

MÖSSBAUER AND MAGNETIC STUDIES OF IRON-ZEOLITE AND IRON-COBALT ZEOLITE CATALYSTS USED IN SYNTHESIS GAS CONVERSION

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Abstract Medium-pore (diameter ~ 6Å) zeolites such as ZSM-5 and silicalite impregnated with Group VIII metals provide selective catalytic pathways for the conversion of synthesis gas to gasoline or olefins. Mössbauer and magnetic studies on these catalysts containing iron or iron plus cobalt are reported. The zeolites were impregnated with metal nitrate solutions, reduced, and carbided to yield showed Fe^{3+} type spectra. The ZSM-5 (14.7 % Fe) and Silicalite (13.6 % Fe) samples exposed to H_2 (450 C) showed an approximate 85% reduction to the metallic state. The carbided ZSM-5 (14.7 % Fe) revealed a spectrum of Hagg carbide (Fe_3C_2), an active component of the catalyst. The used catalysts showed mixtures of Hagg carbide (Fe_3C_2) and cementite (Fe_3C). It is suggested that the selectivity of ZSM-5 (5.6 % Fe, 4.5 % Co) resulted from iron-cobalt alloy formation.

Keywords Mössbauer Studies, Selective Catalyst, Zeolite, Carbided

چکیده زئولیت های دارای اندازه متوسط (قطر ۶ آنگستروم) مانند ZSM-۵ و سیلیکات های آبستن شده با گروه VIII فلزات، می توانند به عنوان کاتالیست های گزینشی برای تبدیل گازهای سنتز H_2 و CO به بنزین و آلفین عمل نمایند. مطالعات ماسباور و مغناطیسی این نوع کاتالیست ها محتوی آهن یا آهن - کبالت گزارش شده است. این کاتالیست ها به وسیله محلول های نیترات دار فلزی به روش آبستنی تهیه شده اند که بعد از مرحله احیا و تماس با گاز CO تبدیل به مشتقات Fe^{3+} می شوند. نمونه های ZSM-۵ با ۱۴/۷٪ آهن و سیلیکات با ۱۳/۶٪ آهن وقتی که با گاز H_2 تماس داده می شوند، در حدود ۸۵٪ احیا شده و به Fe (آهن فلزی) تبدیل می شوند. همین نمونه ها زمانی که با گاز CO تماس داده می شوند، به Fe_3C_2 که یک ترکیب فعال کاتالیست است، تبدیل می شوند. نمونه های استفاده شده نیز به مخلوطی از Fe_3C و Fe_3C_2 تبدیل می شوند. این مطالعات نشان می دهند که قابلیت گزینش در کاتالیست زئولیت ZSM-۵ با ۴۵٪ Co و ۵/۶٪ Fe به دلیل تشکیل آلیاژ آهن - کبالت است.

1. INTRODUCTION

The catalytic conversion of synthesis gas ($CO+H_2$) to gasoline-range hydrocarbons and olefins using bifunctional zeolite catalysts is of much interest today [1]. The medium-pore (diameter~6Å) zeolite ZSM-5 in combination with iron or with iron-cobalt was shown to yield a high fraction of aromatics in the product, resulting in a favorable

octane number (> 80). It was indicated that the bimetallic iron-cobalt on ZSM-5 could alter the product selectivity, mainly in reducing the shift conversion of $CO + H_2O$ to CO_2 from the high shift yields of iron on ZSM-5. The aromatics in the product decreased by the addition of cobalt to the zeolite.

In contrast to ZSM-5, Silicalite lacks aluminum, although the two appear to possess similar crystal

structures [1]. They crystallize with the orthorhombic space group $Pnma$ or $Pn2_1a$ with $a = 20.1 \text{ \AA}$; $b = 19.9 \text{ \AA}$; $c = 13.4 \text{ \AA}$. The framework structure consists of five-membered rings of $Si(Al)-O$ tetrahedral. The pore structure consists of intersecting channels defined by ten rings of oxygen atoms. The elliptical straight channels of cross section $5.7 \text{ \AA} \times 5.1 \text{ \AA}$ along the b -axis and the circular zigzag channels of diameter 5.4 \AA interconnect the straight channels.

While the silicon/aluminum ratio in ZSM-5 can be varied from 3 to over 100, Silicalite has essentially no aluminum. Hence it appears that Silicalite is the limiting form of ZSM-5 when the aluminum concentration is vanishingly small. A comparison of the properties of ZSM-5 and Silicalite is shown in the reference [2].

Owing to the absence of cations that can be exchanged with protons, Silicalite has no acidity, while HZSM-5 is a highly acidic zeolite. Recent investigations have shown that the difference in selectivity for synthesis gas conversion by ZSM-5 (iron) and Silicalite (iron) catalysts results from the previously mentioned difference in acidity. The main influence was on the production of aromatics and olefins; the former the nonacid Silicalite (iron) catalyst.

Mössbauer and magnetic investigations, described here, were conducted to determine the state of iron and iron-cobalt in the zeolite catalyst at different stages of catalyst preparation and use. Among the several aims of the investigation were the determination of:

- The valence state of the transition metal in the freshly impregnated state;
- The extent of reduction on exposure to H_2 ;
- The active catalytic species after carbiding with synthesis gas;
- The species present in the used catalyst; and
- In the case of iron-cobalt, the possible formation of bimetallic or alloy clusters and their influence on the selectivity of the catalyst.

2. EXPERIMENTAL PROCEDURE

2.1. Preparation of Samples ZSM-5 and Silicalite were prepared using methods described

in the literature [3,4]. X-ray Powder diffraction patterns revealed no phases other than ZSM-5 or Silicalite. The metal component was introduced by gradually adding the metal nitrate solution to the zeolite until incipient wetness was reached. The impregnation with the metal (Fe or Fe + Co) nitrate solution was carried out for 1 h under vacuum to enable the nitrate solution to enter the pore of the zeolite. The material is dried initially with constant stirring over a boiling water bath, and further dried in air at 110°C for 12 h. The amount of iron and cobalt in the samples was determined by standard wet chemical techniques and atomic absorption.

