JOURNAL OF CATALYSIS 97, 261–263 (1986)

Iron Alloy Fischer–Tropsch Catalysts

VI. FeCo on ZSM-5

A series of Fe and FeCo catalysts on ZSM-5 support were prepared and characterized in comparison with a similar Y-supported series (*1*). Shape selectivity is important in determination of product distribution of ZSM-5 materials, particularly in leading to a significant aromatic product fraction.

The NH_4ZSM-5 (Si/Al ~ 28) was supplied by PETC, Department of Energy.[1] HZSM-5 (80–120 mesh) was prepared by treatment at 400°C overnight and impregnated samples prepared as before (*1*). Ion exchange was attempted, however at the metals loadings involved significant exchange was not obtained. A list of the impregnated samples is given in Table 1.

Particle size and distribution. X-Ray characterization employed Fourier line profile analysis (*2*) and particle sizes of Fe samples were checked by H_2 chemisorption with generally good agreement. Both oxidized and reduced HZSM-5 samples checked rather well in average particle size with Y catalysts of similar weight loading. Reduced Fe/HY was 7.5 vs 6.0 nm for Fe/HZSM-5; reduced FeCo/HY 8.0 vs 7.8 nm for FeCo/HZSM-5. Corresponding values for the oxides were 11.5 vs 13.0 and 10.2 vs 13.0 nm, respectively. Lattice contraction, as one goes from oxide to metal, has been reported previously for SiO_2 supports (*3*). Size distributions were rather broad, about 5 to 20 nm, for both oxide and metal. A major difference was the formation of a FeCo alloy phase not observed for Y-supported catalysts. In this note "oxide" is after treatment O_2, 500°C, 24 h (O_2, 500°, 24) and "metal" (reduced) after further treatment H_2, 425°C, 24 h (H_2, 425°, 24).

Fe/HZSM-5; reduction and carburization. Mössbauer spectroscopy was used for characterization after oxidation, reduction, and carburization (1 : 1/H_2 : CO, 250°, 10). The oxide is predominately ferromagnetic α-Fe_2O_3 with about 5% superparamagnetic oxide. Reduction gives over 95% Fe^0, while Fe/Y was only partially reduced under these conditions. Carburization gives mostly ε'-carbide with a minor amount of χ-phase. The overall behavior of Fe/HZSM-5 is similar to that of Fe/SiO_2 (*2, 3*).

FeCo/HZSM-5; reduction and carburization. Again a characteristic oxide pattern is obtained after O_2, 500°, 24, but the spectrum fit indicates the presence of two phases (Table 2). Two six-line patterns were also obtained after reduction, the dominant one for FeCo alloy and a second for Fe metal as in Fe/HZSM-5. Carburization leaves the alloy unchanged, but Fe is converted into χ-carbide as shown in Table 2. Again the material is similar to FeCo/SiO_2 (*3*); no alloy was found for FeCo/HY (*1*).

CO and water-gas shift activities. The Fe/HZSM-5 catalysts are comparable in CO activity to Fe/HY, 20 vs 35 × 10^{-3} s^{-1} at 1% conversion, increasing to 21 vs 16 × 10^{-3} s^{-1} at 3% conversion. FeCO/HZSM-5 is about 1.5 times more active than FeCo/

TABLE 1

Catalysts Investigated

Fe/HZSM-5	Fe: 4.94 wt%
Co/HZSM-5	Co: 4.60 wt%
FeCo/HZSM-5	Fe: 3.84 wt% + Co 1.02 wt%

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[1] We are indebted to Dr. V. V. S. Rao of PETC for his help.

0021-9517/86 $3.00

TABLE 2

Room-Temperature Mössbauer Parameters, FeCo/HZSM-5

Treatment	Isomer shift (mm/s)	Quadrupole splitting (mm/s)	Hyperfine field (kOe)	Relative area
Oxidation				
Phase (1)	0.13	0.27	465.7	0.16
Phase (2)	0.43	0.41	512.9	0.84
Reduction				
Fe metal	0.04	0.02	333.4	0.29
FeCo alloy	0.07	0.02	350.0	0.71
Carburization				
χ-Carbide	0.11	0.48	183.0	0.23
FeCo alloy	0.09	0.04	347.5	0.77

HY (20 vs 15 × 10^{-3} s^{-1}), as is Co/HZSM-5 vs Co/HY (~13 vs 2 × 10^{-3} s^{-1}); in both of these cases turnover is essentially conversion-independent. The differences for FeCo can well arise from differences in alloy formation, while diminished product inhibition on HZSM-5 may be due to secondary reactions absent on HY. Shift activity of the HZSM-5 is about twice that of the Y series (i.e., about the same as for SiO_2 supports) except for Co which is low in all cases.

