Selective Formation of Propene from CO + H_2 or C_2H_4 with $Fe_3(CO)_{12}$ supported on Inorganic Oxides. Mechanistic Implication in Fischer–Tropsch Synthesis

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Summary When a catalyst derived from $Fe_3(CO)_{12}$ supported on magnesia is treated either with CO + H_2 or C_2H_4 propene is formed selectively; this can be explained on the basis of a carbene + olefin $\rightleftharpoons$ metallacyclobutane mechanism.

The mechanism of carbon–carbon bond formation in Fischer–Tropsch synthesis is not yet clearly understood. Three types of mechanisms are commonly invoked which imply: (i) insertion of CO into a metal–alkyl bond to produce a metal–acyl;[1] (ii) insertion of a methyl fragment into a metal–alkyl bond, or (iii) hydroxycarbene condensation.[3] We present here data which favour a carbene mechanism and we propose a mechanism of homologation for Fischer–Tropsch synthesis.

In a typical experiment $Fe_3(CO)_{12}$ (0·026 g) was chemisorbed in a sealed tube on a magnesia support (96 m^2/g) (0·4 g) which had previously been treated at 400 °C for 16 h and 10^{-4} Torr. The supported cluster was thermally decomposed under 10^{-4} Torr at 130 °C for 16 h, the resulting catalyst contained 1·8 wt % Fe/MgO. Introduction of $CO + H_2$ (760 Torr) in a molar ratio of 2 : 1 using glass equipment was followed by a stepwise increase in temperature from 25 to 200 °C. Analysis of the gas phase gave the results in the Figure (a). At 176 °C the conversion of CO into hydrocarbons was *ca.* 1% with mainly propene (32·0%), methane (26·1%), ethylene (9·2%), but-1-ene (7·3%), *cis*-but-2-ene (3·6%), *trans*-but-2-ene (5·5%), and C_5 (7·6%) being formed in the proportions indicated. All the paraffins except methane were present in much smaller amounts than the olefins.

A similar experiment was carried out with $Fe_3(CO)_{12}$ (0·025 g) supported on silica Aerosil 'O' (200 m^2/g) (0·5 g) which had previously been treated at 500 °C for 16 h under 10^{-4} Torr. The results in the Figure (b) indicate the same kind of selectivity for propene, the higher olefins (butenes, pentenes, hexenes, and heptenes) are mainly the α-olefins (>90%). The Figure (c) shows typical results obtained in Fischer–Tropsch synthesis with a dynamic reactor using a catalyst derived from $Fe_3(CO)_{12}/Al_2O_3$.[4]

The high selectivities for propene, which can be as high as 45%, and the low selectivities for ethylene, which can be as low as 5%, suggest that ethylene could be a primary product which would undergo, on these particular catalysts, a secondary reaction leading selectively to propene. It was

