MAGNETIC STUDIES OF FINE FE AND CO SPECIES FORMED IN FE/ZEOLITE CATALYSTS

M. Oskoie

Water and Energy Research Center, Sharif University of Technology
P.O. Box 11155-8639, Tehran, Iran
osk1258@yahoo.com

Abstract   Magnetic, Mössbauer, and I.R. studies of nanosize particles of Fe and Co species dispersed in a cage of aluminosilicates structure, in relation to syngas (CO+H_2) Fischer Tropsch conversion. The difference in the catalytic activity of such species have shown dependancy on their degree of dispersion. The carbonyl impregnation gave ultra-fine Super Paramagnetic Fe_3O_4, whereas the nitrate impregnation gave larger size particles of Fe_3O_4 or α-Fe_2O_3. The active Fe_5C_2 component was converted to Fe_3C during the above reaction.

Keywords   Nanosize, Super Paramagnetic, Fine Particles, Mossbauer

چکیده   مطالعات مغناطسی، موسباور وطیف .I.R نشان می‌دهند که توزیع ذرات Fe و Co نانوسایز در داخل ساختار (فیزیکی) آلومینوَسیلیکات ها شکل گرفته و برای تبدیل گاز ستنز H_2 + CO (یا واکنش فیشر تروپ) گزارش شده است. اختلاف فعالیت کاتالیست های نمونه های اشاره شده در بالا نشان می‌دهد که این اختلاف مربوط به شکل توزیع ذرات است. نمونه هایی که از روش کاربنیل بارور شده به دست می‌آید مربوط به اندازه ذرات ابرپارامغناطیس Fe_3O_4 (دارای سایز کوچکتر از تک حوزه مواد فرومغناطیس) است، در حالی که نمونه هایی که با روش نیترات بارورشده تهیه شده اند دارای ابعاد فیزیکی بزرگتری (دارای چندین حوزه مغناطیسی) نسبت به روش قبلی هستند و از مواد Fe_3O_4 یا α-Fe_2O_3 تشکیل شده اند. ترکیب Fe_5C فعال به Fe_3C در طول واکنش تبدیل شده است.

1. INTRODUCTION

The magnetic properties of clusters which are magnetically ordered materials (Ferro, ferri, and antiferromagnetic) were shown to behave differently than those of the corresponding bulk materials [1-4]. Such fine particles exhibit a superparamagnetic (S.P.) behavior, which has attracted considerable attention with regards to the newly emerging area of "nanosize" magnetic systems. In the realm of chemical physics the Superparamegnetic particles have shown to play an important role as an active catalysts, providing not only the system's high surface area, but also a suitable and appropriate energy to perform the reaction [4-9].

The technological relevance of such system lies in synthesizing catalysts for the hydrogenation of CO to get CH_4 and, more particularly, to obtain the gasoline range hydrocarbons via Fischer-Tropsch

(F-T) reaction. The cage structure alumino-silicates known as zeolites (with sub classifications such as mordenites, Silicalite) impregnated with Group VIII metals in highly dispersed form, provides promising catalysts for selective conversion of syngas (CO+H_2) to liquid hydrocarbons [10,11]. The catalystic activities and the selectivity of these F-T catalysts are strongly influenced by the transition of the metal component (s), impregnated into the zeolite support. The method of incorporating metal into the support, is the percentage of loading and the degree of (metal species) dispersion, the degree of reduction to the S.P. metallic state, the number of acid sites in the substrate, the nature of interaction between metal and the support, and so on [11-14]. Mössbauer and magnetic measurement studies are becoming increasingly important in the characterization of catalysts used in syngas conversion [15-17].

The above studies prompted us to investigate

the subdomain particles of Fe produced in two medium pore zeolites, ZSM-5 and Silicalite. Magnetic measurements, Mössbauer and I.R. spectroscopes were used to characterize various catalysts. This paper discusses the results of said studies.

ZSM-5 and Silicalite have similar crystal structures [18] with the pore diameter in 0.5 to 0.6 nm range; however, only the former category possesses acidic function. The acid sites are effective in the catalytic cracking and isomerization of hydrocarbons [19] and for the conversion of methanol and olefins to aromatics [20].

