Efficient Conversion of CO + H_2 into Acetylene at Atmospheric Pressure using a Graphite-based Catalyst

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A 3 : 1 mixture of H_2 : CO (total pressure 1 atm) is converted with *ca.* 20% efficiency and *ca.* 95% selectivity into acetylene at 100 °C over a catalyst generated by partially de-intercalating a (first stage) sandwich compound C_9FeCl_3 with potassium naphthalenide: the catalyst maintains its performance for several days under these conditions.

Our aim in studying various kinds[1] of graphite intercalates as catalysts in the conversion of 'syngas' (CO + H_2 mixtures) to hydrocarbons was to circumvent limitations imposed on the product distribution[2] by the polymeric nature of the reaction of Fischer–Tropsch catalysts.[3] The hope here was that geometric restrictions would be imposed upon active intermediates if the elementary process of chain addition takes place in the interlamellar region[4] of the expanded graphite matrix. These hopes were not realized, probably because catalysts composed of or derived from graphite intercalates exert their influence more *via* electronic than geometric factors. However, a remarkably efficient, readily prepared, relatively air-stable and long-lived 'de-intercalation' catalyst for the synthesis of acetylene has been discovered.

Typical selectivities and activities as well as their variation as a function of temperature and time are summarized in Figure 1. The catalyst in these experiments was natural graphite (1 mm flakes, S40, Kropfmuhl[5]) intercalated with $FeCl_3$ from a u.v.-irradiated suspension in CCl_4.[6] The highly unstable intermediate product was reduced subsequently with a 0.05 M solution of potassium naphthalenide in tetrahydrofuran.[7] The catalytic activity of this product does not deteriorate after several weeks storage in air. A distinctly different[1] catalyst is obtained when the reduction is carried out with hydrogen gas at elevated temperatures.[8] Under carefully controlled conditions the synthesis and performance of both types of catalysts can be reproduced within the experimental error in Figure 1.

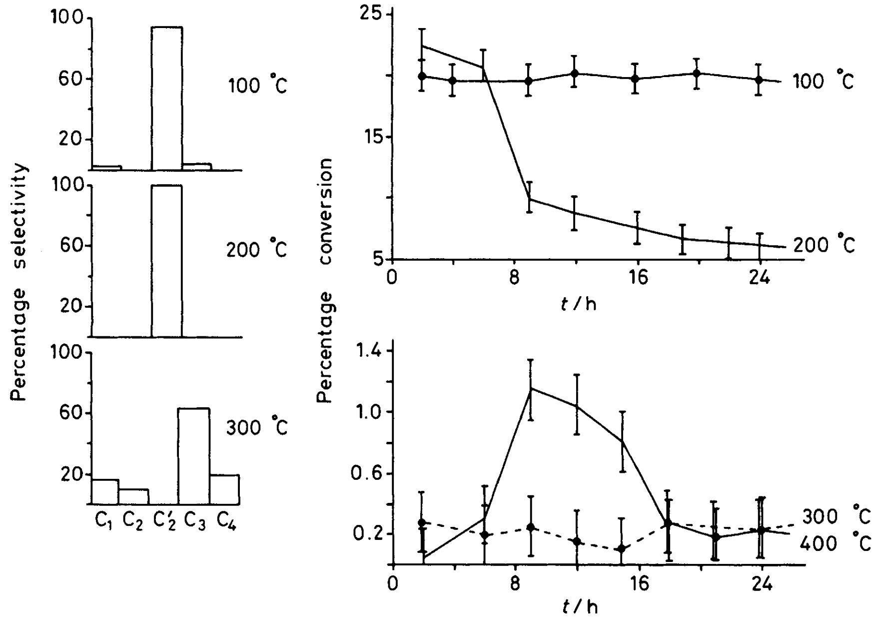

Figure 1. The performance of a typical catalyst: product distributions are quoted after 3 h of conversion at each temperature (with in each case a new batch of catalyst). The errors in the percentage conversion (number of carbon atoms appearing in hydrocarbon *vs.* number of carbon atoms in CO) *vs.* time (*t*) curves are estimated from the deviations of two subsequent runs at each temperature using two different catalysts.

