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Characteristics of Zeolite-Supported Iron Catalysts Prepared from Iron Cyanide Complexes

In a recent article (*1*) a new preparation method of zeolite-supported metal catalysts has been described. The method consisted in reacting a metal-exchanged zeolite with an anionic, metal-containing coordination compound, that resulted in an insoluble complex supported by the zeolite. Subsequent reduction under hydrogen resulted in dispersed metal on the zeolite support. The method described was illustrated by using transition metal cyanide complexes in the reaction and was designed for applications in Fischer–Tropsch catalysis.

For a better physical characterization of zeolite-supported iron catalysts prepared by this method, the Mössbauer spectra of these materials were obtained at room temperature, before and after reduction under hydrogen. The catalyst precursor was prepared by reacting Fe^{2+}–Y zeolite with a solution of $(NH_4)_4[Fe(CN)_6]$ and drying the product in air. Exposure to air caused the oxidation of Fe^{2+} to Fe^{3+} and the compound turned deep blue. The material contained 4.66% iron (dry basis). Details of the preparation method are givne in (*1*). Portions of the catalyst precursor were reduced under hydrogen at 400°C for 1, 4, and 48 h, respectively.

The Mössbauer spectrum of the catalyst precursor shows the presence of an asymmetric doublet (Fig. 1). Computer fitting of the spectrum shows resolution of the asymmetric doublet into a singlet and symmetric doublet. The spectrum is similar to the one ascribed in the literature to "Prussian Blue" (*2*). This asymmetric doublet is due to the superposition of a singlet from the ferrocyanide and quadrupole doublet from the high-spin iron (III) ions. Analysis of the doublet gives a chemical isomer shift I.S. = 0.092 mm/sec and a quadrupole splitting Q.S. = 0.491 mm/sec measured with respect to a Pd source.

Electron microscopic examination of the oven-dried material shows the presence of amorphous "patches" on the crystalline support, suggesting that the precipitate is located on the outer surface of the zeolite particles. It is reasonable to assume that during the reaction Fe^{2+} ions migrate from their initial location in the zeolite cages to the zeolite surface, where they form a precipitate with $[Fe(CN)_6]^{4-}$ ions. Ammonium ions from $(NH_4)_4[Fe(CN)_6]$ are most likely the counterions replacing Fe^{2+} in the zeolite.

Calcination of this material at 400°C under nitrogen results in an increase in the size of the amorphous "patches," indicating an agglomeration of the precipitate on the outer surface of the zeolite particles.

The spectra of the catalyst reduced for 1, 4, and 48 h are shown in Fig. 2. The three spectra show great similarity and indicate that after the first hour the reduction process is practically completed. This contrasts with most iron-based Fischer–Tropsch catalysts with similar iron loading, which require prolonged heating in a reducing atmosphere in order to complete the reduction process. The relatively short reduction time is due not only to improved mass transport at the surface, compared to diffusion through the bulk of the particle, but also to the easy reducibility of the ferrocyanide compound, as was shown by Mittasch *et al.* (*3*).

The spectra in Fig. 2 show a set of four strong Mössbauer peaks, which are part of a six-peak ferromagnetic split component. The other two peaks of this component are

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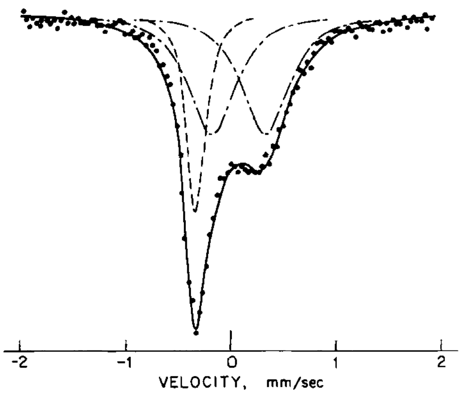

FIG. 1. Mössbauer spectrum of catalyst precursor.

outside the velocity range shown in Fig. 2. In the spectrum of the catalyst reduced for 1 h, the peaks are located at −3.30, −1.00, 0.67, and 2.94 mm/sec. The presence of ferromagnetic iron metal in the hydrogen-treated material shows that the bulk of the iron is in particles greater than 10 nm diameter and thus clearly outside the zeolite cages, whose maximum diameter is about 1.3 nm. Changes of the hyperfine field in the spectra shown in Fig. 2 can be attributed to changes in particle size (*4*). An increase in the hyperfine field, as seen in spectrum C, is likely to be caused by the larger particles formed from agglomeration of the metal after prolonged heating.