2. EXPERIMENTAL

Table 1 lists the catalyst samples investigated in the present study. The transition metal was introduced into the zeolite structure by (a.) impregnation with Fe $(NO_3)_3$ solution till the incipient wetness was reached, and also (b.) impregnating it with the iron carbonyl $Fe_3(CO)_{12}$ using an extraction technique with cyclohexane as the solvent. The weight percentage of impregnated metal species was determined by the atomic absorption technique.

The magnetization measurements on the catalysts were carried out with a Vibrating Sample

TABLE 1. Summary of Synthesis of Catalysts and Phases Detected.

Sample	Description	Impregna Tion	Phase-in Fresh State	Phases in Reduced State	Phases in Carbided State	Phases After Use
SN-1	Silicalite (20 % Fe)	Nitrate	Multi Domain $\alpha - Fe_2O_3$	Fe^0	Fe_5C_2, Fe_3C	Fe_3C, Relatively Small Fe_5C_2
ZN-1	ZSM-5 (14.7 % Fe)	Nitrate	Multi Domain $\alpha - Fe_2O_3$	Fe^0	Fe_5C_2, Fe_3C	Fe_3C, Relatively Small Fe_5C_2
ZN-2	ZSM-5 (5 % Fe + 5% Co)	Nitrate	Multi Domain Fe_3O_4	Fe-Co "Alloy"	Fe_5C_2, Fe-Co "Alloy"	Fe_3C, Relatively Small Fe_5C_2
SN-2	Silicalite	Nitrate	Multi Domain $\alpha - Fe_2O_3$			
ZCO	ZSM-5 (15.2 % Fe)	Carbonyl	Super Paramagnetic Fe_3O_4	Fe^0, Fe_3O_4, Fe^{3+}	Fe_5C_2, Fe_3C, Fe_3O_4, Fe^0	Fe_5C_2, Fe_3C

Magnetometer. Samples were investigated in the range of 78-1200 k and in some applied fields up to 20 kOe. In the case of multiphase specimens the Curie temperatures of individual phases were obtained from the points of inflection in the M vs. T curves.

The Mössbauer spectra were obtained at room temperature with an Austin Associates constant acceleration spectrometer, with a 50 mCi Co^{57} source and a Nuclear Data ND-100 multichannel analyzer. The Mössbauer spectrometer was calibrated using a standard NBS iron foil. The Mössbauer spectra were computer fitted to Lorentzian line shapes. All isomer shifts reported herein are relative to the metallic iron.

The in-situ magnetic and Mössbauer measure-ents were performed on samples at various stages; namely, (a) after impregnation of the zeolite support with $Fe_3(CO)_{12}$ /$Fe(NO_3)_3$; (b) on reduction of the fresh samples in flowing H_2 (30 cc/min) at 723 k for 16 h; (c) on carbiding the reduced samples in 1: 1 H_2 + CO syngas at 523 k for 16 h; and (d) finally the catalyst was used up in the conversion of syngas to gasoline range hydrocarbons.

Infrared spectra were recorded in the spectral region of 4000 to 500 cm with an IBM IR-98 Fourier Transform Spectrometer. An I.R. spectrometer equipped with a DTGS detector and a KBr beam splitter was used. All measurements were performed in vacuum, maintaining a resolution of ~ 4 cm.

The catalytic activity of the samples for the conversion of syngas was determined using a fixed bed micro reactor in conjunction with conventional chromatograph.

3. RESULTS AND DISCUSSION

3.1. I.R. Studies The I.R. spectra obtained from the carbonyl impregnated fresh sample ZCO, showed no evidence of the presence of carbonyl bands. This suggested that decarbonylation (removal of CO) of $Fe_3(CO)_{12}$ had taken place on the ZSM-5 support, during the impregnation procedure. A similar observation was made with mordenites impregnation with $Fe_3(CO)_{12}$. The work on mordenites will be published separately.

3.2. Mössbauer Studies Mössbauer spectra of nitrate impregnated fresh samples SN-1 (Fe/silicalite), SN-2 (Fe + Co/silica-lite) and ZN-1 (Fe/ZSM-5) looked similar. A typical spectrum of the fresh sample SN-1 is shown in Figure 1. This spectrum consists of a well-defined six-line pattern corresponding to a hyperfine field H_f = 517 kOe and was attributed to antiferromagnetic α-Fe_2O_3 in fresh samples of SN-1, SN-2, and ZN-1 in the form of multidomain particles.

