

ZEOLITES

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Cover photograph of **Aquasil** zeolite beads
courtesy of Laporte Industries Limited

Photolytic and thermolytic decomposition products from iron pentacarbonyl adsorbed on Y zeolite

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Zeolite supported iron systems obtained by photolysis and thermolysis of $\text{Fe}(\text{CO})_5/\text{Na}-\text{Y}$ adducts are characterized via evaluation of the respective magnetic isotherms taken with a FONER magnetometer at $T=4.2$ K. Thermolysis under fast heating in inert gas and under fluidized shallow bed conditions completes within a few minutes at ~ 500 K, and gives iron clusters of which at least 70 to 90 wt% is smaller than 1 nm. Prolonged photolysis at 290 K in the same fluidized bed conditions does not result in the formation of 'naked' iron(0) clusters, but gives a limited fraction of magnetically coupled $\text{Fe}_x(\text{CO})_y$ entities. Photodimerization cannot be excluded to be the main reaction path.

Keywords: Iron clusters; thermolysis; photolysis; magnetic isotherms

INTRODUCTION

Small iron clusters stabilized on appropriate supports are of particular interest for studies of catalytic particle size effects as well as for magnetic investigations. Zeolites are excellent supports for these purposes, because they are crystalline, have well defined pore structure, variable electronic¹ and solvolytic properties.

Several techniques have been used to introduce iron clusters into the cavities of large pore zeolites. Since reduction of Fe(II) exchanged^{2,3} Y zeolite is impossible with molecular hydrogen, efforts have been made with stronger reducing agents⁴⁻⁶.

Alternatively, iron(0) species can be introduced by adsorption and subsequent decomposition of iron complexes⁷⁻¹².

In order to dispose of detailed quantitative data on the decomposition process of iron pentacarbonyl adsorbed on different large pore zeolites¹³, the adsorption equilibrium^{14,15} and thermolysis¹⁶ have been studied by thermogravimetric and i.r.—*in situ* techniques, whereas the influence of decomposition methods on the resulting iron particle distributions could be elucidated by magnetic characterization^{17,18}. The advantages of carbonyl decomposition compared to iron reduction are the following:

—The zeolite is not subjected to extensive heating which can cause lattice breakdown and/or strong ionic fields in case of ion exchange with multivalent cations.

—The zeolite is prevented from contamination by oxidized or excessive reducing agents (protons, Na^+ -ions etc.).

—Cation-free, hydrophobic zeolites can also be loaded with metal.

Photolysis of iron pentacarbonyl adsorbed on H-Y has been reported in a ¹³C-n.m.r. study¹² to proceed via a strong complex-support interaction. Carbonyl-free iron clusters were proposed to be the final photolysis products. Since the main photolysis product of $\text{Fe}(\text{CO})_5$ in condensed phases was already identified in 1891 as $\text{Fe}_2(\text{CO})_9$ ²⁰⁻²², the question arises as to the nature of the products obtained by illumination of $\text{Fe}(\text{CO})_5$ adsorbed on zeolites. If this approach could provide 'naked' iron clusters at low temperatures, it should be preferred over the thermal decomposition techniques because sintering will be effectively reduced.

In the present study, a comparison is made between thermolytic and photolytic products from $\text{Fe}(\text{CO})_5/\text{Na}-\text{Y}$ under fluidized shallow bed conditions. The generated iron zeolites are characterized by evaluation of their magnetic isotherms taken under inert conditions at a temperature of $T=4.2$ K.

EXPERIMENTAL

Materials

Synthetic sodium faujasite (FAU) with a Si/Al ratio of 2.46 from Strem Chemicals was treated with a 0.1 M NaCl solution, washed until Cl^- free, air dried and

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stored over saturated NH₄Cl solution to ensure constant humidity. The zeolite samples were degassed in the reactor at 670 K for 36 ks at 10⁻³ Pa, with a heating rate of 0.033 K s⁻¹.

Iron pentacarbonyl (99.5%, Ventron) was coldly distilled in the dark and stored over molecular sieve 5 A in a stainless steel tube connected to the gas dosing system.

