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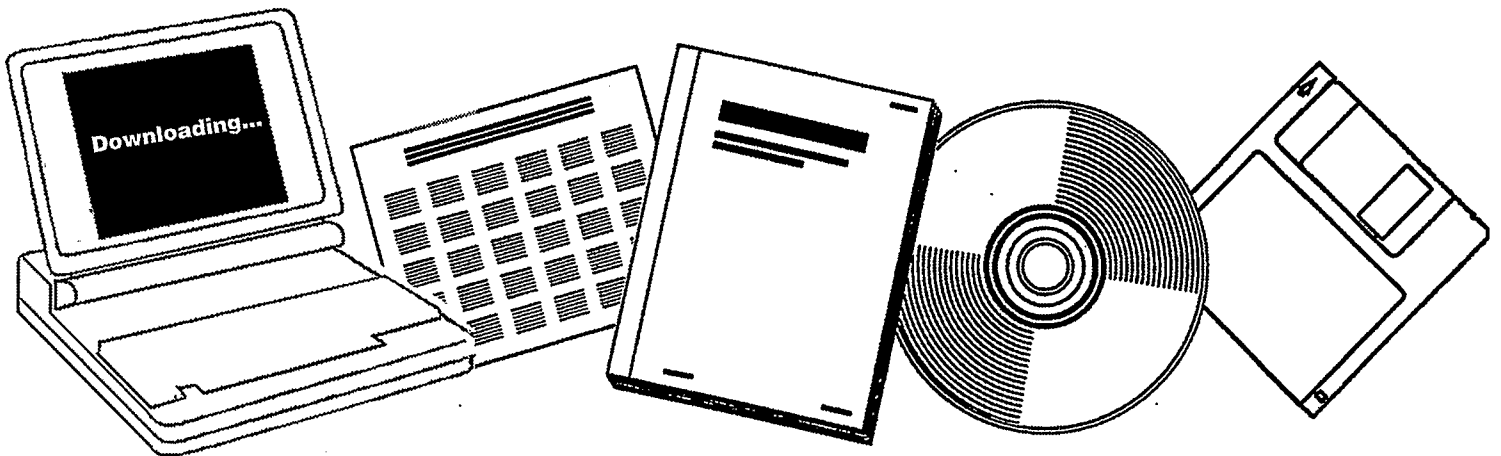
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SPECTROSCOPY OF ZEOLITE FE (AND FE-CO)
SYNFUEL CATALYSTS**

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TRANSMISSION AND BACKSCATTER MÖSSBAUER SPECTROSCOPY OF ZEOLITE Fe (AND Fe-Co) SYN FUEL CATALYSTS

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Abstract.— The reduced and carbided ZSM-5 (14.7% Fe) showed spectra corresponding to (a) Fe⁰ (~85% reduction) and to (b) (Fe₃C₂) respectively. The used catalysts showed mixtures of (b), presumably the active phase, and (c) Fe₃C. The backscatter spectra of Fe-Co (selective) catalyst revealed absence of Fe in the 30 nm layer, which was confirmed by Ion Scattering Spectroscopy. Differences in surface composition and product distribution are discussed.

Introduction.

The catalytic conversion of coal derived synthesis gas (CO + H₂) to gasoline range hydrocarbons and olefins using bifunctional zeolite catalysts is of much current interest (1). The medium pore (dia ~6 Å) zeolite ZSM-5 in combination with Fe or with Fe-Co (2) was shown to yield a high fraction of aromatics in the product, resulting in a favorable octane number (>80). It was indicated (2) that the bimetallic Fe-Co on ZSM-5 could alter the product selectivity, mainly in reducing the shift conversion of CO + H₂O to CO₂, from the high shift yields of Fe on ZSM-5. The aromatics in the product decreased by the addition of cobalt to the zeolite (2). An extensive chapter by Mulay, Lo et al. gives further background information (1).

The zeolite ZSM-5 has space group Pnma or Pn2₁a with a = 20.1 Å; b = 19.9 Å; c = 13.4 Å. The framework structure consists of five membered rings of Si(Al)-O tetrahedra. The pore structure

(Figure 1) consists of intersecting channels defined by 10 rings of oxygen atoms. The elliptical, straight channels of cross-section 5.7 Å × 5.1 Å along the b-axis and circular zig-zag channels of diameter 5.4 Å interconnect the straight channels.