The spectrum of nitrate impregnated fresh sample ZN-2 (Fe+Co/ZSM-5) revealed the presence of multi domain Fe_3O_4 particles in this sample.

A typical spectrum of the fresh sample ZCO (Fe/ZSM-5, carbonyl impregnation) is shown in Figure 2. This spectrum consisted of a strong doublet with an isomer shift of 0.4 mm/s and quadrupole splitting of 0.55 mm/s. This spectrum was created from the presence of ultra-fine super paramagnetic particles of γ-Fe_2O_3/Fe_3O_4. However, the spectrum obtained from heating the fresh sample at 827 k for 4h and subsequent cooling to room temperature had characteristics of bulk Fe_3O_4. Therefore it was inferred that the fresh carbonyl-impregnated sample ZCO consisted of superparamagnetic particles of Fe_3O_4.

The reduced sample was obtained from flowing pure hydrogen gas (purity = 9999.99) at different times. Based on the saturation magnetization of Fe which is about 218 emu/gr, the reduction percentage of the sample was calculated.
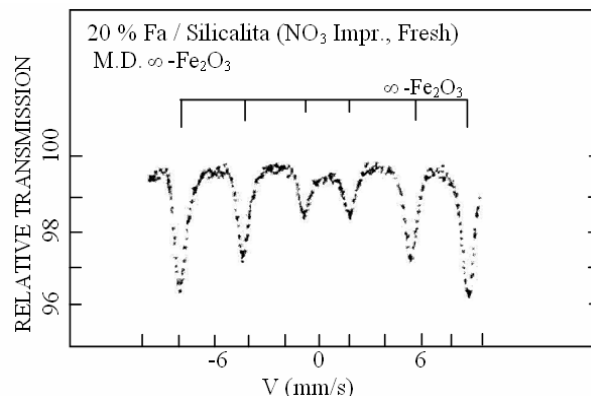
The Mössbauer spectra of reduced samples SN-

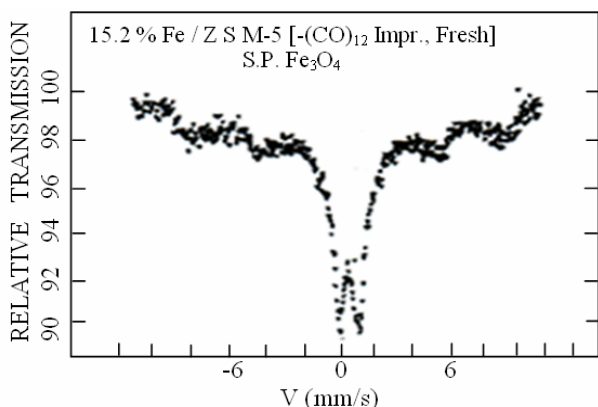**Figure 1**. Mössbauer spectrum of the fresh sample SN-1 (20 % Fe/Silicalite, $Fe(NO_3)_3$ impregnation).

Figure 2. Mössbauer spectrum of the fresh sample ZCO (15.2 % Fe/ZSM-5, $Fe_3(CO)_{12}$ impregnation).

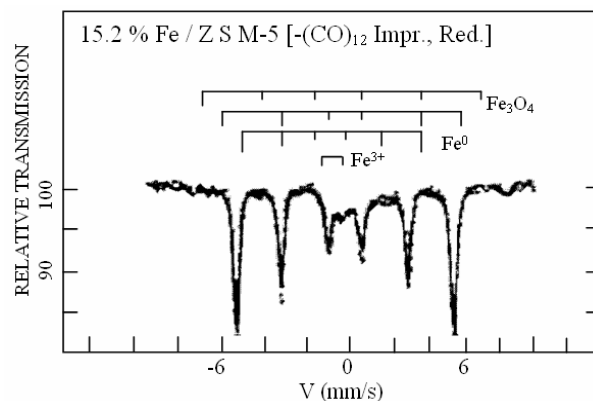**Figure 3**. Mössbauer spectrum of the sample ZCO (15.2 % Fe/ZSM-5, $Fe_3(CO)_{12}$ impregnation) Reduced in flowing H_2 (30 cc/min) at 723 k, for 30 min.