The zeolite impregnated with iron or iron plus cobalt was reduced in flowing H_2 at 450°C for 24 h. It was then carbided in flowing synthesis gas at 250°C for 24 h to yield the active catalyst. The catalysts were tested for synthesis gas conversion in both a fixed-bed micro reactor and a bertly (continuous-flow stirred-tank) reactor. For catalytic testing, these steps on the metal-impregnated zeolite were all carried out in the reactor. For Mössbauer studies, all the samples except the used catalysts were prepared separately under the conditions just described. In the ensuing discussion such samples will be described variously as (a) freshly impregnated, (b) reduced, (c) carbided, and (d) used catalysts. The last mentioned was taken from the reactor after its use for periods lasting from one to three weeks under synthesis gas under temperatures ranging from 280° to 320°C . X-ray diffraction studies were carried out on the samples after steps (a) and (d).

2.2. Characterization Techniques The apparatus used for Mössbauer spectroscopy and magnetic measurements is described separately under the corresponding sections.

3. RESULTS AND DISCUSSION

3.1. Mössbauer Studies The Mössbauer spectra of catalysts listed in Table 1 were recorded utilizing a conventional constant-acceleration spectrometer made by nuclear Science and Engineering Corporation and Nuclear Data ND-100 multichannel analyzer in MCS mode. The spectra were calibrated with a standard NBS iron

TABLE 1. Summary of Mössbauer.

Sample	State
ZSM-5 (14.7 % Fe)	Reduced
ZSM-5 (14.7 % Fe)	Carbided
ZSM-5 (14.7 % Fe)	Used
ZSM-5 (5.4 % Fe + 1.3 % Co)	Reduced
ZSM-5 (5.4 % Fe + 1.3 % Co)	Carbided
ZSM-5 (5.4 % Fe + 4.5% Co)	Used
Silicalite (13.6 % Fe)	Fresh
Silicalite (13.6 % Fe)	Used
Silicalite (4.4 % Fe + 3 % Co)	Reduced
Silicalite (4.4 % Fe + 3 % Co)	Used

foil. The parabolic background observed in the spectra arose from the geometry of the Mössbauer setup. A least-squares program fitting, in progress, has justified our interpretations. The spectra were recorded at room temperature using an 80-mCi⁵⁷Co in Rh matrix.

The Mössbauer spectra of the different catalysts were recorded at various stages; namely, (a) after impregnation with Fe(NO₃)₃; (b) on reduction in H₂ at 450°C for 24 h; (c) on carbiding in 1:1 H₂/CO synthesis gas at 250°C for 24 h; and (d) finally after utilization of the catalyst in the conversion of the synthesis gas to gasoline-range hydrocarbons. The spectra have revealed the existence of various phases, formed at different stages, and have given clues to the nature of the active component(s) responsible for the efficient conversion of synthesis gas into gasoline.

The spectrum of a fresh catalyst in general, consisted of a doublet with an isomer shift of about +0.35 mm/s and a quadrupole splitting of about 0.75 mm/s, which indicate that the valence state of iron in the starting material is Fe³⁺. A typical spectrum for a fresh catalyst of Silicalite

impregnated with 13.6 % iron using Fe(NO₃)₃ is shown in Figure 1.

As discussed in a later section, the magnetization (M) vs. magnetic field (H) measurements on the fresh catalyst gave a magnetic moment of about 5.96_{μB}, which further confirmed that the iron ion is in a high spin Fe³⁺ state. 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. The spectrum of a reduced catalyst consisted of a six-line pattern corresponding mostly to iron metal, in addition to indicating the presence of a small quantity of an oxide, if the catalyst contained only iron, on the one hand; whereas the spectrum of a catalyst consisting of both iron and cobalt clearly indicated the formation of an iron-cobalt alloy on reduction, on the other hand.

The spectrum of reduced ZSM-5 containing 14.7 % iron, shown in Figure 2a, essentially corresponds to that of metallic iron. However, there is a small amount of unreduced iron in the form of an oxide, probably α-Fe₂O₃. The reduction in this case is about 85 %.

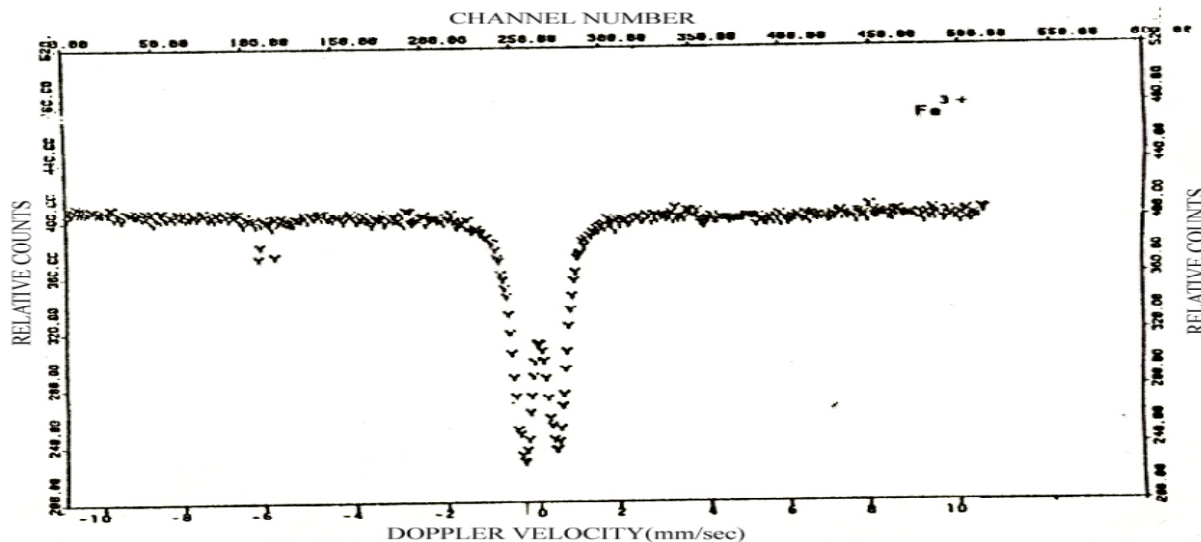


Figure 1. Mössbauer spectrum of silicalite impregnated with 13.6% iron using $\text{Fe}(\text{NO}_3)_3$.

