

Reply to "The Location of Catalytic Iron in Reduced Graphite Ferric Chloride"

It has recently been demonstrated that the lamellar compound of graphite (LCG) with FeCl_3 reduced in H_2 catalyzes the hydrogenation of carbon monoxide and gives hydrocarbons with high selectivity (1, 2). However, it is a disputable problem whether hydrocarbon synthesis takes place at Fe active sites between the intercalated layers or at those on the outer surface of graphite. In our previous work (1), it was shown that FeCl_3 in the intercalated layers was reduced to FeCl_2 and partly to metallic Fe in flowing H_2 at 400°C and that the activity of the reduced LCG catalyst for hydrocarbon synthesis was attributed to metallic Fe. We argued that the Fe active sites were located between the graphite layers on an experimental basis and that the steady-state activity of the reduced FeCl_3 -LCG catalyst did not change at all when treated with a 5 N aqueous solution of HCl. Our further study on the magnetic property of LCG supports our previous conclusion. We measured magnetic susceptibility of the LCG reduced in flowing H_2 at 400°C for 8 hr. It showed strong ferromagnetism due to metallic Fe deposited on the graphite surface, probably formed by reduction of FeCl_3 eluted from the graphite layers. By washing this ferromagnetic substance with a 5 N aqueous solution of HCl, a paramagnetic LCG was yielded. Fig. 1 indicates a linear relationship between temperature and the reciprocal susceptibility of the LCG, showing its paramagnetism. This paramagnetic LCG is the one which had been used as catalyst in our previous work (1). Consequently we believe that metallic Fe on the outer surface of graphite is removed by the HCl treatment. The detailed procedure of the HCl treatment is as fol-

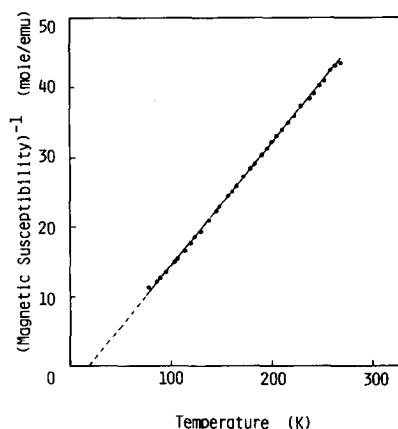


FIG. 1. Linear relationship between temperature and reciprocal magnetic susceptibility of the reduced LCG catalyst after HCl treatment.

lows: The reduced LCG is soaked in a 5 N aqueous solution of HCl for 2 hr and subsequently filtered and washed with pure water and dried at 110°C overnight.

Recently, however, the opposite conclusion was reached by Parkash and Hooley (3). They reported that a 5 N HCl solution could not remove the metallic Fe on the graphite surface because a physical mixture of graphite and FeCl_3 when reduced in H_2 at 400°C and then treated with 5 N HCl solution is still catalytically active for hydrocarbon synthesis. We also prepared a reduced physical mixture of graphite and FeCl_3 in the same manner as described by them (2) and investigated its catalytic activity and selectivity for CO hydrogenation under the same reaction conditions employed in our previous work. As shown in Table 1, the catalytic activity of the physical mixture significantly decreased upon treatment with a 5 N HCl solution. It is, however, shown that the catalytic activity still remains after

TABLE 1

Catalytic Activity and Selectivity of a Reduced Physical Mixture of Graphite and Ferric Chloride^a

	Before HCl treatment	After HCl treatment
Conversion of CO (%)	75.2	17.7
Conversion of CO to hydrocarbon (%)	69.1	16.5
Hydrocarbon distribution ^b (mole%)		
C ₁	61.3	75.0
C ₂	14.3(0.21)	11.5(0.21)
C ₃	13.3(0.66)	8.1(0.76)
C ₄	6.4	3.3
C ₅ +	4.7	2.1

^a Reaction conditions: pressure = 20 atm, temperature = 400°C, H₂/CO = 3, W/F = 2240 g-cat · min/CO-mole.

^b Values in parentheses refer to fractions of olefin: olefin/(olefin + paraffin).

the treatment. Then we carried out a thermogravimetric measurement using the same procedure described previously on the unreduced physical mixture of graphite and FeCl₃ in flowing He after removal of the FeCl₃ from the outer surface of graphite by treatment with HCl solution. The observed thermogravimetric diagram is shown in Fig. 2. On heating, the weight loss took place in two steps: at 300 to 400°C and 600 to 750°C. Such a two-step weight loss agrees with the results obtained for the LCG with FeCl₃ given in our previous work (1). It seems therefore that some part of FeCl₃ in the physical mixture was intercalated to graphite and that the catalytic activity of the HCl-treated physical mixture shown in Table 1 was due to the LCG formed. On the other hand, the catalytic activity of the physical mixture of graphite and Fe(NO₃)₃ when reduced in H₂ and treated with 5 N HCl solution was insignificant.

Another basis of their argument in the paper (3) is that there is no difference in the adsorption isotherms of CO and H₂ on

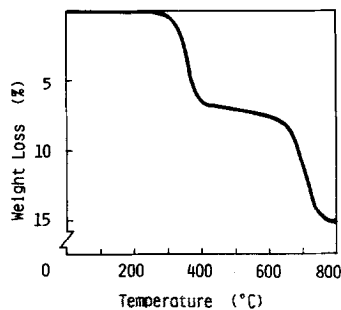


FIG. 2. Thermal gravimetric diagram of the physical mixture of graphite and ferric chloride in flowing He.

FeCl₃-LCG from those on graphite, suggesting that neither CO nor H₂ diffuses into the intercalated layers. Their isotherms, however, were measured at 25°C and under the pressure range 0 to 700 Torr. These conditions are quite different from those for hydrocarbon synthesis. It is our opinion that their results on CO and H₂ uptake have not yet demonstrated that these gases do not diffuse into the intercalated layers under the conditions for catalyst preparation or hydrocarbon synthesis. Consequently, we maintain our conclusion from Ref. (1) that metallic Fe between the intercalated layers is the site for catalytic activity in hydrocarbon synthesis on the LCG catalyst as reported in our previous work.

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Received June 25, 1979