1 (Fe/silicalite) and ZN-1 (Fe/ZSM-5) revealed six-line spectra with a hyperfine field $H_{of} \sim 330$ kOe, which were ascribed to the presence of metallic Fe. However, the six-line Mössbauer spectrum of the reduced sample ZN-2 (Fe+Co/ZSM-5, nitrate impregnation) corresponded to a hyperfine field H_f of ~ 345 kOe, which was found to be much larger than the 330 kOe field, expected for metallic iron Fe°. This large H_f is believed to be due to Fe-Co "alloy" formation in the sample upon reduction; this was further supported by magnetization measurements.

The Mössbauer spectrum of carbided samples SN-1 (Fe/Silicalite, nitrate impregnation) and ZN-1 (Fe/ZSM-5, nitrate impregnation) consisted of superposition of four apparent six-line patterns corresponding to at least two iron-carbon phases. A typical spectrum of carbided sample SN-1 is shown in Figure 4. This spectrum indicated the presence of the Hägg carbide (Fe_5C_2) and Cementite (Fe_3C). The former has three inequivalent sites whereas the latter has only one [21].

The spectrum of carbided sample ZN-2 (Fe+Co/ZSM-5, nitrate impregnation) is shown in Figure 5. This spectrum indicated the presence of Hägg carbide (Fe_5C_2) in the sample. In addition, a sextet was found to correspond to "Fe-Co" alloy. It was noted that the amount of carbides formed in this catalyst were smaller than those containing Fe only. Apparently the presence of Co inhibited the formation of carbides. This could be due to the
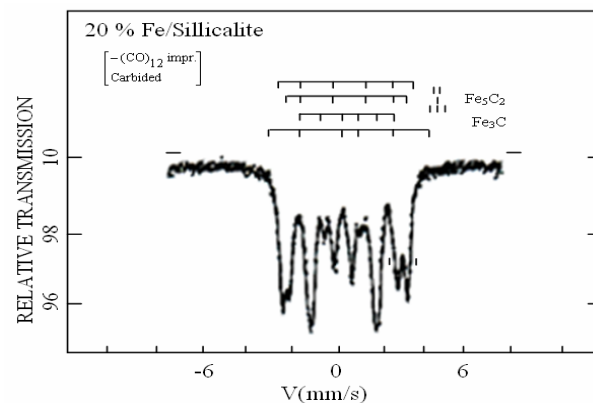

Figure 4. Mössbauer spectrum of the carbided sample SN-1 (20 % Fe/Silicalite, $Fe(NO_3)_3$ Impregnation), carbided with 1: 1 H_2/CO for 16h at 325 k.

existence of Co atoms on the outside of Fe-Co alloy clusters.

The spectrum of ZCO (Fe/ZSM-5, carbonyl impregnation) sample, after 9h of carbiding indicated the presence of Fe_5C_2 and Fe_3C, in addition to that of Fe_3O_4 and Fe° (Figure 6). However, the spectrum obtained after 19h of carbiding did not reveal the presence of Fe°.

Mössbauer spectra of the used catalysts SN-1, SN-2, ZN-1, and ZN-2 (all impregnated with iron nitrate) consisted of three or more magnetically split hyperfine spectra. The spectrum of the sample ZN-1 is shown in Figure 7, which is explained in terms of the Hägg carbide (Fe_5C_2) presence
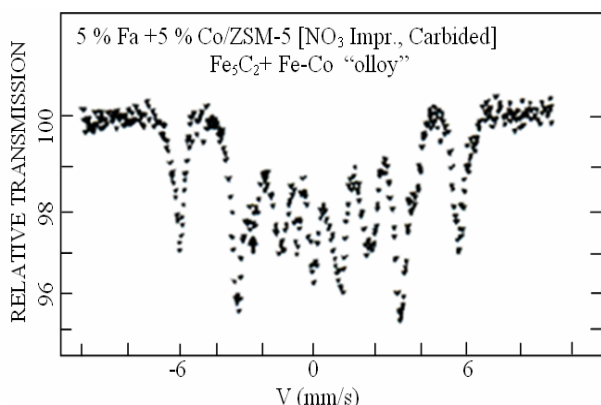
Figure 5. Mössbauer spectrum of carbided sample ZN-2 (9 % Fe + 9 % Co/ZSM-5, Fe(NO$_3$)$_3$ Impregnation) carbided with 1: 1 H$_2$/CO for 16 h at 523 k.
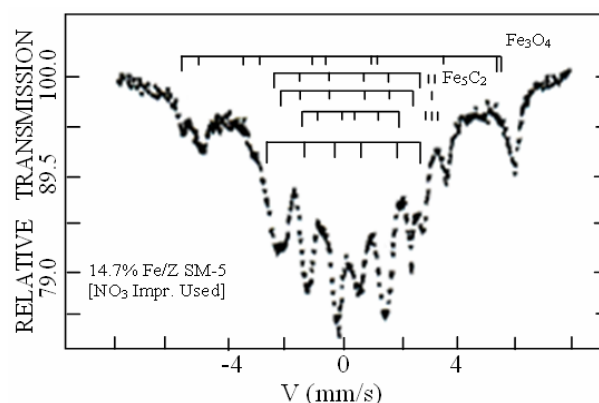