This is also confirmed by the magnetization measurements, which indicated an approximate 15 % lowering in the observed saturation magnetization of iron.

The spectrum of reduced ZSM-5 containing 5.4 % iron and 1.3 % cobalt, shown in Figure 2b,

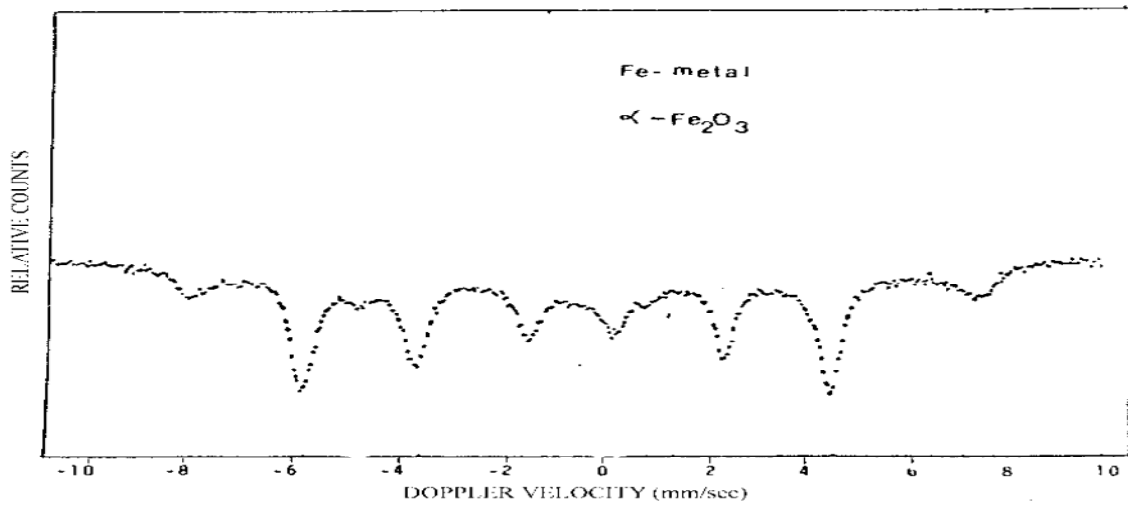
revealed a six-line pattern corresponding to an average internal magnetic field of about 340 kOe, and indicates the formation of an iron-cobalt alloy.

A typical spectrum of reduced Silicalite containing 4.4 % iron and 3.0 % cobalt is shown in Figure 3. The spectrum consists of a well defined six-line pattern corresponding to an internal magnetic field of 345 ± 3 kOe, which is much larger than the 330-kOe field expected for metallic iron. Second, the isomer shift observed is 0.18 mm/s with respect to iron metal, which indicates that the electron density at the iron nucleus is smaller in the iron-cobalt alloy than in iron metal. This decrease in the electron density in the iron-cobalt alloy is consistent with the experimental results reported by Van der Woude and Sawatsky [5]. The formation of an iron-cobalt alloy is supported further by the magnetization measurements on this catalyst, which indicated

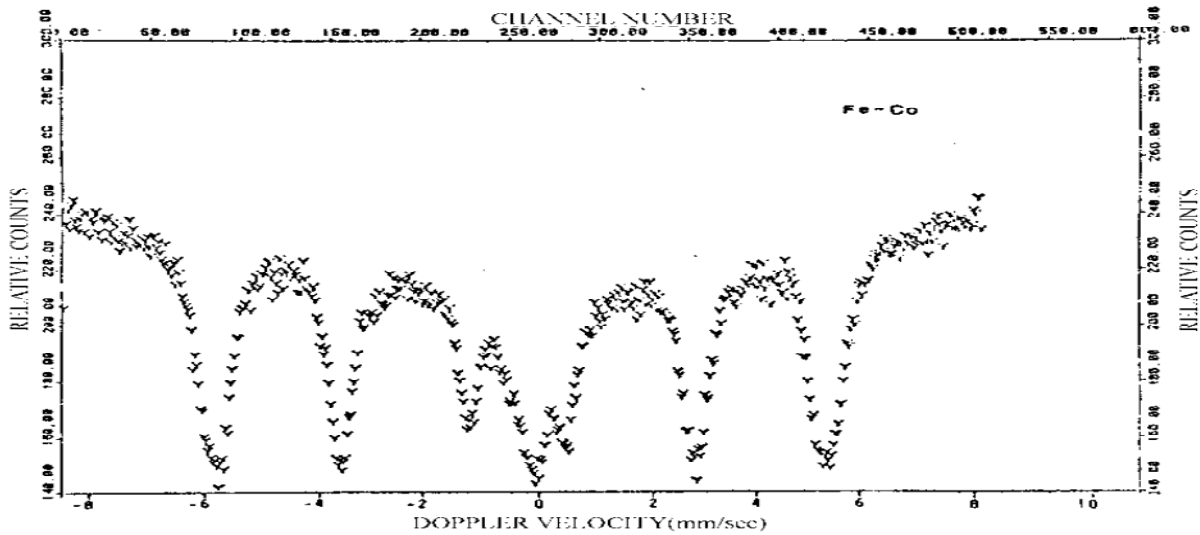
a magnetic moment intermediate between the moments corresponding to iron and cobalt.