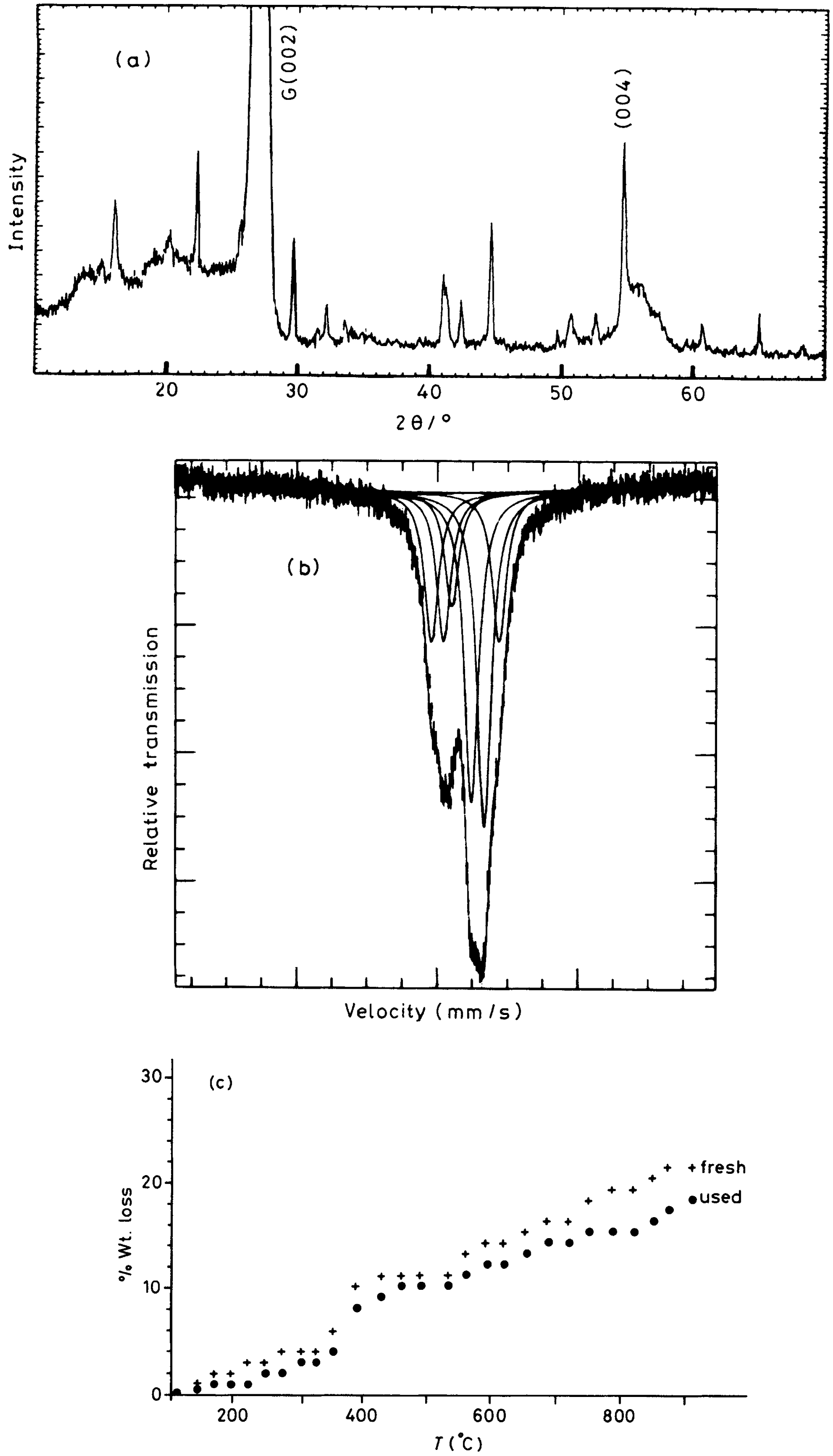

Figure 2. Analytical results: (a) powder diffractogram illustrating the multiphase nature of the catalyst: iron oxide lines (sharp) are superimposed on a hardly recognisable (00l) pattern of the residual graphite intercalate (broad lines); (b) room temperature Mössbauer spectrum of the fresh catalyst showing the presence of iron(III) oxides (superparamagnetic Fe_2O_3 and FeOOH) in addition to intercalated and partially hydrated $FeCl_3$; (c) TGA traces for fresh and used catalyst; note the stepped de-intercalation pattern is only slightly affected after the use of this compound as catalyst.