Figure 7. Mössbauer spectrum of used sample ZN-1 (14.7 % Fe/ZSM-5, Fe(NO$_3$)$_3$ Impregnation) after syngas reaction at 553 k for 24 h.
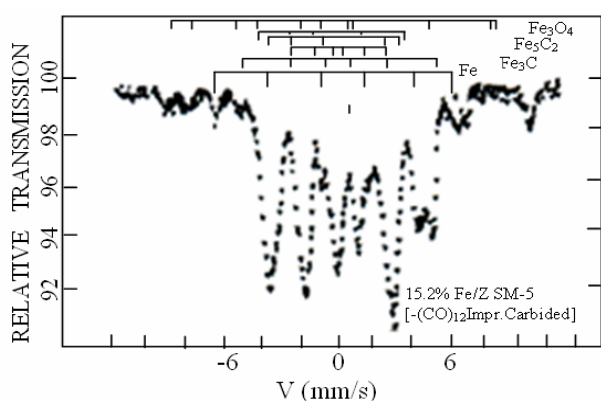

Figure 6. Mössbauer spectrum of carbided sample ZCO (15.2 % Fe/ZSM-5, Fe$_3$(CO)$_{12}$ Impregnation). 9 h of carbiding with 1: 1 H$_2$/CO at 523 k.

Cementite (Fe$_3$C) and Fe$_3$O$_4$. It should be noted that, the Cementite content had relatively increased at the expense of the Hägg carbide (the active component of the catalyst) used samples, comparing with what was found in the carbided samples.

The Mössbauer spectrum of the carbonyl impregnated sample ZCO, obtained after 24h of syngas reaction at 523 k was identical to the one obtained after carbiding (Figure 6). Very little change was observed in the spectrum recorded even after 72h of syngas reaction at higher temperature (553 k). This seems to indicate that carbonyl

impregnated catalysts are more stable than nitrate impregnated catalysts, with respect to the active component Fe$_5$C$_2$ at different temperatures over longer periods of time as reaction Proceeds.

3.3. Magnetic Studies The magnetization measurements of the nitrate impregnated fresh samples SN-1, SN-2, and ZN-1 exhibited large coercive force (Hc = 8 kOe) and low magnetization (ó$_s$ = 0.5 emu/g. of Fe). Bohr magneton numbers for these samples were close to 5.9 [22]. Hysteresis loops and low magnetization obtained for these samples, closely resembled the formation of α-Fe$_2$O$_3$ particles. These observations confirmed that, the above samples contained multidomain particles of antiferomagnetic α-Fe$_2$O$_3$, as observed from Mössbauer spectroscop.

A high value (120 emu/gr.) of Fe was observed during saturation magnetization for the fresh sample ZN-2, indicating the presence of multidomain particles of Fe$_3$O$_4$, which could be detected by Mössbauer spectroscop.