The spectra of carbided catalysts consist of superposition of at least two apparent six-line patterns corresponding to at least two different iron-carbon phases. A typical spectrum of carbided ZSM-5 with 14.7 % is shown in Figure 4a. This spectrum represents the presence of Hagg carbide (Fe_5C_2) and cementite (Fe_3C). The former has three inequivalent iron sites, whereas the latter has only one. 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. A doublet due to Fe^{3+} was not apparent in Figure 4a.

The spectrum of carbided ZSM-5 containing 5.4 % iron and 1.3 % cobalt, shown in Figure 4b, indicates the presence of both Fe_5C_2 and Fe_3C in addition to a strong doublet. Apparently fewer carbides have been formed in this catalyst than in those containing no cobalt; it appears that the presence of cobalt has somewhat inhibited the formation of carbides. The doublet may be attributable partly to super paramagnetic behavior. Similar spectra also have been observed in the case of Silicalite based catalysts as well.



(a)



(b)

Figure 2. (a) Mossbauer spectrum of reduced ZSM-5, 14.7 Fe and (b) Mossbauer spectrum of reduced ZSM-5 5.4 % Fe, 1.3 % Co.

The spectra of used catalysts are in general very complicated and seem to consist of three or more magnetically split hyperfine spectra. A typical

Spectrum of used ZSM-5 with 14.7 % iron is shown in Figure 6. This spectrum can be explained in terms of the presence of Hagg carbide,

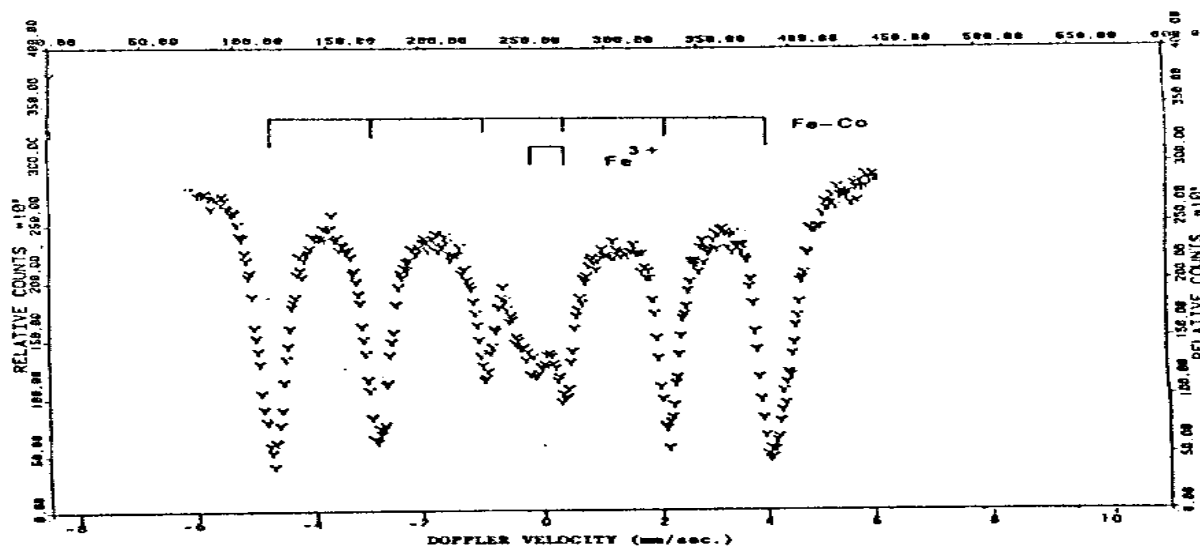


Figure 3. Mössbauer spectrum of reduced silicalite (4.4 % Fe, 3 % Co).

cementite, and Fe_3O_4 . It is noteworthy that the cementite content has relatively increased at the expense of the Hagg carbide in the used catalyst as compared to that found in the carbided catalyst (See the lines marked by arrows in Figure 5a and Figure 5.)

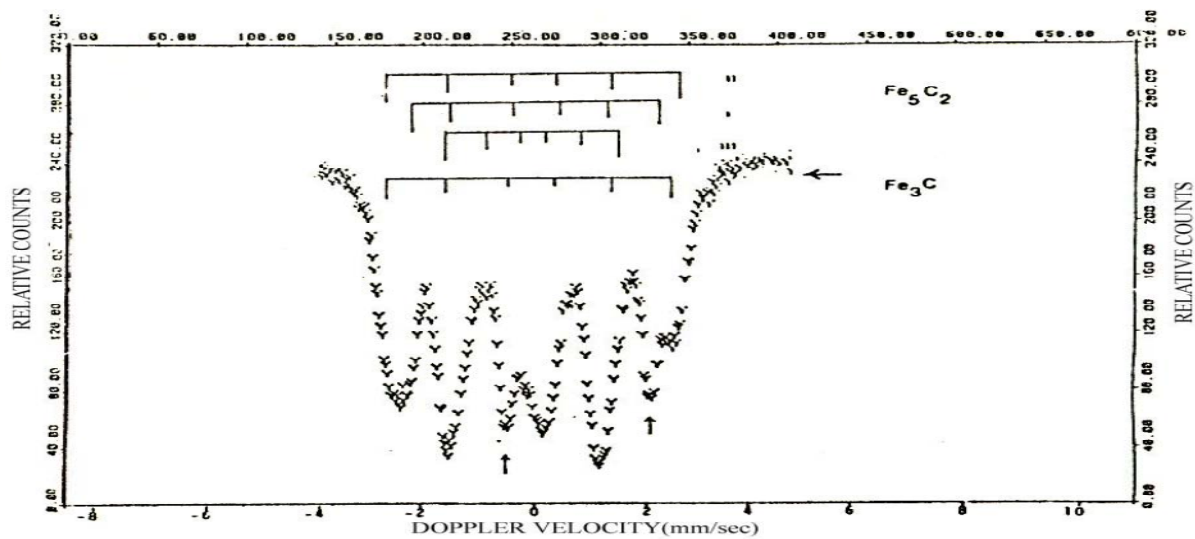
The spectrum of used ZSM-5 with 5.6 % iron and 4.5 % cobalt shown in Figure 6 consisted of a six-line pattern corresponding to an internal magnetic field of 344 ± 3 kOe and an isomer shift of $+ 0.15$ mm/s with respect to iron metal, and appears to indicate the formation of an iron-cobalt alloy. It is to be noted that the carbides, which were present in the case of used ZSM-5 containing only iron, are surprisingly absent in this case. Once again, the presence of a large amount of cobalt appears to inhibit the formation of carbides in these samples. The x-ray powder patterns showed the presence of a bcc iron-cobalt alloy phase in addition to the ZSM-5 phase.

