side reaction that is concurrent with intercalation. For instance, it has been claimed that intercalating CrO_3 in graphite modifies its ability to oxidize an alcohol (1). However, this ability is caused by the production, during intercalation, of lower oxides of chromium (2). A second possibility is that the electron density on the two basal planes of each graphite flake has been changed because of the charge transfer that accompanies intercalation. This possibility has been used to explain the catalytic formation of HBr from its elements in the presence of graphite-metal chloride compounds (3). A third possibility is that catalysis or oxidation, etc., occurs within the layer plane system and, therefore, in a different fashion than with graphite or with the pure substance before intercalation. In this case the reacting species must diffuse between the layer planes and the products must diffuse out. This has often been assumed to occur but whether it does or does not occur has, in our opinion, yet to be demonstrated. We have studied this possibility by determining the composition pressure isotherms of a gaseous reactant on graphite and on graphite-ferric chloride. If diffusion does occur between the intercalated layers then the isotherms for the graphite-ferric chloride should show a much higher reactant composition at one or more pressures. Because the recent energy crisis has redirected attention to the catalytic synthesis of hydrocarbons via the Fischer Tropsch route (4-6) we chose to study the isotherms of H_2 , of CO and of their mixture (1:1) on graphite, on graphite-ferric chloride and on a mixture of graphite and ferric chloride. The data should tell us whether all three of the above possibilities should be considered in explaining any catalytic activity or only the first two.

To further the scope of our investigations, the catalytic formation of hydrocarbons from H_2 and CO on graphite-ferric chloride and on a mixture of graphite and ferric chloride was also investigated.

Graphite (G_0) was of Madagascar origin, acid purified and sieved to -40 + 45 mesh. Graphite-ferric chloride of stoichiometry C_8FeCl_3 (G_1) was prepared from G_0 and anhydrous FeCl_3 by the two temperature tube method (7) and then washed free of FeCl_3 . Mixture of graphite and FeCl_3 (G_M) was prepared by standard incipient wetness technique (4) where G_0 was impregnated with FeCl_3 solution of concentration equivalent to C_8FeCl_3 followed by overnight drying at 110°C . There was no intercalation, whatsoever, in this case.

Before proceeding with the adsorption measurements, the surface of the graphite was cleaned by outgassing the previously 110°C oven dried samples for a period of ~ 16 hr in high vacuum (10^{-6} Torr) at room temperature. High temperature evacuation was not appropriate because of thermal instability of G_1 .

The specific surface area (using BET equation) and pore-size distribution (using Kelvin's equation) in the range $20\text{-}400 \text{ \AA}$ diameter were determined from the N_2 adsorption isotherms at 77°K using Micromeritic surface area and pore volume analyzer. The same gas adsorption apparatus was used for H_2 and CO isotherms determined at 25°C and up to 700 Torr initial pressure. Equilibrium period of 90 min was allowed for every point of isotherm.

For adsorption isotherms from H_2 and CO mixture (1:1) a sample flask having a side arm (~ 3 cm) fitted with a septum using stainless steel fittings was used. After 90 min equilibrium period, gas mixture was analyzed on a Fisher Gas Partitioner using molecular sieve column. From the analysis, the amounts of H_2 and CO adsorbed individually from their mixture was computed.

Catalytic formation of hydrocarbons over G_1 and G_M , previously activated in a rapid flow of H_2 (12/min) in situ at 375°C for 48 hr, using a mixture of H_2 and CO (2:1) was studied in a fixed bed laboratory reactor at 325°C and 90 psi pressure. For product analysis, a Hewlett-Packard 7620A gas chromatograph with silica gel column was used in conjunction with an electronic Hewlett-Packard 3380A integrator.

Results and Discussion

N_2 -BET surface area of G_0 upon intercalation with FeCl_3 (G_1) remained unchanged ($0.3 \text{ m}^2/\text{g}$) whereas simple impregnation of FeCl_3 (G_M) showed a slight increase. The percentage of pore volume composed of pores less than 40 \AA in radius was ~ 47 which reduced to ~ 33 for G_1 and ~ 26 for G_M .