Magnetization per gram of the sample (emu/gram) was plotted as a function of H/T for the carbonyl impregnated fresh sample, which can be seen in Figure 8, also the results of thermo magnetic analysis (TMA) are shown in Figure 9. A very good superposition of data points in Figure 8 for two different temperatures, 85 k and 218 k. This data confirmed further by Mössbauer study of superparamagnetic for Fe$_3$O$_4$ clusters.
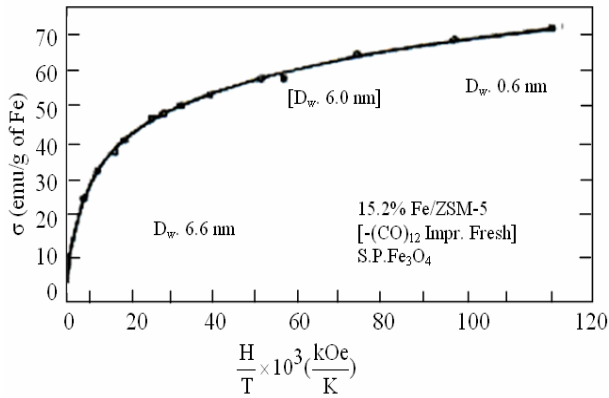
Figure 8. Magnetization (ó) as a function of H/T for the fresh sample ZCO (15.2 % Fe/ZSM-5 Fe₃(CO)₁₂ impregnationn). 85 k, 284 k.

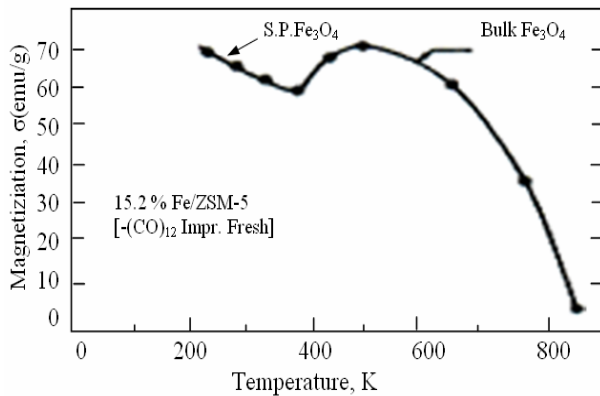**Figure 9**. Magnetization (ó) vs. temperature for the fresh sample ZCO (15.2 % Fe/ZSM-5, Fe₃(CO)₁₂ impregnation).

The increase in magnetization in Figure 9 around 500 k can be attributed to the growth of the fine superparamagnetic particles of Fe_3O_4 into a ferromagnetic bulk form. The value of Tc = 850 k was determined from the same figure which agreed well with the reported Curie temperature for bulk Fe_3O_4 [21].

Using low-field (LF) and high-field (HF) approximations of the well known Langevin function [22], the particle diameter D for the superparamagnetic fresh sample ZCO (carbonyl impregnation) was calculated to be D_{LF} = 6.6 nm, D_{HF} = 5.6 nm, giving an average particle diameter of 6 nm. The particle size distribution for the

system was obtained, based on langerin function assuming a log-normal distribution. The results of this calculation shown in Figure 10 indicated that the particle diameter falls within a narrow range of about the mean value, 6 nm.

The magnetization measurements of reduced samples SN-1, and ZN-1 indicated that these samples had been reduced to almost 100 % under the reducing conditions, mentioned earlier.

The reduced samples SN-2 and ZN-2 (Fe + Co, nitrate impregnation) showed a large statestical value of magnatic saturation = 297 emu/(g. of Fe-Co), which is considerably greater than the óₛ of metallic Fe (~218 emu/gr. of Fe). A very high value of óₛ for the above samples were attributed to the formation of "Fe-Co" alloy, a conclusion drawn from Mössbauer study. The observed value of óₛ in this instance, is surprisingly the largest reported for any ferromagnetic alloy containing Fe + Co.

Thermo magnetic measurements on the reduced sample ZCO (Fe/ZSM-5, carbonyl impregnation) yielded a Curie temperature Tc = 920 k, a value smaller than that of Fe° in bulk form. This lowering of Tc may be attributed to the superparamagnetic behavior of small particles formed in the channels of ZSM-5.
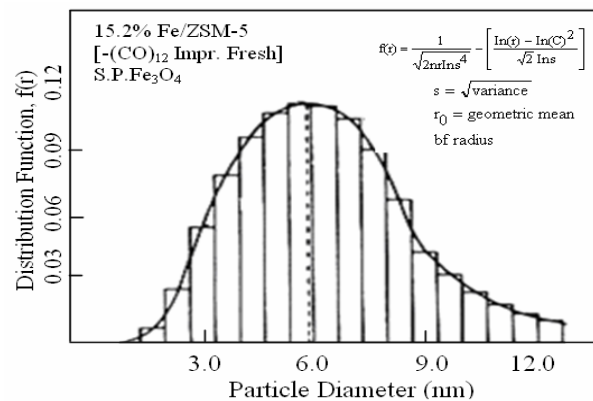
Results of the thermo magnetic measurements