The spectrum of used Silicalite containing 13.6 % iron is shown in Figure 7. It consists of both Hagg carbide and cementite and is similar to that observed for ZSM-5 with 14.7 % iron, except that this spectrum does not indicate the presence of

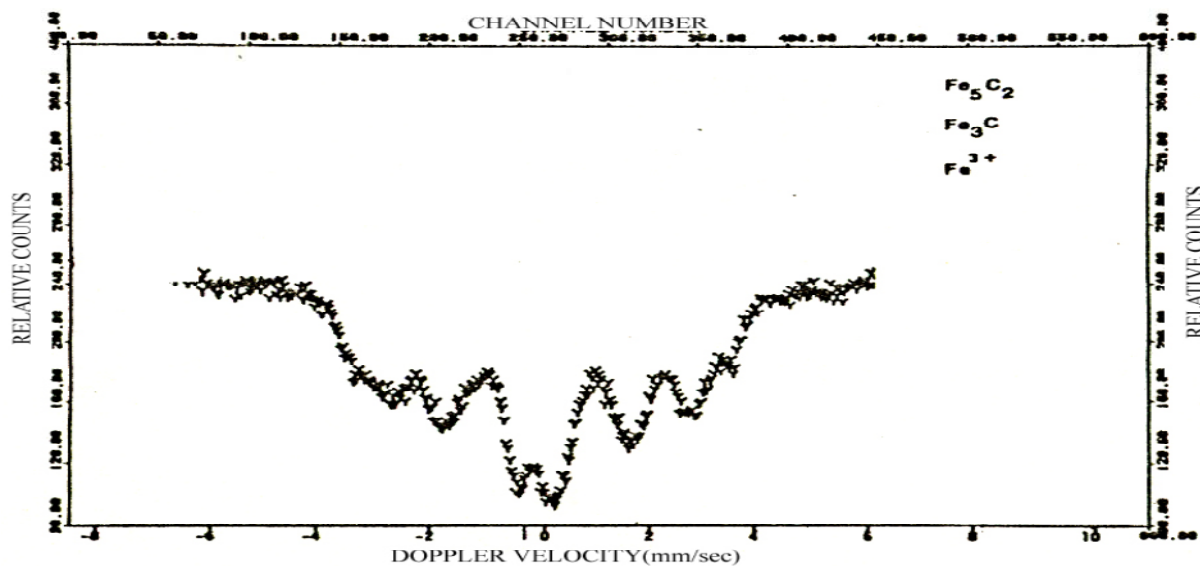
any oxide. The spectrum of used Silicalite containing both 5 % iron and 5 % cobalt is shown in Figure 8. This spectrum also contains Hagg carbide and cementite in addition to a strong doublet. However, the relative amounts of Hagg carbide and cementite present in this catalyst appear to be considerably less than those in the catalyst containing only iron. Thus, the presence of cobalt appears to hinder the formation of carbides in the Silicalite-based catalysts as well. Preliminary low-temperature studies have shown that the central doublet is partly a result of superparamagnetic behavior of a magnetic phase.

The stick diagrams on various Mössbauer spectra shown are the approximate line positions for Hagg (Fe_5C_2) and cementite (Fe_3C) phases [6].

The observation that the carbided ZSM-5 containing only iron 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



(a)



(b)

Figure 4. (a) Mössbauer spectrum of carbided ZSM-5 14.7 % Fe and (b) Mössbauer spectrum of carbided ZSM-5 5.4 % Fe, 1.3 % Co.

hot spots on the catalyst resulted in the conversion of the active Hagg carbide to the relatively inactive cementite phase. This could partly be the reason

for the reduction in activity of these catalysts, amounting to about a 30 % decrease over a period of 2-weeks exposure to synthesis gas at 280°C.

