Partially Degraded Iron Complexes as Stable Catalysts for the Selective Hydrogenation of Carbon Monoxide to Alkenes

Ruud Snel

Chemical Engineering Research Group, Council for Scientific and Industrial Research, P.O. Box 395, Pretoria 0001, Republic of South Africa

A new class of active, stable, and selective catalyst for the hydrogenation of CO to alkenes has been prepared by partial decomposition of Fe complexes.

Highly disperse metal catalysts for the selective hydrogenation of CO to alkenes were derived from Fe carbonyls[1] by thermal activation. They were shown to exhibit a selectivity for alkenes of up to 70%, as well as hydrocarbon distributions that deviate strongly from those predicted by Schulz–Flory statistics.[2] However, the stability of the catalysts was poor and within two days on stream the product spectrum had shifted to that normally observed with iron catalysts. In this communication we report on the first *active* and *stable* iron catalysts exhibiting similar selectivities.

Amorphous mixed-metal complexes can be obtained from solutions containing metal salts and polyfunctional hydroxy-acids.[3] Several different iron citrate complexes containing other metals at different concentrations were prepared by this means. Partial combustion of the complexes yielded a variety of materials with the general formula $Fe_xM_yO_zC_a$, in which M represents one or more different metals. Scanning Auger electron microscopy revealed that in the outermost surface layer of these materials the value for a is generally *ca.* 0.5 and decreases to approach zero at the fourth atomic sub-surface layer. The density of the catalyst precursors is very low, typically ranging from 200 to 400 kg m^{-3}.

Catalytic reaction experiments were carried out with the partially reduced materials in a fixed-bed microreactor system with on-line gas chromatographic analysis of the products, which has been described elsewhere.[4—7] The reaction conditions were 2.0 MPa and 543 K. Synthesis gas with a H_2/CO ratio of 0.5 was passed at an hourly space velocity (V.H.S.V.) = 1000.

The conversion rate of CO into hydrocarbons (r_{HC}) in a typical experiment with a catalyst containing no other metal but iron (catalyst A) is compared with the rate obtained with a fused iron ammonia synthesis catalyst (BASF S6-10, catalyst B). The catalytic activity of A was more than an order of magnitude higher than that of B (Figure 1). Activity maintenance is very good. After reaching a maximum, the rate of hydrocarbon synthesis levelled out at a constant value of

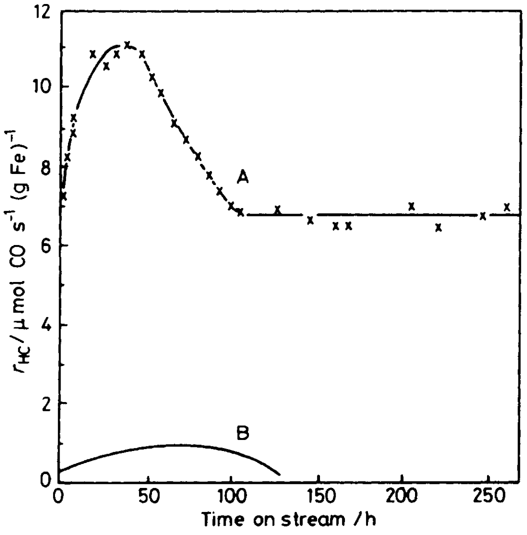

Figure 1. Comparison of the magnitude of the rate of hydrocarbon synthesis over catalysts A and B, and of their stability.

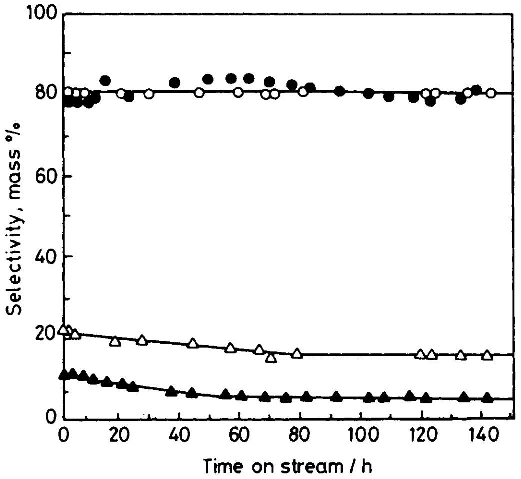

Figure 2. Comparison of selectivities obtained with catalysts A (●, ▲) and B (○,△): ○,● C_2—C_5 alkenes; △,▲ methane.

