Catalytic Synthesis of Low Molecular Weight Olefins from CO and H_2 with $Fe(CO)_5$, $Fe_3(CO)_{12}$, and $[HFe_3(CO)_{11}]^-$ Supported on Inorganic Oxides

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Summary $Fe(CO)_5$, $Fe_3(CO)_{12}$, and $[HFe_3(CO)_{11}]^-$ supported on inorganic oxides such as Al_2O_3, La_2O_3, MgO, or SiO_2, exhibit, after decomposition under CO + H_2, a very high selectivity in Fischer–Tropsch syntheses for low molecular weight olefins.

FISCHER–TROPSCH synthesis with iron-based catalysts usually produces a variety of paraffins and olefins which range from C_1 to *ca.* C_{20}.[1] We report here that $Fe(CO)_5$ or $Fe_3(CO)_{12}$ supported on inorganic oxides (*e.g.*, Al_2O_3, La_2O_3, MgO, SiO_2) exhibit, in Fischer–Tropsch synthesis, a very high selectivity for low molecular weight olefins.[2]

The catalysts were prepared by impregnation of γ-Al_2O_3 (200 $m^2 g^{-1}$), La_2O_3, SiO_2 (320 $m^2 g^{-1}$), and MgO with $Fe(CO)_5$ or $Fe_3(CO)_{12}$ in n-pentane solution. The solvent was removed under vacuum and the catalyst (40 g) was placed under argon in a flow reactor. The solids were usually thermally activated under a flow of CO + H_2 (CO : H_2 = 1 : 1, P_{total} = 10 bars) and the reaction was carried out for *ca.* 90 h under differential conditions in the temperature range 180—270 °C. Typical results are given in Table 1. Most of the iron-based catalysts exhibited a selectivity towards olefins higher than *ca.* 50%, the product distribution showing a sharp maximum for C_2—C_3 hydrocarbons. By comparison, a conventional iron catalyst obtained by impregnation of the same γ-alumina with $Fe(NO_3)_3$, followed by calcination in air and reduction under H_2, exhibited a completely different product distribution with a minimum selectivity for C_2-olefins and a wide range extending as far as C_{16}. Also, the selectivity towards olefinic compounds was only 38%. Since the same alumina was used for both types of catalysts, the porosity of the support does not

TABLE 1. Activities and selectivities of the catalysts in Fischer–Tropsch synthesis

Catalyst	Fe[a]/ wt %	T/°C	% Conversion[b]	Selectivity to hydrocarbons[c]	Fraction of olefins[d]	% Product distribution				
						C_1	C_2	C_3	C_4	C_5+
$Fe_3(CO)_{12}/Al_2O_3$	0·82	270	3·3	100	57·0	18·8	72·7	7·4	1·1	ϵ
$Fe_3(CO)_{12}/SiO_2$	0·49	260	5·3	44·4	50·3	22	17·5	22	19·5	19[f]
$Fe(CO)_5/Al_2O_3$[h]	1·85	260	3·3	100	42·8	46·5	13·5	18	13	9[f]
$Fe(CO)_5/La_2O_3$[h]	0·30	270	3·4	44·2	58·1	29	20	22	17·5	11·5[f]
$Fe(CO)_5/La_2O_3$+py[e]	0·30	270	6·1	44·1	62·8	25·5	19	24	18	13·5[f]
$Fe(CO)_5/SiO_2$	2·80	265	5·1	42·6	68·9	20·5	21	30·0	21·5	7[f]
$Fe(CO)_5/SiO_2$+py[e]	4·60	270	6·1	86·2	63·4	22	18	25·5	18·5	16[f]
$Fe(CO)_5$/MgO[h]	0·50	265	1·4	100	60·3	21	17	24	29	9[f]
$Fe(NO_3)_3/Al_2O_3$	8·1	270	19·4	62·6	38·4	22	10·6	16·3	15·2	35·9[g]

[a] Wt % metal determined at the end of the test.

[b] Conversion is defined as:

$$100 \times \frac{\sum_{n=1}^{n=5} n(C_nH_{2n+2}) \quad + \quad \sum_{m=2}^{m=5} m\,(C_mH_{2m}) \quad + \quad (CO_2)\text{ produced}}{(CO)\text{ input}}$$

[c] Selectivity to hydrocarbons is defined as:

$$100 \times \frac{\sum_{n=1}^{n=5} n(C_nH_{2n+2}) \quad + \quad \sum_{m=2}^{m=5} m(C_mH_{2m})}{\sum_{n=1}^{n=5} n(C_nH_{2n+2}) \quad + \quad \sum_{m=2}^{m=5} m(C_mH_{2m}) \quad + \quad (CO_2)\text{ produced}}$$

[d] Fraction of olefins in hydrocarbons is defined as:

$$100 \times \frac{\sum_{m=2}^{m=5} m(C_mH_{2m})}{\sum_{n=1}^{n=5} n(C_nH_{2n+2}) \quad + \quad \sum_{m=2}^{m=5} m(C_mH_{2m})}$$

[e] Support pretreated with pyridine before impregnation. [f] Mainly C_5 hydrocarbons. [g] Mainly C_5 to C_{12} hydrocarbons. [h] On basic support a fraction of $Fe(CO)_5$ is transformed into $HFe_3(CO)_{11}^-$ (ref. 8).

TABLE 2. Activities and selectivities of the catalysts in Fischer–Tropsch synthesis.