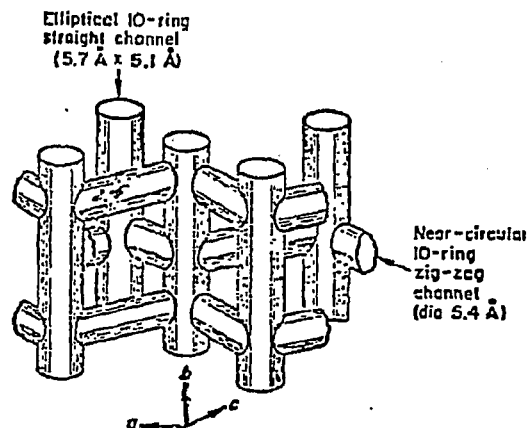


Fig. 1. Possible model of the pore structure of ZSM-5.

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The Mössbauer spectra were obtained to characterize the fresh, the reduced, the carbided and the used ZSM-5 with Fe or Fe-Co at the microscopic level. The backscatter work was undertaken to see if the iron was on the top 30 nm layer of

the Fe-Co catalysts formed with the ZSM-5 system. Salient features of such work are reported in this paper.

Experimental.-

The preparation of samples is described in ref (1). The Mössbauer spectra were recorded with a constant acceleration spectrometer (Austin Science Associates Inc.) with a 75 mCi Co^{57} source in Rh matrix, Nuclear Data-100 multi-channel analyzer and a Reuter-Stokes gas proportional counter (90% krypton and 10% methane). Typical spectra reported here were calibrated with respect to a Fe foil. Lorentzian lines were computer fitted with a subroutine for the calculation of χ square and MISFIT. For back-scatter experiments a conversion Electron Detector (made by Ranger Engineering Corp., Fort Worth, TX, U.S.A.) was used. A continuous gas flow of helium containing 6% CH_4 (Matheson Co., Philadelphia, PA, U.S.A.) was maintained in the detector as specified.

Results and Discussion.-

The spectrum of a fresh catalyst, in general, consisted of a doublet which indicated that the valence state of iron in the starting material was Fe^{3+} , and in a high-spin state (3). It should be noted that the magnitude of the quadrupole splitting and isomer shift significantly depend upon the nature of the support used and the size of the iron particles (4). The ZSM-5 containing reduced Fe only, showed a six-line spectrum corresponding to mostly Fe-metal, besides indicating the presence of a small quantity of an oxide; whereas, the spectrum of a catalyst consisting of both Fe and Co clearly indicated the formation of a Fe-Co alloy on reduction. For example, the spectrum of reduced ZSM-5 containing 5.4% Fe and 1.3% Co, shown in Figure 2, revealed a six-line pattern corresponding to an average internal magnetic field of about 340 kOe and indicated the formation of an Fe-Co alloy (5).

The spectra of carbided catalysts (14.7% Fe)

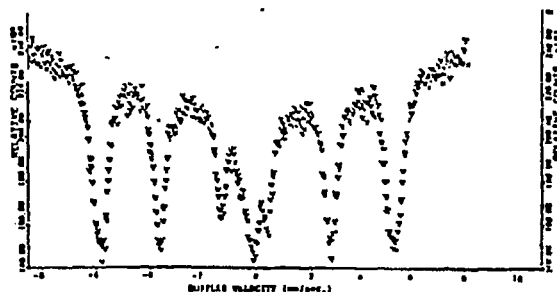


Fig. 2. Mössbauer spectrum of reduced ZSM-5 (5.4% Fe and 1.3% Co).

consist of superposition of at least two apparent six-line patterns, which showed the presence of Hagg carbide (Fe_5C_2) and cementite (Fe_3C). The possibility of the presence of small quantities of less stable ϵ' and ϵ carbides ($\text{Fe}_{2.2}\text{C}$ and Fe_2C) cannot be ruled out (6).

