Anchoring of Hydridic Clusters by Acid–Base Reactions: New Method for the Preparation of Highly Active Fischer–Tropsch Catalysts

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Hydridic complexes such as $HFeCo_3(CO)_{12}$ can be effectively supported on basic supports such as silica modified by amino donor functions in an acid–base reaction to give highly active Fischer–Tropsch catalysts which give rise to an unusual product distribution.

Conventional Fischer–Tropsch catalysts prepared by precipitation of iron or cobalt salts convert synthesis gas in a rather unspecific reaction into n-alkanes and alkenes of a wide molecular weight range.[1] An approach which narrows the product distribution involves the control of the size of the metal particles on the surface of the catalyst. This can be achieved by supported cluster catalysts as shown by Basset *et al.* Using $HFe_3(CO)_{11}^-$ on γ-Al_2O_3 an unusually high selectivity for propene formation in the initial phase of the synthesis was observed. Unfortunately aggregation occurred under synthesis conditions leading to a growth of particle size and a loss of selectivity.[2]

We now report a new method for supporting hydridic complexes on inorganic supports such as silica. This method was chosen to prevent sintering effects. A chemical rather than a physical technique of metal fixation was applied, assuming that strong metal–support interactions would stabilize highly divided metal particles on the catalyst's surface. Amino functions were used as anchoring groups.

The aminated supports were prepared by condensation of $(EtO)_3Si[CH_2]_3NH_2$ with SiO_2 (Grace, pellet size 1—2.5 mm; Brunauer–Emmett–Teller area 579 m^2/g; pore volume 1.09 ml/g) with elimination of EtOH.[3]

Support of $HFeCo_3(CO)_{12}$, which was prepared according to the method of Chini *et al.*,[4] was carried out using the acid–base reaction (1), where SIL is the silica gel matrix. The

$$SIL\text{–}[CH_2]_3\text{–}NH_2 + HFeCo_3(CO)_{12} \rightarrow SIL\text{–}[CH_2]_3\text{–}NH_3^{+}\text{-}FeCo_3(CO)_{12}^{-} \qquad (1)$$

aminated silica gel (15 g) was treated with a solution of $HFeCo_3(CO)_{12}$ (5 g) in acetone (100 cm^3) at 30—40 °C for 4 h. After extraction with pentane (300 ml) and drying *in vacuo* the dark brown catalyst precursor (19.5 g) was obtained. Its i.r. spectrum (KBr pellet) showed absorptions at 2075 m, 2010s, 1970w, and 1815m cm^{-1}, in good agreement with the i.r. data reported by Chini[4] for $NEt_4^+FeCo_3(CO)_{12}^-$, indicating deprotonation but preservation of the cluster's framework. A relatively high metal content of 1.9 wt % Fe and 6.0 wt % Co was determined by atomic absorption spectrometry. It should be noted that this method leads to supported cluster catalysts of a highly reproducible metal content.

The electronic spectra (KBr matrix) of the cluster catalyst showed absorptions at 408 nm and 588 nm; *cf.* $HCoFe_3(CO)_{12}$ (320 and 525 nm) and $NEt_4^+FeCo_3(CO)_{12}^-$ (382 and 510 nm).[†] It was also possible to regenerate $HFeCo_3(CO)_{12}$ from the supported cluster catalyst by extraction with a solution of KOH in methanol followed by the work-up procedure used by Chini *et al.*[4] $HFeCo_3(CO)_{12}$ was isolated in 40% yield based on the metal content of the supported cluster catalyst and was characterized by u.v.–visible, i.r., and mass spectroscopy.[4]

Decarbonylation–activation of the catalyst was carried out in a stream of hydrogen of atmospheric pressure at 200 °C and a space velocity of 1000 h^{-1}. Hydrocarbons in the C_1—C_5 range could be detected during this activation procedure and the black catalyst pellets were kept in an inert atmosphere prior to use.