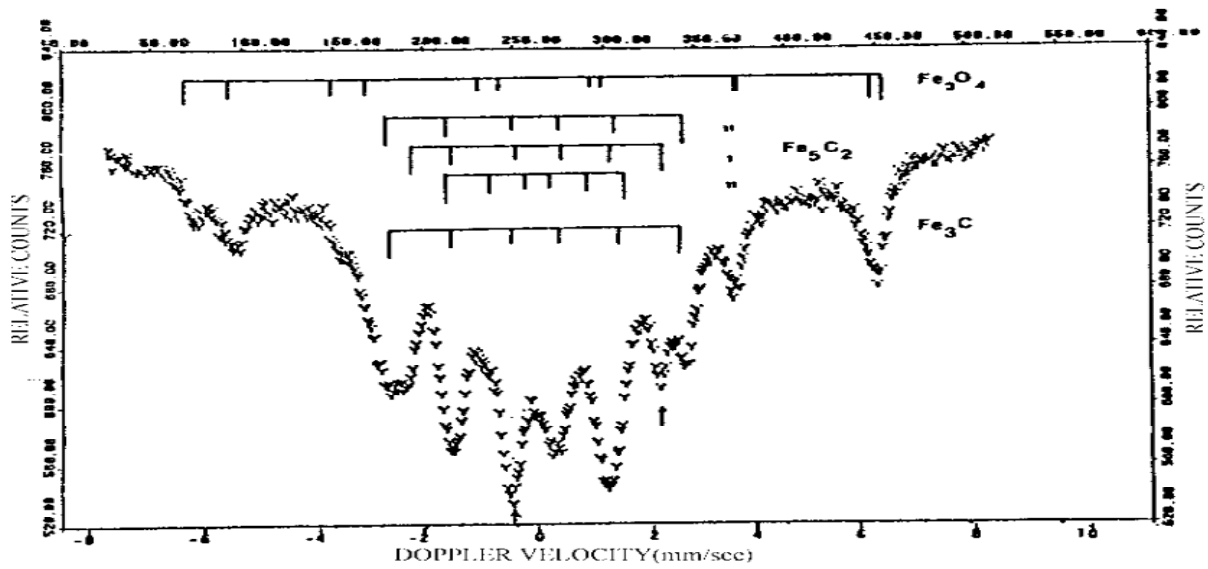


Figure 5. Mössbauer spectrum of used ZSM-5 (14.7 % Fe).

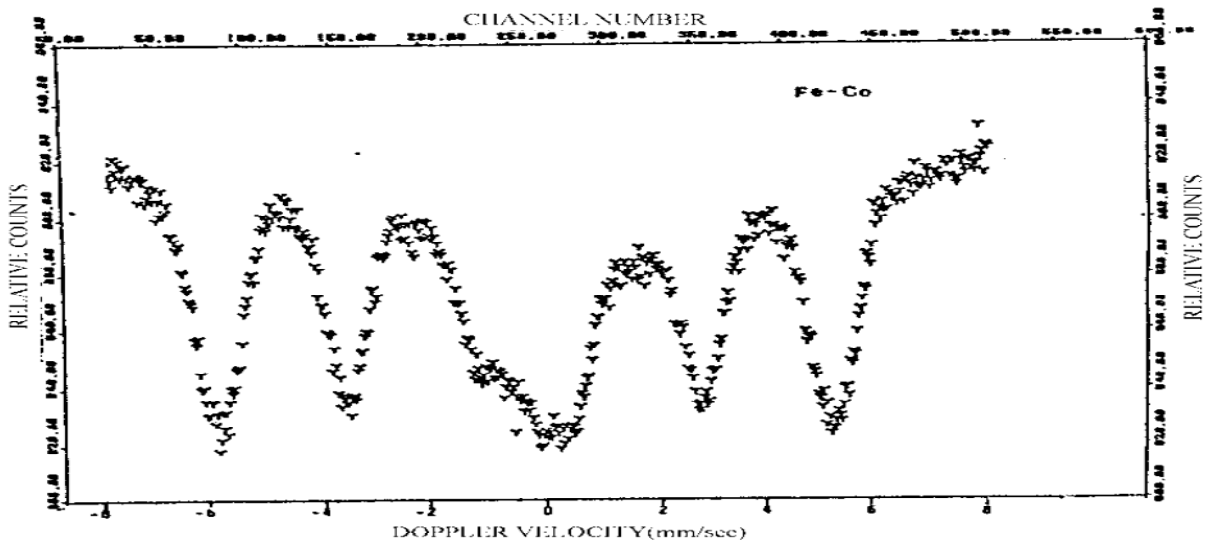


Figure 6. Mössbauer spectrum of used ZSM-5 (5.4 % Fe, 4.5 % Co).

3.2. Magnetic Measurements The magnetization and susceptibility measurements were performed using the Faraday technique [7] Cahn RH electrobalance was used for these

measurements.

The freshly impregnated zeolites indicated the presence of Fe^{3+} species from an analysis of the paramagnetic susceptibility, which showed an

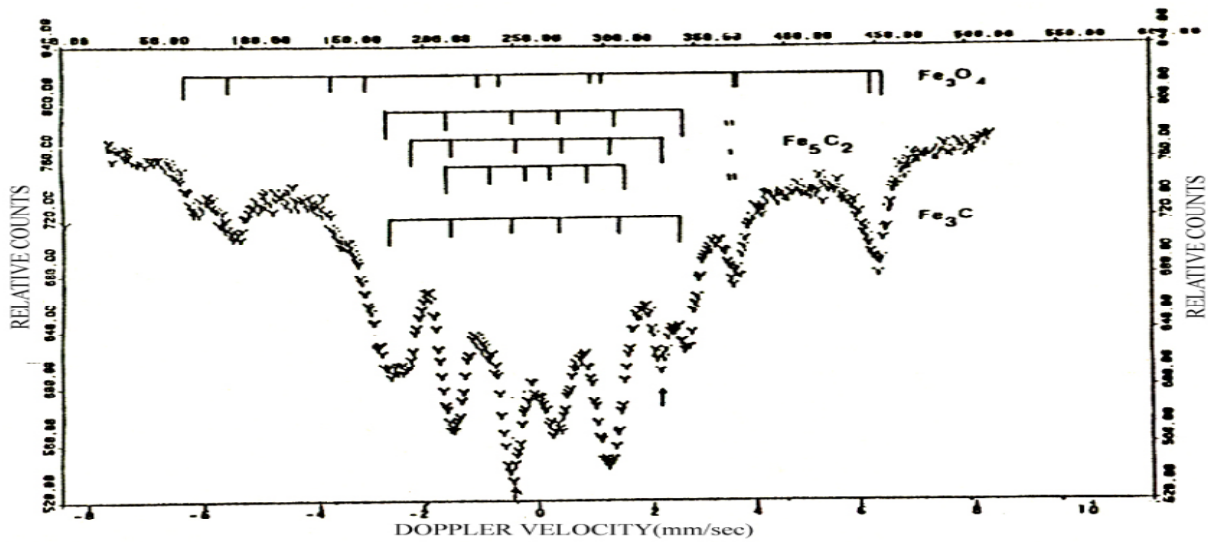


Figure 7. Mössbauer spectrum of used silicalite (13.6 % Fe).