Adsorption isotherms of H_2 , CO from pure gases and from their mixture (1:1) are shown in Fig. 1. The amounts of H_2 as well as of CO uptake for G_0 and G_1 were almost identical at any pressure up to one atmosphere while for G_M the uptake of both H_2 and CO was ~ 5 times greater. Similarly the concurrent sorption of H_2 and CO from their mixture was almost of the same magnitude (although $\sim 70\%$ higher compared to sorption from pure components) for G_0 and G_1 while for G_M it was far greater. This observation, repeated several times, that upon intercalation of G_0 with FeCl_3 there was no increased uptake of either H_2 or CO , was of significant consequence. It rules out the possibility that the modified

chemical or catalytic activity of metal intercalated graphite is the result of diffusion of reacting species between the layer planes; because, if this had been the case, then the isotherm for G_I would have shown a much higher uptake at one or more pressures. Experimental evidence of this fact, probably for the first time, is apparent from our studies.

In comparison to H_2 and CO adsorbed individually, the adsorption of both the gases is enhanced invariably, especially for G_I and G_M , when adsorbed simultaneously from their 1:1 mixture. This behaviour is akin to several metal catalyst systems reported in the literature (8). Mutual enhancements for the adsorption of both H_2 and CO during simultaneous course of adsorption are attributed partly due to complex formation between the adsorbed species and partly due to 'cooperative work functions'. Tamaru (9) and Tsuchiya and Shiba (10) are of the opinion that the oppositely oriented chemisorbed dipoles of $H\delta^+$ and $C\delta^-$ alter the work function of the metal in opposite manner; the increase caused by one is partly offset by the other and finally enhances the limiting adsorption of H_2 and CO . Enhancement is more pronounced for G_M than G_I .

The catalytic activity for hydrocarbon synthesis is observed when G_I or G_M is heated above $300^\circ C$. We believe that the activity develops by the thermal decomposition of $FeCl_3$ to $FeCl_2 + Cl_2$ and is caused only by that fraction that diffuses out of the graphite. For G_I , this product has been shown (11) to have a Mossbauer spectrum isomer shift which is the same for heating in H_2 or N_2 or a vacuum. However, above $350^\circ C$ in H_2 it is known that some metallic iron is produced. Now, the $FeCl_2$ and any Fe may behave differently when adsorbed on graphite that had been intercalated (G_I) than on graphite that had not been intercalated (G_M). Any difference could be

caused by the charge transfer to the basal planes from intercalated material in G_I and the fact that some of this intercalated material remains in the structure after heat treatment.

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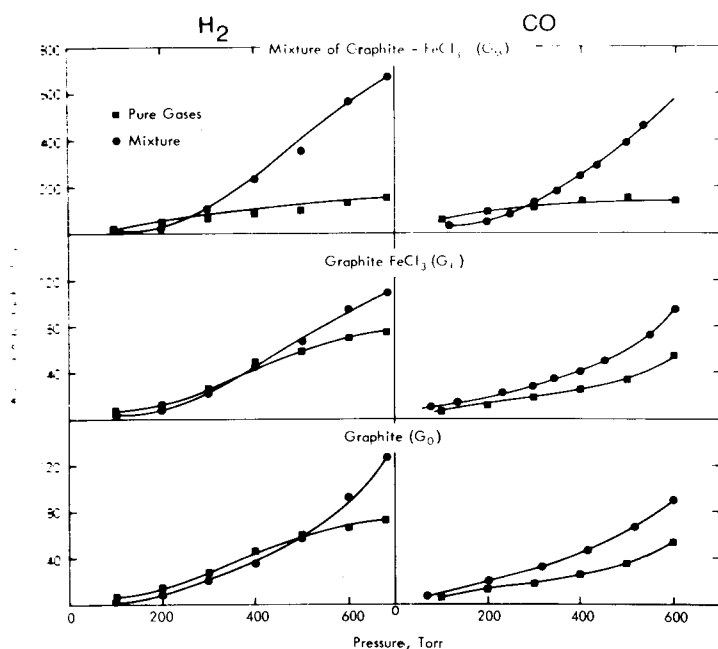


Fig. 1 H_2 and CO adsorption isotherms from pure gases and their 1:1 mixture