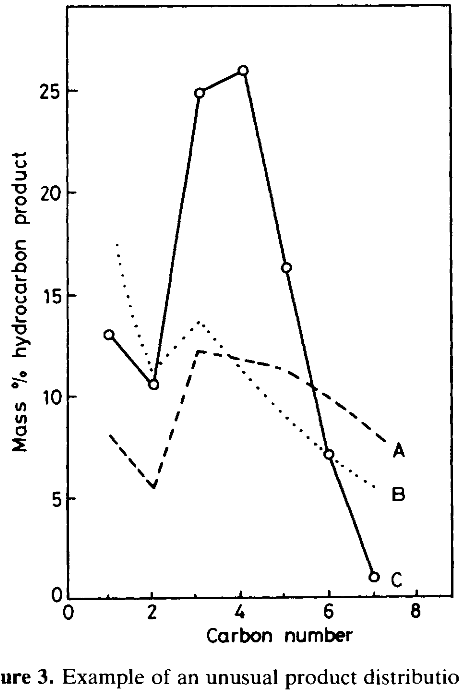

Figure 3. Example of an unusual product distribution.

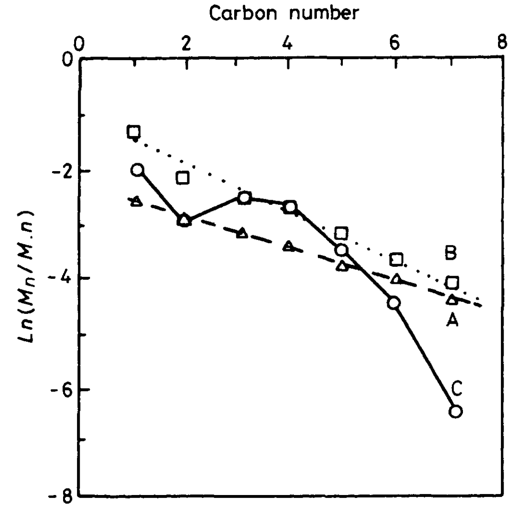

Figure 4. Example of a deviation from normal Schultz–Flory behaviour. Catalysts A and B follow Schultz–Flory statistics with growth probabilities of 0.75 and 0.65 respectively. [Data from Figure 3 expressed in terms of the ratio of the mass of a hydrocarbon with *n* carbon atoms (M_n) to the total mass of hydrocarbons *M*, times *n*.]

7 μmol s^{-1} g^{-1}, which was still being maintained after 306 h on stream, at which point the experiment was terminated.

The selectivity behaviour of A also compares very well with that of B. The percentage of alkenes in the C_2—C_5 hydrocarbon product fraction obtained with A easily matched that obtained with B (Figure 2). This indicates that high alkene selectivities, usually only obtained by alkali promotion,[8] can also be achieved in an entirely different manner since catalyst A is not alkalized but catalyst B is.

Methanation is an undesirable side-reaction that is substantially suppressed by the use of catalyst A. In fact, the product obtained with B contains more than twice as much methane as that obtained with A. The selectivity maintenance of both catalysts is very good.

When other metals, *e.g.* Ca (atomic ratio Fe/Ca = 1, catalyst C), are incorporated into the catalyst, very unusual product distributions are obtained. The concentration of the C_3—C_4 fraction is more than double that normally obtained under the same conditions (Figure 3). Although it is often suggested that Fischer–Tropsch product distributions always adhere to Schulz–Flory statistics,[8] in this case a substantial deviation is observed (Figure 4). It should be stressed that this result was not obtained only in the initial stages using a fresh catalyst or at very low conversion levels where deviations are known to be possible.[9] In this particular case the catalyst was in a steady state, working at a conversion level of *ca.* 50%.

We conclude that partially degraded Fe complexes form a new class of very stable and active Fischer–Tropsch catalyst, some of which exhibit unusually high selectivities towards lower alkenes and an exceptionally low methane selectivity.

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