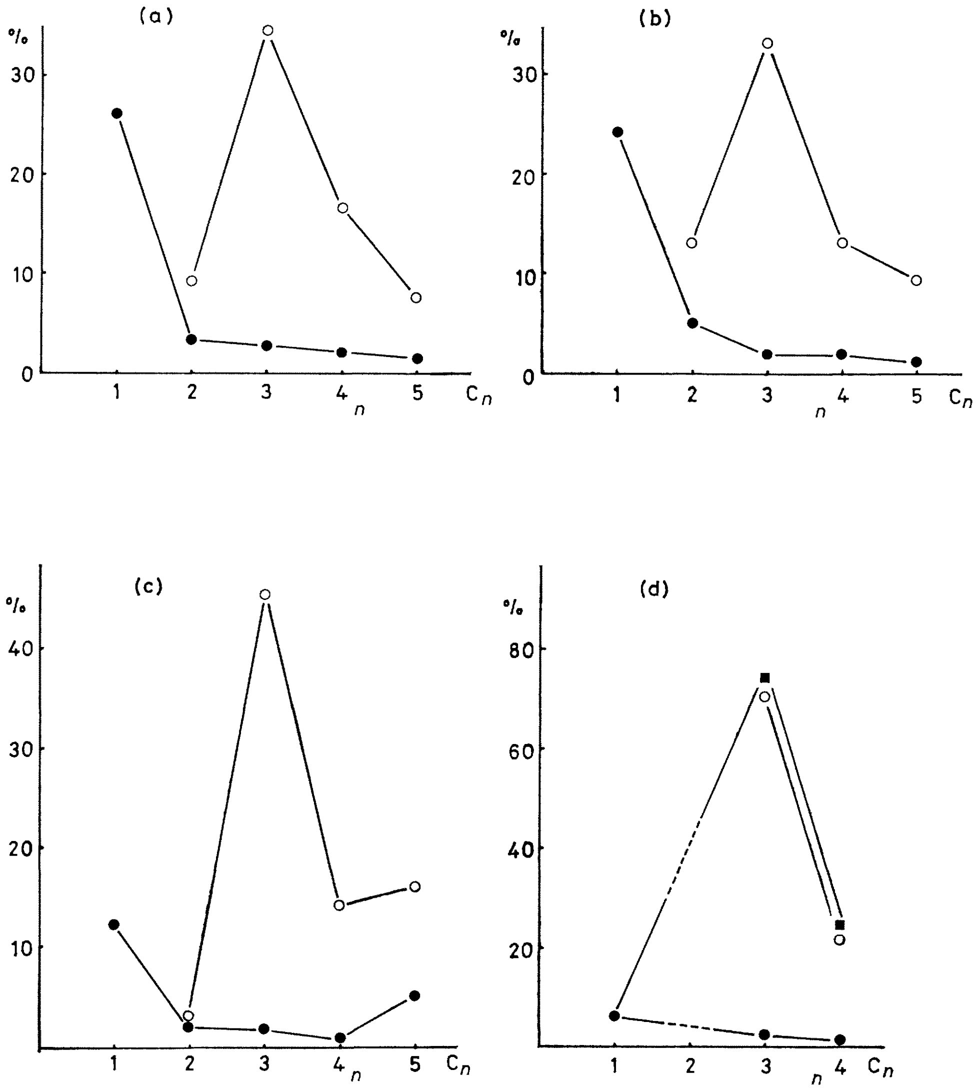


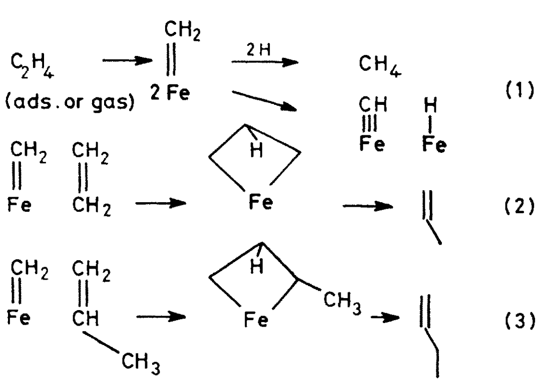
FIGURE. Selectivities in the reactions $CO + H_2$ (a—c) or C_2H_4 (d) with the following catalysts: (a) $Fe_3(CO)_{12}/MgO$, (b) $Fe_3(CO)_{12}/SiO_2$, (c) $Fe_3(CO)_{12}/Al_2O_3$, (d) $Fe_3(CO)_{12}/MgO$. ○ = olefins, ● = paraffins, in (d) ■ = olefins + paraffins. In (a)—(c), small amounts of products larger than C_5 have been neglected, whereas in (d) products larger than C_4 have been neglected, and C_2H_4, and C_2H_6 produced by self-hydrogenation of C_2H_4, are not represented.

therefore logical to study the behaviour of ethylene on such catalysts.

In another experiment $Fe_3(CO)_{12}$ (0·100 g) was chemisorbed in a sealed tube on the same magnesia support (1·5 g) which had previously been treated at 400 °C for 16 h under 10^{-4} Torr. The supported cluster was thermally decomposed *in vacuo* (10^{-4} Torr) at 130 °C for 16 h to give a grey solid containing 2 wt.% Fe/MgO. Introduction of C_2H_4 (200 Torr) on to this catalyst was followed by thermal treatment at low temperatures (90 to 170 °C) in order to avoid high conversions and secondary reactions. At 170 °C [Figure (d)] 1% of ethylene was converted mainly into propene (70%), methane (5·9%), but-1-ene (11·3%), *cis*-but-2-ene (4·5%), and *trans*-but-2-ene (5·7%). Above 170 °C the selectivity for methane increased whereas the distribution of olefins did not vary. After this experiment, the gas phase was removed *in vacuo* and the catalyst was tested at 172 °C under CO + H_2; high selectivity for propene was again observed.

The above results clearly show that rather high selectivities for propene can be reached on the same catalysts (or closely related catalysts) and at the same temperature either from a mixture of CO + H_2 or from C_2H_4 alone. Consequently some elementary steps leading to propene in both cases are likely to be the same: ethylene would be a primary product formed from CO + H_2 which would undergo a secondary reaction leading selectively to propene.

Methane formation from C_2H_4 implies a cleavage of the olefin into C_1 surface groups according to equation (1). Selective formation of propene from such surface species may be accounted for by equation (2); the co-ordination of ethylene to the metallacarbene would give a metallacyclobutane. This step would be followed by β-hydrogen transfer to the α-carbon and is in agreement with model reactions of olefins with tantalum–carbene complexes.[5] Selective formation of higher α-olefins, especially on a silica surface in which double bond migration is avoided, either with CO + H_2 or with C_2H_4, implies a selective co-ordination of propene or of higher α-olefins to the metallacarbene fragment followed by a selective β-hydrogen transfer to the most substituted carbon of the metallacyclobutane [equation (3)]. Such selectivities would be due to steric and (or) electronic reasons as already suggested by Rooney in the case of selective homologation of alkanes on tungsten films.[6] More recently, Rooney[7] has suggested that such a mechanism could also be involved in Fischer-Tropsch synthesis.



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