Gas dosing system and quartz reactor

Controlled degassing of the zeolites under high vacuum (10⁻³ Pa), loading of the zeolites with dry vapour of Fe(CO)₅ as well as thermal and photochemical decomposition of the Fe(CO)₅/FAU adducts was carried out in a stainless steel gas dosing system with metal/viton valves and a quartz reactor¹³ (Figure 1).

The reactor allowed decomposition under inert gas/fluidized bed conditions and inert sample preparation for the FONER magnetometer and Mössbauer spectroscopy. Deep frozen iron pentacarbonyl was carefully outgassed and slowly allowed to warm up at a temperature of 273 K, while the vapour was in contact with 180–450 mg dehydrated zeolite sample at $T=295$ K. An equilibrium pressure of 870 Pa saturates the faujasite pore system¹⁵.

The adsorption was allowed to equilibrate for 14 ks. After evacuating the system for one hour, the Fe(CO)₅/FAU adducts were thermally or photochemically decomposed in the horizontal, 20×50 mm bed section of the quartz reactor. The fluidized bed was generated by a horizontal vibration of the reactor with $\nu=50$ Hz and about 1 mm amplitude. The *thermolysed* sample F/0.17 was decomposed at a heating rate of 0.17 K s⁻¹ up to 470 K in a 48 kPa helium atmosphere under fluidized bed conditions. After heating for 1.2 ks at 470 K, the sample was outgassed at 373 K for 22 ks under vacuum (10⁻³ Pa). The iron content of this sample amounted to 3 wt%.

The *photolysed* sample F/UV was decomposed by irradiation of the Fe(CO)₅/FAU adduct with the ultraviolet light of a Pen Ray 11 SC-1 Hg-lamp (UV-Products, $\lambda_{\max}=254$ nm, 40 Wm⁻² in 25 mm distance) at a temperature of $T=290$ K.

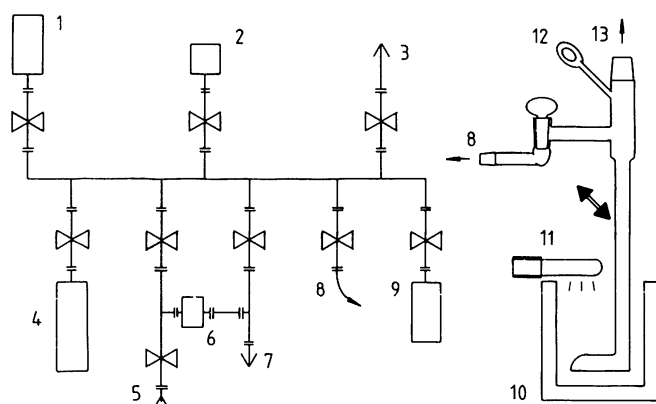


Figure 1 Gas dosing system and reactor for decomposition of Fe(CO)₅/zeolite adducts. 1, buffer volume; 2, high vacuum measuring tube; 3, connection to turbomolecular pump; 4, absorber for Fe(CO)₅ (molecular sieve 13X); 5, inert gas inlet; 6, Baratron capacitance manometer; 7, vacuum pump; 8, connection to quartz reactor; 9, reservoir with dry Fe(CO)₅; 10, shallow bed quartz reactor; 11, u.v. lamp; 12, sample bulb; 13, connection to transfer apparatus for FONER samples

Magnetization measurements

Immediately after the preparation procedure, the reactor was connected with a transfer system for FONER-sample preparation under inert conditions. About 20 mg iron zeolite sample were transferred into a quartz tube (2.5 mm diameter) under vacuum, pressed with a quartz rod, sealed off and introduced into the helium cryostat (JANIS) of a calibrated FONER vibrating sample magnetometer (P.A.R.). The magnetization curve was taken at 4.2 K in magnetic fields up to 6 T. For evaluation of the magnetic isotherms, corrections for sample holder and quartz tube were taken into account.