The catalyst prepared by this procedure is highly active in Fischer–Tropsch synthesis as shown in Figure 1. At atmospheric pressure 20% conversion of synthesis gas (CO–H_2) is observed at 240 °C. An unusually narrow product distribution was observed with a maximum at C_6 and a low selectivity for methane formation of 12.5%. Also a high alkene content was found: >95% in the C_3—C_5 range. Increase of pressure led to further improved conversions of up to 40% at 40 bar. At the same time the selectivity for methane formation increased to 32—35% and that for alkene formation decreased. This reflects the enhanced hydrogenation activity of the catalyst at elevated pressures. In contrast to conventional catalyst systems increase of pressure favours the formation of short-chain products. Thus, the product distribution shows a maximum at C_5 at 20 bar which is further shifted to C_3 at 40 bar. Following a suggestion of Schulz,[5] the deviation from the Schulz–Flory distribution in the C_1—C_5 range at atmospheric pressure can be interpreted in terms of a high degree of incorporation of the primary product ethylene into the growing chain on the catalyst's surface. Increase in synthesis gas pressure leads to a lower partial pressure of ethylene favouring chain growth by insertion of C_1 units in a conventional Fischer–Tropsch-process ending up in the usual Schulz–Flory product distribution.

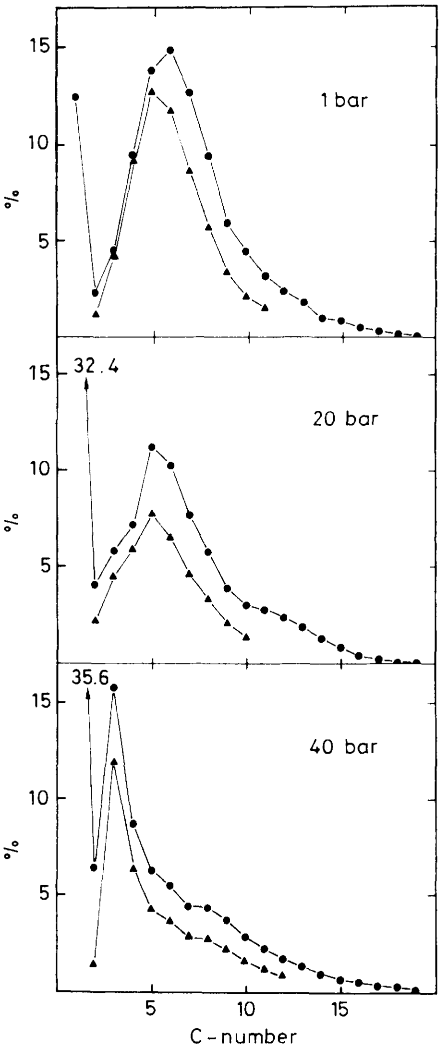

Figure 1. Product distribution in Fischer–Tropsch synthesis using $SIL[CH_2]_3NH_3^+FeCo_3(CO)_{12}^-$ as the catalyst precursor at 1, 20, and 40 bar of CO–H_2 (1 : 1); ●, total hydrocarbons; ▲, alkenes. Conditions: fixed bed reactor, 30 cm^3 catalyst volume, 500 h^{-1} space velocity, *T* 240 °C, fresh catalyst, steady-state conditions after 3 h, sampling period 3 h.

It is noteworthy that this catalyst showed an almost constant activity during an operation period of up to 220 h at a synthesis gas pressure of 40 bar. During this period a significantly increased selectivity for formation of oxygenated products was found. It should be emphasized that supporting hydridic complexes on aminated silica by an acid–base reaction is a general method. This has not only been exemplified for $HFeCo_3(CO)_{12}$ as described here, but also for HCo-

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[†] The disparity between the electronic spectra of the supported catalyst and the model clusters suggests that some other metal chromophore is present, although it is probable that a large proportion of the metal atoms are present in the form of clusters.

$(CO)_4$, $HRuCo_3(CO)_{12}$, and '$H_2Fe_3(CO)_{11}$' which was generated *in situ* from $Fe(CO)_5$ and water. It should also be mentioned that the high catalytic activity was achieved in the absence of any promoters such as K_2O. Possibly the amino groups of the support are transformed under synthesis conditions into metal nitride phases. Preparation of nitrided iron catalysts has been reported by Anderson by treatment with ammonia.[6] In this case iron nitride phases were detected on the catalyst's surface and a high selectivity for formation of oxygenated products was observed. The supported catalyst $HFeCo_3(CO)_{12}$/aminated silica is at present being characterized by surface analytical methods in order to determine the presence of nitride phases.

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