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The Location of Catalytic Iron in Reduced Graphite Ferric Chloride

Iron is a well-known catalyst for the synthesis of hydrocarbons from CO + H_2 by the Fischer–Tropsch method. The behavior is a function of the support for the Fe. If that support is graphite which had been intercalated with $FeCl_3$ before reduction to Fe^0 there are many claims that the catalytically active Fe^0 is located between the layers of carbon atoms where the $FeCl_3$ had been in the intercalated state. Hence any modified behavior can be attributed to a state of the intercalated Fe^0 which would be different from that of Fe^0 adsorbed on the carbon atoms at the edges of the layers or on the two outer basal planes. If this difference is the source of the modification, it also requires that the reactants must diffuse between the layers to reach the intercalated Fe^0 and that the products must diffuse out. We did report (*1, 2*) that if every space is filled with $FeCl_3$ before reduction at 400°C with H_2 then the adsorption isotherms of H_2 and of CO are the same on that solid as on graphite itself or on a reduced physical mixture of graphite and ferric chloride. We therefore concluded that neither H_2 or CO diffuse between the layers and that the catalytically active Fe^0 is on an outer surface. We have measured isotherms on an H_2-reduced stage II compound (alternate spaces filled) and have found the same result (Fig. 1). It was necessary to show this because Herold and Lagrange (*3*) have shown that whereas benzene will not intercalate stage I (every space filled) C_8K it will intercalate stage II (alternate spaces filled) $C_{24}K$. Our work shows that graphite ferric chloride does not behave in this fashion. Neither the reduced stage I nor stage II compound intercalates CO or H_2 and hence any catalytic behavior is caused by Fe^0 on the surface. Our work also shows that there is no Fe^0 between the layers because in order to produce it there, H_2 would have to diffuse into that region. The above-mentioned data rule this out.

In a recent paper (*4*) the opposite conclusion was reached. The experimental basis for this claim is the absence of any change in catalytic activity when reduced graphite ferric chloride is treated with 5 *M* HCl. Because this reagent does not intercalate the compound it cannot dissolve Fe^0 between the layers but may dissolve surface Fe^0. Hence the active Fe^0 must be intercalated. However, we have shown that a physical mixture of graphite and ferric chloride, after reduction with H_2 at 400°C and then treatment with 5 *M* HCl, is still catalytically active with CO and H_2. In this system, the Fe^0 was on the outer surface of the graphite and must have been in a form that was insoluble in 5 *M* HCl at 20°C. This could also have been the case described in (*4*). Certainly some of the Fe^0 in that system must have been on the outer surface—we think all of it—and yet the catalytic activity was not changed by 5 *M* HCl. This shows that in their case too, the acid did not dissolve this Fe^0 on the surface because if it did, the activity would have changed.

Another claim in the paper (*4*) was that the graphite ferric chloride compound reduced in H_2 gave a higher ratio of hydrocarbon to CO_2 than did the physical mixture of graphite and $Fe(NO_3)_3$. We reported the reverse to be true (*2*). The explanation of this difference could be that they used $Fe(NO_3)_3$ in their physical mixture whereas we used $FeCl_3$. At 400°C these give, respec-

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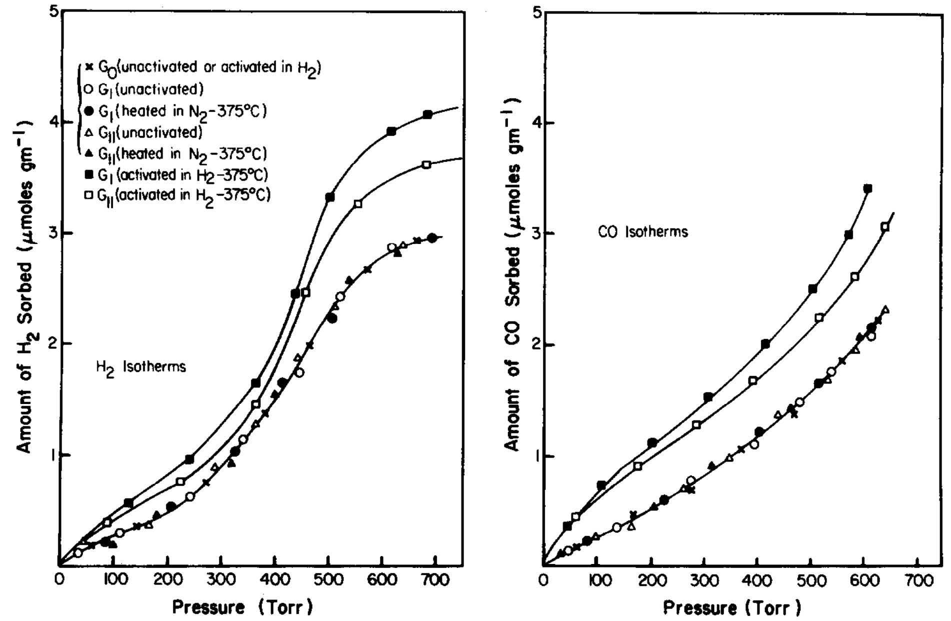

FIG. 1. Adsorption isotherms of H_2 and CO at 25°C on graphite (G_0), C_8FeCl_3–stage 1 (G_I), and $C_{15}FeCl_3$–stage 2 (G_{II}).

tively, iron oxide and $FeCl_2$ before reduction. Hence the Fe^0 produced could well be in different states in the two cases. Another difference is that they used Union Carbide spectroscopic powder and we used Madagascar flakes about 500 μm in diameter. There are two grades of spectroscopic powder—SP1 and SP2. The former is a natural flake about 60 μm across; SP2 is a synthetic graphite. All this shows of course that explanations of modified catalytic behavior must be made with great caution. It is our opinion that the assumption that catalytic activity may occur between the layer planes of intercalated graphite has not yet been demonstrated.

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