The spectra show some additional absorption bands at 2.0 and −0.21 mm/ sec, which account for about 30% of the total iron in the sample. These could be due to smaller, superparamagnetic iron metal particles or to Fe^{2+} ions which did not react with the ferrocyanide ions. It has been shown that Fe^{2+} ions in iron-exchanged Y zeolites cannot be reduced under hydrogen to metallic iron (*5*). However, the broadness of these additional absorption bands and the strong overlap with the ferromagnetic metallic iron spectrum makes an exact assignment difficult.

The materials described have proved to have interesting catalytic properties in Fischer–Tropsch reactions. Table 1 illustrates the hydrocarbon distribution obtained during the conversion of synthesis gas over a

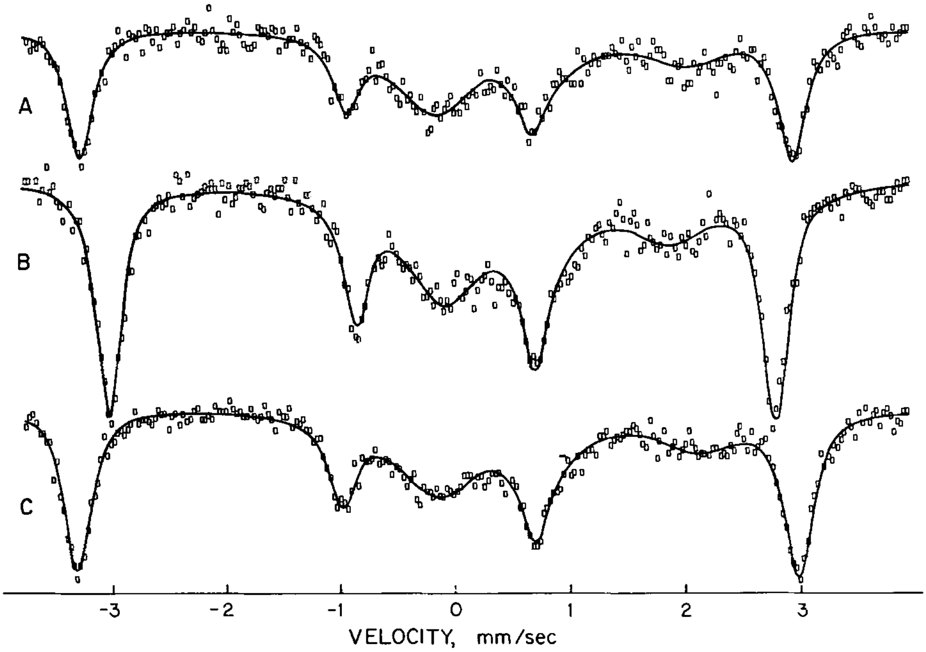

FIG. 2. Mössbauer spectra of catalysts reduced under hydrogen at 400°C for (A) 1 h; (B) 4 h; (C) 48 h.

TABLE 1

Conversion of Syngas over Fe/Y Catalyst

	Test No.					
	1	2	3	4	5	6
Reaction conditions						
H_2/CO ratio	1/1	1/1	1/1	2/1	2/1	2/1
T (°C)	300	300	300	300	300	300
GHSV (H^{-1})	200	200	200	200	200	200
Time on stream (h)	0.25	1.0	20	0.25	1.0	20
χ_T (mole%)[a]	34	27.5	14	21	14	9
χ_{HC} (mole%)	18	14	6	14	9	6
S_{HC} (mole%)	53	51	43	67	64	67
HC distribution (mole%)						
CH_4	42.5	45.0	58.8	53.6	52.5	59.5
C_2H_4	0.3	1.3	11.6	—	0.8	3.1
C_2H_6	26.5	27.6	12.4	27.6	29.8	24.8
C_3H_6	1.0	1.8	4.6	0.9	0.8	2.4
C_3H_8	15.1	11.8	5.4	11.9	10.2	6.6
C_4H_8	10.5	9.8	7.2	5.2	5.9	3.5
C_4H_{10}	2.0	1.1	—	0.8	—	—
C_5H_{10}	2.0	1.7	—	—	—	—
Total C_2–C_4 (mole%)	55.5	53.3	41.2	46.4	47.5	40.5
C_2^{2-}/C_2 total (mole%)	1.1	4.5	48.3	—	2.6	11.1
C_3^{2-}/C_3 total (mole%)	6.2	13.2	46	7	7.3	26.7
C_4^{2-}/C_4 total (mole%)	84	89.9	100	86.6	100	100
$S^*_{CH_4}$ (at.%)	20.8	23.0	35.5	31.3	30.8	38.1
$S^*_{C_2\text{–}C_4}$ (at.%)	74.2	64.5	68.7	68.7	69.2	61.9
$S^*_{C_5}$ (at.%)	5.0	4.3	—	—	—	—