The spectrum of carbided ZSM-5 containing 5.4% Fe and 1.3% Co, indicated the presence of both Fe_5C_2 and Fe_3C besides a strong doublet. Apparently small amounts of carbides seem to have been formed in this catalyst as compared to those containing no Co. It appears that the presence of Co had somewhat inhibited the formation of carbides. The doublet appeared to be due partly to superparamagnetic behavior. The spectrum of used ZSM-5 with 5.6% Fe and 4.5% Co shown in Figure 3 consisted of a six-line pattern corresponding to an internal magnetic field of 344 kOe and an isomer shift of +0.15 mm/sec with respect to Fe-metal and appears to indicate the formation

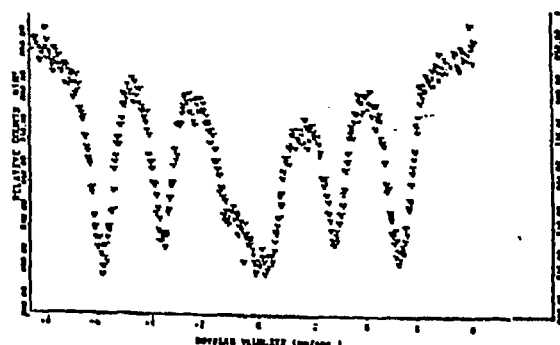


Fig. 3. Mössbauer spectrum of used ZSM-5 (5.6% Fe and 4.5% Co)

of an Fe-Co alloy. It is to be noted that the carbides, which were present in the case of used ZSM-5 containing only Fe are surprisingly absent in this case. Once again, the presence of a large amount of Co appears to inhibit the formation of carbides in these samples.

The observation that the carbided ZSM-5 containing only Fe has relatively more Hagg carbide compared to cementite and that the used catalyst has, in contrast, relatively more cementite than Hagg carbide suggests that the Hagg carbide has been converted into cementite during the course of the reaction. Since synthesis gas conversion is exothermic, it is possible that local hot spots on the catalyst resulted in the conversion of the active Hagg carbide to the relatively inactive cementite phase. This could be partly the reason for the reduction in activity of these catalysts amounting to about thirty per cent. decrease over a period of two weeks exposure to synthesis gas at 280°C. Further, CEMS and ISS show that the differences in selectivity between ZSM-5 (Fe) and ZSM-5 (Fe, Co) catalysts arises from the presence of bimetallic transition metal (TM) clusters in the latter, with consequent changes in the average number of 3d-electrons per TM atom.

At this juncture, we describe exploratory results on the backscatter (i.e., CEMS) spectroscopy. The calibration of the backscatter apparatus was checked with the same standard Fe foil, which was used for transmission work. No Fe type spectra were obtained with the Fe-Co systems; namely (a) 5.4% Fe and 1.3% Co systems; namely (a) 5.4% Fe and 1.3% Co and (b) 5.6% Fe and 4.5% Co even after running the experiment for several days at a time. This indicated that the Co atoms were preferentially on the surface (top 30 nm layer). Thus, the role of Co in enhancing the selectivity in synfuel formation could be confirmed by backscatter Mössbauer spectroscopy. This octane selectivity

is particularly significant with the 5.4% Fe - 1.3% Co composition as shown in Table 1.

Table 1. Berty Reactor Results on ZSM-5-Based Catalysts Containing Fe-Co Process Conditions: $H_2/CO = 1$, $P = 300$, $psig$, $T = 280^\circ C$

Catalyst (ZSM-5*)	(14.1% Fe)	(5.4% Fe, 1.3% Co)	(5.6% Fe, 4.5% Co)	(9.0% Co)
CO conversion %	61.5	23.1	30.8	53.5
H ₂ conversion %	40.1	38.8	46.5	87.2
Product composition %				
CO ₂	52.1	24.8	28.8	27.6
H ₂ O	19.2	44.0	38.5	37.3
CH ₄ + oxygenates	28.8	31.2	32.6	35.1
CH ₄ + oxygenates comp. %				
CH ₄	25.5	44.0	47.6	42.6
C ₂ H ₄ + C ₂ H ₆	13.7	10.8	14.4	4.4
C ₃ H ₆ + C ₃ H ₈	8.9	7.1	11.1	6.0
C ₄ H ₈ + C ₄ H ₁₀	6.3	4.7	5.5	3.0
C ₅ + 6 oxygenates	45.7	33.4	21.4	43.3
Liquid prod. comp. %				
Aromatics	18	23	5	1
Olefins	67	37	51	66
Saturates	13	28	38	30
Oxygenates	2	12	6	3
% gasoline (BP<204°C)	91	90	54	88
Research octane no.	87.0	90.3	72.7	57.8
*SiO ₂ /Al ₂ O ₃ = 30				

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