Figure 10. Particle size distribution for the fresh sample ZCO (s15.2 % Fe/ZSM-5, Fe₃(CO)₁₂ impregnation), determined by assuming log-normal distribution. The log-normal distribution of a crystallite of radius r can be represented by f(r) = $(1/\sqrt{2\pi} r \ln S)$ exp $[-((\ln r - \ln r_0)/\sqrt{2} \ln S^2]$ where r_o is the geometric mean of the distribution and S is the square root of the variance of the distribution.

for the carbided sample SN-1 is shown in Figure 11. A similar curve was obtained for sample ZN-1 after it was carbided. From the observed magnetic transition temperatures (Tc) the phases in both carbided samples were identified to be the Hägg carbide and Cementite. Results of the thermomagnetic analysis on the carbided sample ZCO is presented in Figure 12.

A summary of the results obtained from Mössbauer and magnetic studies is given in Table1.

4. CONCLUSION

The studies indicated that with carbonyl impregnation, a relatively finer dispersion of superparamagnetic clusters of Fe-oxides is obtained in the as-impregnated catalysts. A comparison of the carbided and used spectra samples, further showed that the active phase taking part in the conversion of syngas, by Fe/ZSM-5 and Fe/Silicalite is the Hägg carbide (Fe_5C_2), which is converted to Cementite (Fe_3C) during the syngas reaction. The carbonyl impregnated catalysts are more stable, with respect to Fe_5C_2 active component, at different temperatures over longer periods of time, than the nitrate impregnated catalysts. The catalysts were tested for syngas ($CO + H_2$) conversion in a Berty reactor. The carbonyl impregnated catalysts yielded the most gasoline-range hydrocarbons (C_5-C_{11}) in the products obtained in the Fischer-Tropsch reaction. The superior performance of the carbonyl impregnated samples is believed to be influenced by a higher degree of superparamagnetic dispersion or nanosize of the metal species achieved in these samples. Furthermore, the Fe/ZSM-5 gave~75 % of the gasoline range hydrocarbons, whereas superparamagnetic (Fe + Co) clusters in general enhanced the formation of the gasoline range hydrocarbons to ~ 94 %.

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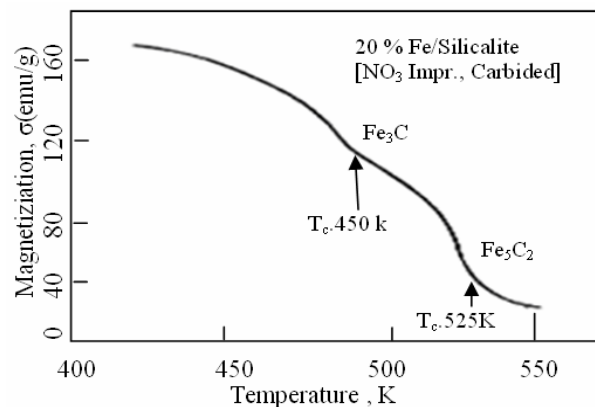
Figure 11. Magnetization (ó) vs. temperature for the carbided sample SN-1 (20 % Fe/Silicalite, Fe (NO_3)$_3$ impregnation).
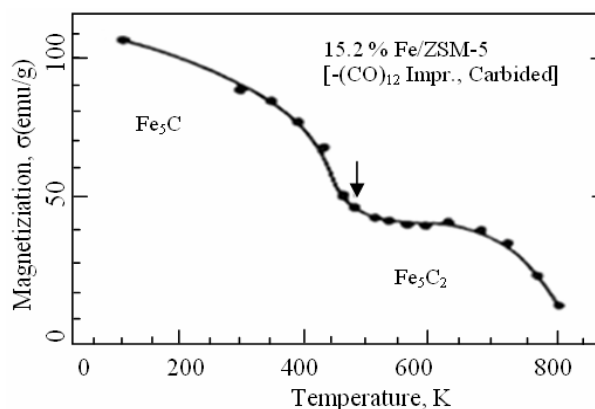

Figure 12. Magnetization (ó) vs. temperature for the carbided sample ZCO (15.2 % Fe/ZSM-5, $Fe_3(CO)_{12}$ impregnation).

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