Note. Catalyst composition: 4.6% Fe on Y zeolite.

[a] χ_T = mole percentage CO converted; χ_{HC} = mole percentage CO converted into hydrocarbons. Selectivity for hydrocarbons $S_{HC} = (\chi_{HC}/\chi_T) \times 100$; $S^*_{C_i} = (iC_i/\Sigma iC_i) \times 100$, where C_i represents molar concentrations of hydrocarbons with i carbon atoms in the molecule.

zeolite-supported iron catalyst, prepared by the method described. The CO hydrogenation was carried out in a continuous-flow reactor, attached to a Hewlett–Packard model 5830A gas chromatograph. The conversions are shown after different times on stream, and for two different H_2/CO ratios (2 and 1) at atmospheric pressure. Steady state is reached after 3 to 4 h on stream.

The data show rather high selectivity for C_2–C_4 hydrocarbons. Longer times on stream favor higher olefin/paraffin (C_n^{2-}/C_n) ratios. In the case of C_4 hydrocarbons, only the olefinic form appears in significant amounts. The high selectivity for low-molecular-weight hydrocarbons contrasts with the wide range of hydrocarbons obtained with conventional iron-based catalysts (*6*).

The Schulz–Flory distribution (*6*) of hydrocarbons obtained by this reaction after 20 h on stream is plotted in Fig. 3 for the H_2/CO ratios of 1 and 2. For most catalysts used in Fischer–Tropsch reactions, the Schulz–Flory equation applies to hydrocarbons from C_3 or C_4 onward (*6–8*). Usually too much CH_4 and low quantities of C_2 hydrocarbons are found in the mixture. However, in our case, considerably more C_2 is obtained. For the H_2/CO ratio of 2, the distribution of C_1–C_4 hydrocarbons follows

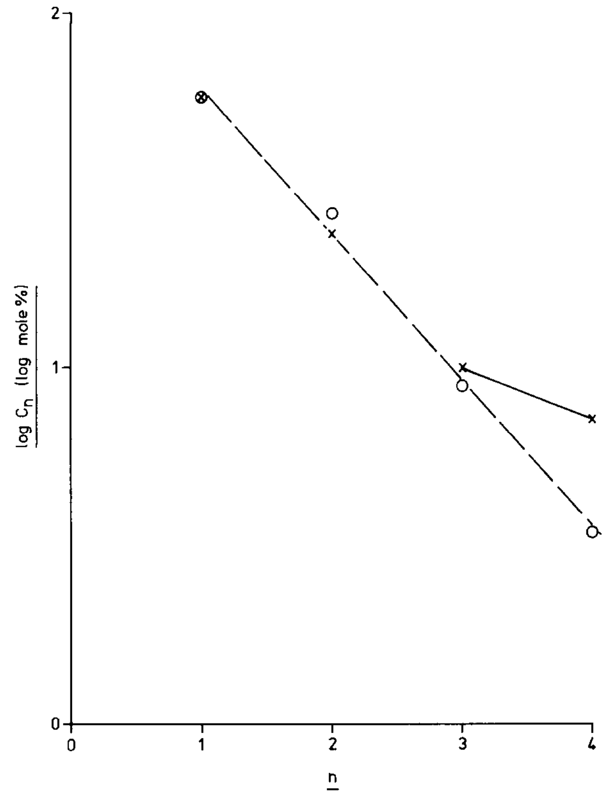

FIG. 3. Schulz–Flory distribution of hydrocarbons obtained in Fischer–Tropsch reaction over reduced Fe/Y catalysts: n = Carbon number; ×—for H_2/CO ratio of 1; O—for H_2/CO ratio of 2; reaction temperature, 300°C.

a linear relationship, which is unusual for an iron-supported catalyst. A more detailed study of different catalysts prepared by the method described in (*1*) is in progress.

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