Product selectivities. Selectivities in comparison with SiO_2 and HY supports (*1*, *3*) are given in Table 3. They are considerably different. Notable is the relatively large fraction of aromatics, 10–15%. Of this there is a large proportion of substituted benzenes (ca. 40% xylenes at 3% conversion) that appear to increase with conversion. Such aromatics deviate from the chain growth mechanism as can be seen from the two probability plots of Fig. 1 in which aromatics have both been included and excluded from the distribution. There is not much difference between Fe and FeCo evident in Table 3 (in spite of alloy formation), however even Co/HZSM-5 is similar to Fe/HZSM-5 except for shift activity, again indicative of an important role of the zeolite in product selectivity.

Conclusions. The impregnation procedure employed gives particles of ca. 10 nm on both HZSM-5 and HY. The decrease in dimension upon reduction indicates the crystallites, though external to the pore structure, are stabilized and no sintering occurs. The HZSM-5 support produces a high percentage of high-molecular-weight and aromatic products compared to HY and SiO_2 (α values are reported in (*2*)). Adherence of HZSM-5 supported catalysts

TABLE 3

Product Composition at 3% CO Conversion

Product composition (%)	Fe/HZSM-5	Fe/HY	CO/HZSM-5	Co/HY	FeZSM-5	FeY	FeCo/ HZSM-5	FeCo/HY
CO_2	28.7	22.2	10.0	6.4	28.5	16.2	19.5	25.4
H_2O	45.2	53.0	57.6	64.4	42.7	55.4	52.6	50.2
CH_n	26.1	24.9	32.4	29.2	28.8	28.4	27.9	24.4
CH_n, %								
C_1	44.9	52.3	52.0	57.1	40.7	52.6	48.7	51.4
$C_2^=$	3.3	5.1	3.8	3.6	3.2	7.2	2.7	6.4
C_2	12.5	9.0	10.8	7.7	11.5	8.6	10.5	11.3
$C_3^=$	4.3	3.8	1.4	6.3	3.8	6.5	3.7	5.3
C_3	5.3	11.2	5.8	4.4	4.8	8.8	5.7	4.4
C_4 (total)	5.8	8.4	6.8	9.6	5.9	9.7	8.5	6.4
C_5^+ Aliphatic	9.6	17.5	9.0	11.4	9.7	6.8	9.4	14.9
Aromatic	12.3	0	10.4	—	16.4	—	10.7	—
$C_2^=/C_2$	0.26	0.53	0.35	0.47	0.28	0.84	0.26	0.56

Note. Data for Y and HY catalysts from Ref. (*1*).

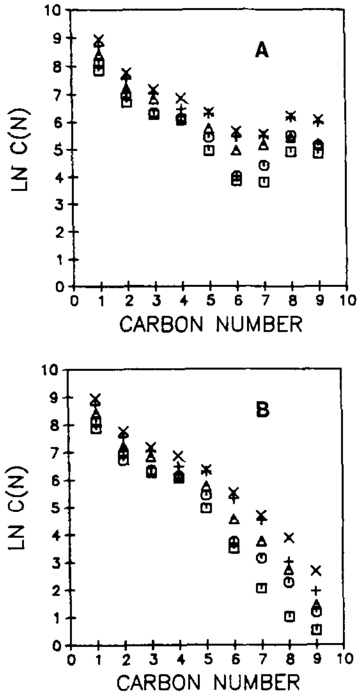

FIG. 1. Chain growth probability plots for Fe/HZSM-5. (A) Total product distribution. (B) Production distribution excluding aromatics at CO mole percentage conversion of: □, 1.72; ○, 2.27; △, 3.34; +, 4.25; ×, 5.25.

to linear chain grouth probability is observed only if the aromatic product fraction is excluded. These observations agree with the proposals of Dejaifve *et al.* (*4*) for reactions involving a combination of synthesis and aromatization steps. Similarity of the product distribution with different metals suggests a reaction pathway in which the metal function serves as an initiator with subsequent migration of intermediates to the internal pore structure. Unfortunately, neither this view nor the present data have much to say about oxygenate formation.

ACKNOWLEDGMENT

This research was supported by the Exxon Education Foundation and the Stauffer Chemical Company.

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Received May 3, 1985