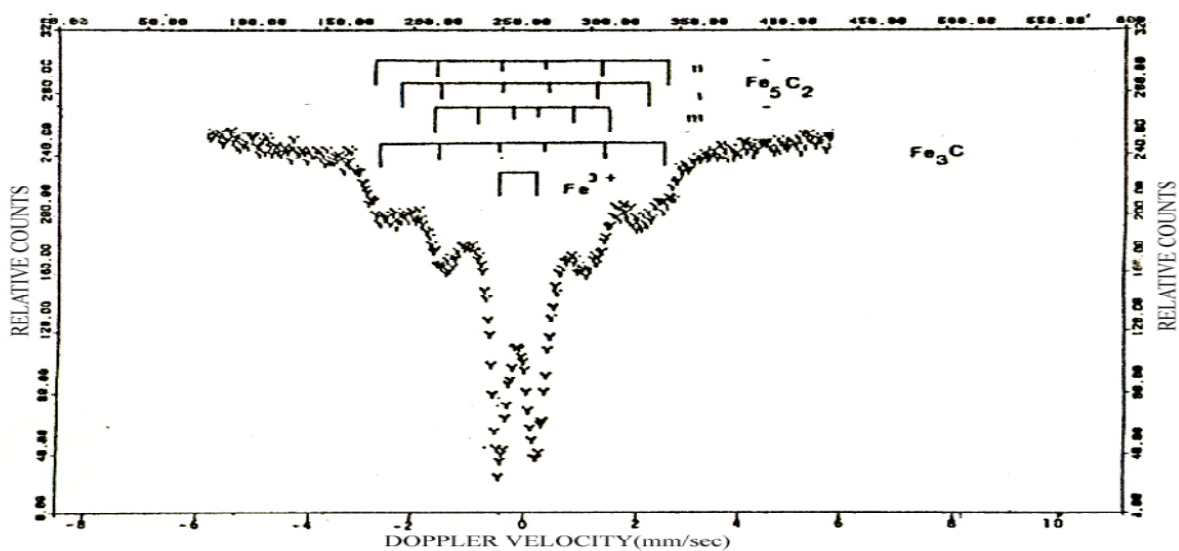


Figure 8. Mössbauer spectrum of used silicalite (4.4 % Fe, 3 % Co).

effective moment of about 5.96 Bohr magnetons.

The magnetization studies on the reduced samples of ZSM-5 (14.7 % Fe) and Silicalite (13.6 % Fe) indicate that iron is in the metallic

state with 86 % and 85 % reduction, respectively.

The magnetization vs. temperature curves for ZSM-5 (11.1 % Fe) are shown in Figure 9. The carbided sample of ZSM-5 (11.1 % Fe) appears to

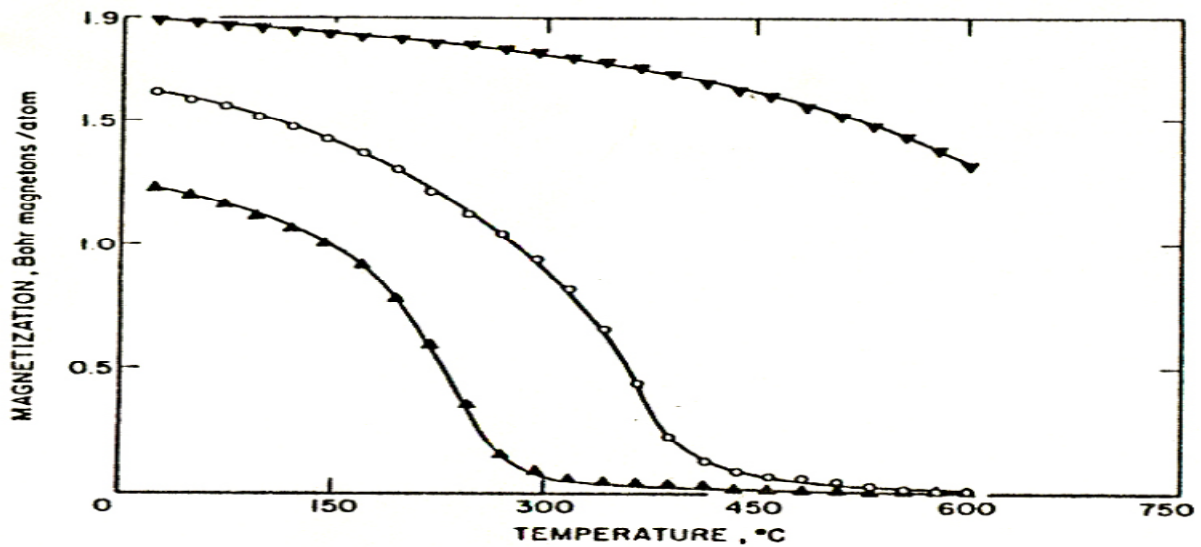


Figure 9. Magnetization (Bohr magnetons/iron atom) as a function of temperature for ZSM-5 (11.1 % Fe) ($H = 6300$ gauss; (\blacktriangledown) reduced; (\blacktriangle) carbided; (\circ) used).