Catalyst	Metal[a] wt/%	T/°C	% Conversion[b]	Selectivity to hydrocarbons[c]	Fraction of olefins[d]	% Product distribution C_1	C_2	C_3	C_4	C_5
$Rh_4(CO)_{12}/Al_2O_3$	2·7	180	4·3	100	2·5	84·8	5·5	6·2	3·4	0·1[f]
$Rh_6(CO)_{16}/Al_2O_3$	2·9	200	2·7	79·5	27·7	28·5	14·5	32·5	22·5	2[f]
$Ir_4(CO)_{12}/Al_2O_3$	3·5	180	11·8	100	0·8	77·9	13·1	6·2	2·4	ϵ
$Ru_3(CO)_{12}/Al_2O_3$	2·4	180	14·7	100	4	49·0	22·8	18·0	9·9	0·3[f]
$Os_3(CO)_{12}/SiO_2$	3·1	200	9	100	8·9	85·5	2·7	2·3	9·0	0·5[f]

Footnotes a—f as for Table 1.

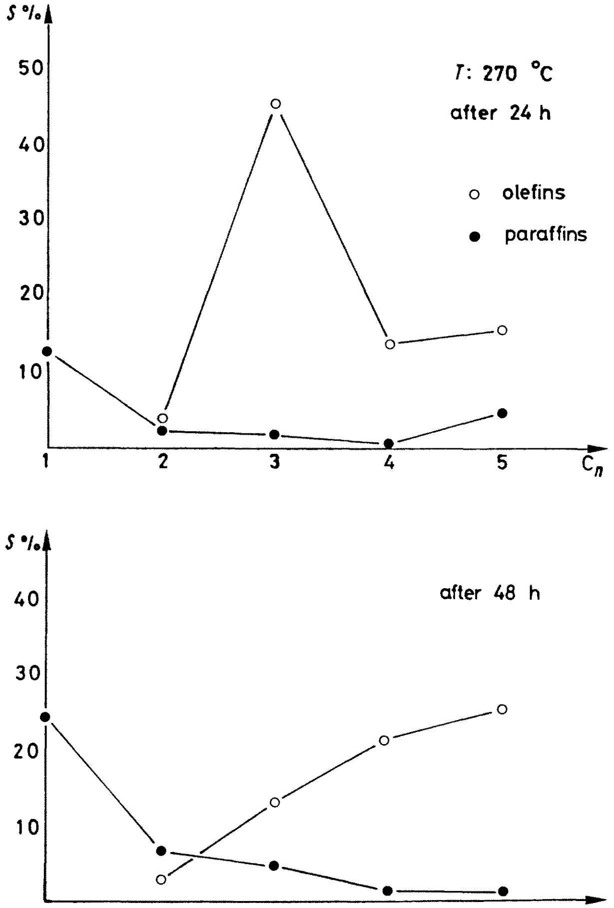

FIGURE. Selectivities observed in Fischer–Tropsch synthesis with the precursor catalyst: $HFe_3(CO)_{11}^-/Al_2O_3$.

seem to be responsible for the low molecular weight olefins observed, but rather, the small dimensions of the iron particles obtained from the carbonyl precursor[3] (*vide infra*).

In order to obtain very small iron particles with an homogeneous distribution on the surface, we have prepared the supported anionic cluster $HFe_3(CO)_{11}^-$ by impregnation of γ-alumina by pentane solutions of $Fe(CO)_5$ or $Fe_3(CO)_{12}$.[4] In contrast with the previously described method, only a fraction of $Fe(CO)_5$ or $Fe_3(CO)_{12}$, chemisorbed as $HFe_3(CO)_{11}^-$, is on the surface, which is washed several times with n-pentane in order to remove weakly adsorbed $Fe(CO)_5$ or $Fe_3(CO)_{12}$. The anionic hydrido cluster, which has a surface $\geqslant Al^+$ counter cation, has been thermally decomposed under $CO + H_2$. This decomposition produces iron particles which cannot be detected by electron microscopy and which have a size smaller than *ca.* 20 Å. The particles of metallic iron have been characterized in separate experiments by e.s.r. spectroscopy and low temperature ferromagnetic resonance.[5]

The catalyst prepared in this way exhibits a very high selectivity towards propylene (45%) during the first hours of the run. Then the selectivity declines slowly with time and hydrocarbons of higher molecular weight are obtained (Figure).

Electron microscope measurements, carried out at the end of the run, indicate the presence of very large iron particles of *ca.* 200—500 Å. The results seem to indicate that the low molecular weight olefins are produced when small iron particles are present whereas a broader molecular weight distribution may be connected with the larger particles of iron.

If molecular clusters of noble metals [$Rh_4(CO)_{12}$, $Rh_6(CO)_{16}$, $Ir_4(CO)_{12}$, $Ru_3(CO)_{12}$, and $Os_3(CO)_{12}$] are supported on silica or alumina[6] the product distribution also favours low molecular weight hydrocarbons (Table 2). However, most of them are saturated. No alcohols or oxygenated hydrocarbons are formed as could be expected from the results of Ichikawa.[7]

In conclusion, the use of a metal carbonyl and preferentially a molecular cluster as a precursor for Fischer–Tropsch catalysts, leads to a limitation of the chain growth and hence to a high selectivity for low molecular weight hydrocarbons. Further, the comparison of our results with those of Ichikawa[7] clearly indicates that the nature of the cluster and the nature of the support govern the nature of the products and their distribution, namely olefinic hydrocarbons, saturated hydrocarbons, or oxygenated compounds.

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