Table 1. Mössbauer parameters of the fresh catalyst (300 K).

I.s. (*mm/s*)	Q.s. (mm/s)	Linewidth (mm/s)	Area (%)
0.48(1)[a]	0.79(1)	0.31	25
0.29(1)[b]	0.74(1)	0.29	41
0.21(1)	—	0.30	10
0.48(1)	—	0.29	24

[a] Superparamagnetic Fe_2O_3. [b] FeOOH (at 78 K: six line pattern).

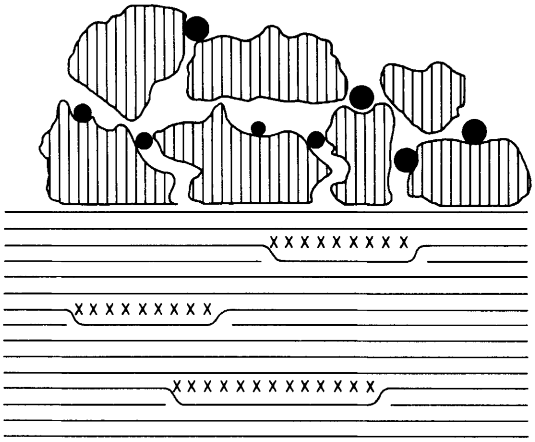

Figure 3. Diagrammatic representation of the interaction of different chemical species in the catalyst: black: potassium promotor, hatched: iron oxide particles; crosses, residually intercalated $FeCl_3$.

As is so common in heterogeneous catalysis the catalyst itself is polyphasic and multicomponent.†[2] On the basis of *X*-ray diffraction, Mössbauer spectroscopy, thermogravimetric analysis (TGA), energy dispersive micro-analysis, and electron microscopy, we argue (see typical results in Figure 2 and Table 1) that the active catalytic entity probably consists of potassium-promoted Fe_2O_3 supported on a residual intercalate of iron chloride graphite. The interaction of the apparently small iron oxide particles (superparamagnetic at 300 K and no hyperfine splitting down to 78 K) with the still intercalated graphite is the prime characteristic which distinguishes the present catalyst in its performance from a physical mixture of the identified ingredients;[1] under our experimental conditions the physical mixture is only slightly active and lacks selectivity.[9]

We believe that, on the atomic level, the situation represented diagrammatically in Figure 3 embraces most or all of the essential ingredients of the active catalyst. Further studies are required to characterize the active site in more detail.

In all other reported[4,10] instances of 'graphite intercalates' as catalysts for the 'syngas' conversion no highly efficient production of acetylene has been described. Previous studies[4,10,11] have tended to neglect both the instability of graphite intercalates in the gaseous environment of the Fischer–Tropsch synthesis and in air and the fact that the basis of the catalytic action is likely to be an interface between two or more chemically distinct structures.

In summary, we believe that the mode of action of the graphite intercalate derived catalysts is electronic rather than geometric: under reaction conditions the near-surface regions of the catalyst are likely to be de-intercalated, and the interlamellar distance in these outer regions is reduced to 335 pm. On the other hand, metal oxide particles (formed as a consequence of the de-intercalation) may interact strongly with the graphitic support. The enhanced metal–support interaction in the present system (when compared with pure graphite as support) probably results from the lowering of the Fermi level[12] as a direct consequence of residual intercalation. This electronic effect extends throughout the entire support.

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† Starting graphite intercalate: C_9FeCl_3; chemical composition after reduction: Fe 14.1%; Cl 19.6%; K 3.8%; surface area 3.9 $m^2 g^{-1}$.