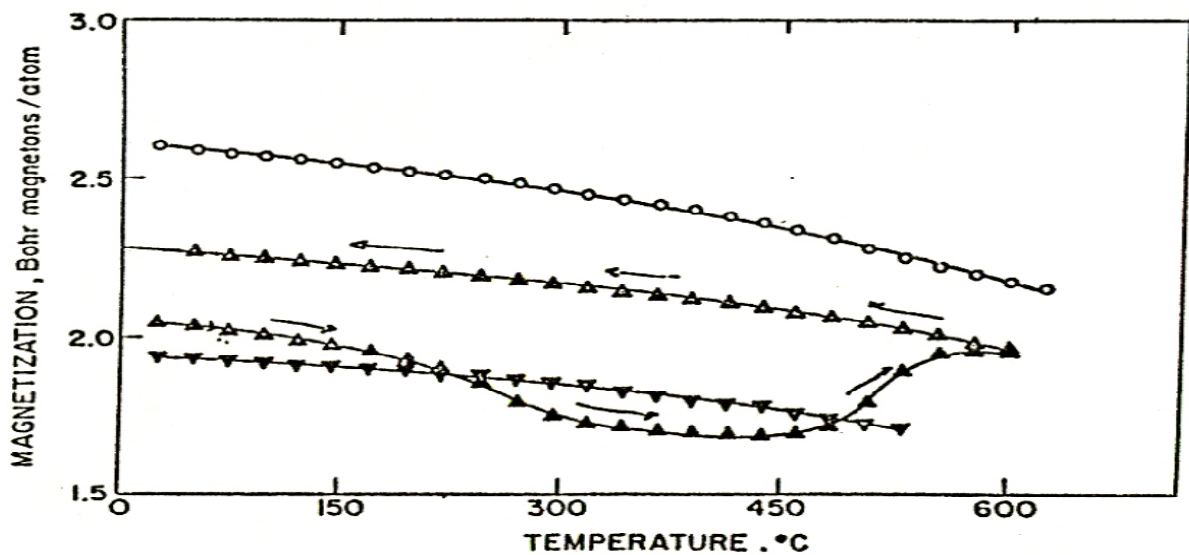


Figure 10. Magnetization as a function of temperature for ZSM-5 (5.6 % Fe, 4.5 % Co). The bohr magneton number represents the weighted average of the two components present. ($H = 6300$ gauss; (\blacktriangledown) reduced; (\blacktriangle) carbided; (\circ) used).

be the high curie point form of the Hagg carbide with $T_c = 540$ K. The used sample of ZSM-5 (11.1 % Fe) exhibited a magnetic transition with $T_c = 650$ K, which corresponds to the hcp phase of

(Fe_2C). The magnetic transition of cementite (Fe_3C) was masked in the M vs. T curve shown in Figure 9 since T_c of Fe_3C is about 490 K, well below that of the hcp carbide. The hcp phase of

Fe₂C is considered to be stable (18) below 470 K in an atmosphere of synthesis gas. Its presence in the used sample may indicate that it was formed while the catalyst was cooled after the reaction.

The magnetization data (Figure 10) on ZSM-5 (5.6 % Fe, 4.5 % Co) show that the reduced, carbided, and used samples have large magnetic moments (1.94, 2.04, and 2.61_{μB} per transition metal atom, respectively, at room temperature) and

high Curie points (> 900°C), which cannot be accounted for on the basis of individual iron and cobalt particles.

The magnetic data indicate the composition to be that of an iron-cobalt alloy, supporting the conclusions derived from the Mössbauer analysis. Hence, one can conclude that the difference in selectivity between ZSM-5 (11.1 % Fe) and ZSM-5 (5.6 % Fe, 4.5 % Co) catalysts (see Table 2) arises

TABLE 2. Product Compositions from the Catalysts ZSM-5 (11.1 % Fe) and ZSM-5 (5.6 % Fe, 4.5 % Co) in a Berty Reactor, Showing the Influence of Cobalt Addition to the Catalyst* .

	Catalyst	
	ZSM-5 (11.1 % Fe)	ZSM-5 (5.6 % Fe, 4.5 % Co)
Temperature	300	280
CO Conversion, %	68.2	37.8
H ₂ Conversion, %	38.7	41.3
Space Velocity	1500	1400
Product Composition (%)		
CO ₂	52.0	9.8
H ₂ O	19.4	51.8
CN _n + Oxygenates	28.6	38.4
Hydrocarbon and Oxygenate Composition (%)		
C ₁ -C ₄ hydrocarbons	83.1	74.3
C ₅ +and Oxygenates	16.9	25.7
Composition of C ₅ + and Oxygenates (%)		
Aromatics	72	10
Olefins	3	46
Saturates	24	37
Oxygenates	1	7
% Gasoline range (BP < 204°C)	75	94
Research octane No.	96	81
*Process condition: H ₂ /CO = 2, P = 21 bar.		

from the presence of bimetallic transition-metal clusters in the latter, with consequent changes in the average number of 3d electrons per transition metal atom [8,9]. The M vs. T curve (Figure 10) of the carbided sample of ZSM-5 (5.6 % Fe, 4.5 % Co) indicated an irreversible formation of a second phase with a higher moment above a temperature of 450°C. This phase has not yet been identified.

4. CONCLUSIONS

A comparison of the spectra of carbided and used ZSM-5 with iron to those with both iron and cobalt, and their relative yields of aromatics (see Table 2) in the conversion process, and an overall consideration of all spectra and magnetic measurements indicate that: (a) the plausible active phase taking part in the conversion of the synthesis gas by iron-containing ZSM-5 and Silicalite is the Hagg carbide which is converted into cementite during the catalytic reaction; (b) the difference in selectivity between ZSM-5 (Fe) and ZSM-5 (Fe+Co) results in decreasing carbide formation. This suggests that the iron-cobalt alloy phase may itself be the active species in cobalt-rich catalyst compositions.

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