Zero-valent Iron Catalyst derived from $Fe(CO)_5$ supported on KOH-doped Alumina: High Activity for the Hydrogenation of Ethylene

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A supported zero-valent iron catalyst derived from $Fe(CO)_5$ was prepared by the use of alumina doped with KOH; it was characterised using the i.r. band of adsorbed NO and its activity is comparable to that of the promoted iron catalyst in hydrogenation of C_2H_4.

Recently, Hucul and Brenner[1] reported that the formation of zero-valent metal catalysts from metal carbonyls supported on γ-Al_2O_3 is accompanied by oxidative decarbonylation involving hydroxyl groups of the alumina, and that the use of a highly dehydrated alumina with carbonyls of Cr, Mo, and W allows the synthesis of zero-valent metal catalysts which are very active in the hydrogenation of C_2H_4.[2] We now report our results in this area. We used alumina doped with KOH to prepare a novel zero-valent iron catalyst derived from $Fe(CO)_5$, which is as active in the hydrogenation of C_2H_4 as the reduced doubly promoted iron ammonia synthetic catalyst or an evaporated film of Fe.[3]

Three catalysts A, B, and C were synthesised. The alumina support for catalyst A was formed by impregnating γ-Al_2O_3 with 1M KOH (JRC-ALO-1 from the Catalysis Society of Japan) and filtering off and drying the solid at 200 °C for 5 h. The KOH-doped alumina was outgassed at 450 °C for 1 h, and exposed to $Fe(CO)_5$ vapour. The prepared sample was heated *in vacuo* in a stepwise fashion from room temperature to 400 °C in 1 h intervals to decompose the iron carbonyl on the alumina. Atomic absorption analysis (a.a.a.) gave 0.8 wt % Fe and 9.4 wt % of K. Catalyst B was prepared in an identical manner to catalyst A except that the γ-Al_2O_3 support was not impregnated with KOH. 0.2 wt % of Fe was detected by a.a.a. Catalysts A and B had surface areas of 160 and 187 $m^2\ g^{-1}$, respectively, after decarbonylation at 400 °C for 1 h.† Catalyst C was a doubly promoted iron ammonia synthetic catalyst containing in addition to iron oxide, 0.33 wt % of K_2O and 2.55 wt % of Al_2O_3 which was reduced overnight at 450 °C in a stream of hydrogen followed by outgassing at 450 °C for 1 h.[4]

In order to characterise the state of iron on catalyst A or B

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† The surface area of γ-Al_2O_3 was decreased from 185 to 153 $m^2\ g^{-1}$ by doping with KOH.

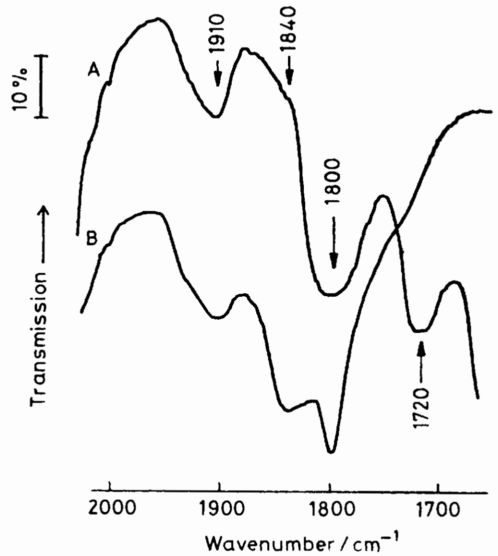

Figure 1. I.r. spectra of chemisorbed NO. $T = 25$ °C; $P = 200$ Torr. (A) Catalyst A (containing 0.8 wt % Fe and 9.4 wt % K on γ-Al_2O_3); (B) Catalyst B (containing 0.2 wt % Fe on γ-Al_2O_3). Catalysts A and B were activated at 300 °C for 1 h.

the adsorption of NO was studied using i.r. spectroscopy (200 Torr, room temp.). As shown in Figure 1, catalyst A gave strong bands at 1800 and 1720 cm^{-1} due to the stretching vibration of NO adsorbed on iron and bands at 1910 and 1840 cm^{-1} due to NO on the alumina support. These results are in agreement with those obtained by Bandow, Ohnishi, and Tamaru[5] for the reaction of iron vapour with NO at low temperature. They attributed the band at 1800 cm^{-1} to NO adsorbed on oxidised iron and the band at 1720 cm^{-1} to that adsorbed on metallic iron particles. Catalyst B, though, only gave a weak shoulder at *ca.* 1745 cm^{-1} (Figure 1). There is, therefore, much more zero-valent iron on catalyst A than on B, since A gives the 1720 cm^{-1} stretch typical of adsorbed NO.

The hydrogenation of C_2H_4 was performed with an equimolar mixture (60 Torr) of C_2H_4 and H_2 at 0 °C or at room temperature in a recirculating system. Figure 2 shows typical results of the reaction at 0 °C using catalyst A activated at 400 °C for 1 h‡ in comparison with those using catalyst B or C.

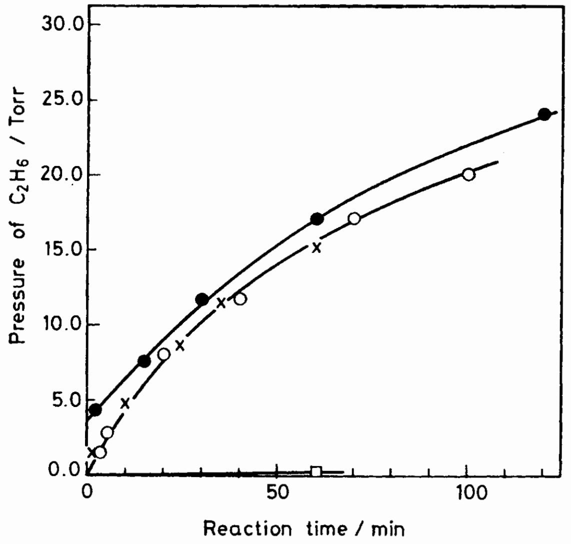

Figure 2. Hydrogenation of C_2H_4. $T = 0$ or 25 °C, C_2H_4 : $H_2 = 1:1$ ($P = 60$ Torr); ○ ●: Catalyst A (containing 0.8 wt % Fe and 9.4 wt % K on γ-Al_2O_3), 1 g; □ : Catalyst B (containing 0.2 wt % Fe on γ-Al_2O_3), 1 g; × : Catalyst C (containing 70 wt % Fe, 0.33 wt % K_2O and 2.55 wt % Al_2O_3), 0.5 g. Catalysts A and B were activated at 400 °C for 1 h.

Catalyst A has a much greater activity than catalyst B, and is as active as catalyst C. Even after reducing catalyst B with H_2 at 400 °C for 1 h its activity was not enhanced. It is noteworthy that the activity of catalyst A is roughly comparable to that of an Fe film.[3]

Zero-valent metals on alumina have been reported to be oxidised by the H^+ of the hydroxyl group of alumina.[1] The i.r. spectrum of the KOH-doped alumina gave a weak band due to the OH stretching vibration at *ca.* 3600 cm^{-1}. Therefore, we suggest that replacement of H^+ on alumina with K^+ prevents oxidation of zero-valent iron due to decarbonylation.

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‡ Complete decarbonylation above 300 °C (as indicated by i.r.) was required to ensure high catalytic activity. Detailed results will be reported elsewhere.