The samples did not show hysteresis. Therefore, to a first approximation, the evaluation of the magnetic isotherms was carried out in terms of superparamagnetism. This implies that the magnetic measuring time (~100 s) is sufficient for attainment of spin equilibrium. Particle anisotropy, magnetic interaction and chemically inhomogeneous phases are neglected.

Under these assumptions, the numerical reconstruction of the measured magnetic isotherms by a sum of different Brillouin functions²³ $B_l(x)$,

$$B_l(x) = M/M_\infty = \frac{2l+1}{2l} \coth \frac{2l+1}{2l} x - \frac{1}{2l} \coth \frac{1}{2l} x$$

with $x = I g \mu_B B / kT$ and M = magnetization, M_∞ = saturation magnetization, I = cluster spin quantum number, g = Lande factor, μ_B = Bohr's magneton, B = magnetic field, k = Boltzmann's constant, T = temperature, gives approximated weight fractions of particles with different cluster spin quantum numbers I . Since small magnetic particle moments were found by the magnetic measurements, the quantum mechanical Brillouin function $B_l(x)$ applies rather than the classical Langevin approach²⁴.

In order to obtain the saturation magnetization M_∞ , the iron content of the samples was determined by X-ray fluorescence and neutron activation techniques. The total relative error in iron weight is $\pm 15\%$. Chemical analysis was found to be too risky due to the small amount of iron (0.5 mg) and the severe conditions to be used for the solvation of Y zeolite.

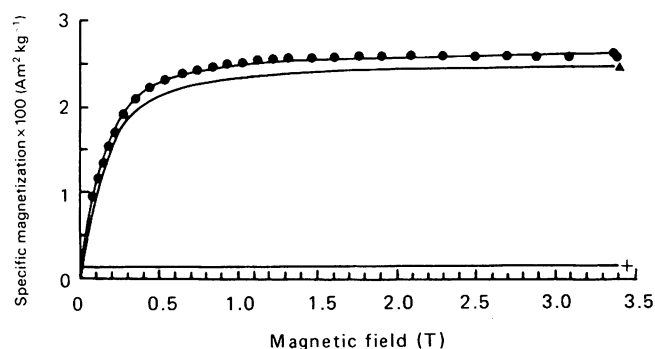


Figure 2 Magnetization curve of sample F/0.17 taken at $T=4.2$ K, fitted by the sum of two Brillouin functions. (●) measured values. (▲)-curve, Brillouin function $B_l(x)$ with $l=37$. (+)-curve, Brillouin function with $l=1105$. Upper-curve, Brillouin fit according to the sum of the Brillouin functions of the single fractions. Other parameters are given in Table 1

Table 1 Cluster spin quantum number *l* distribution for a thermolysed Fe(CO)₅/FAU adduct (sample F/0.17)^a

<i>l</i> , N ^b	particle size ^c V ^{1/3} (nm)	weight fraction ^d (%)	<i>q</i> -value ^e (%)
37	0.76	95	119
1105	2.35	5	

^a Decomposition parameters are given in the experimental section

^b A Landé factor $g = 2.06$ was used in the Brillouin function²⁵. l equals N , the number of atoms, because a value of $l = 1$ per atom was assumed as in bulk iron. $M_{\infty}(T=0)/N\mu_B \equiv n_{\text{eff}} = 2.22$, $l = n_{\text{eff}}/g = 1.08$ ²³

^c Calculated assuming bcc structure and atomic radius $R = 0.124$ nm, according to $V^{1/3} = 0.227 \cdot N^{1/3}$ ²⁶

^d Mass fraction of the respective discrete particle size fraction

^e Ratio between experimental saturation magnetization $M_{\infty, \text{exp}}$ as derived from the Brillouin fit and the bulk value $M_{\infty}(4.2 \text{ K}) = 1.752 \cdot 10^6 \text{ Am}^{-1}$

RESULTS AND DISCUSSION

1 Thermolysis of a Fe(CO)₅/FAU adduct in a fluidized bed (Sample F/0.17)

Characterization of the sample was done via evaluation of the magnetization curve at $T = 4.2$ K, which is shown in Figure 2. The cluster spin quantum number distribution obtained from the fit procedure is given in Table 1, together with other parameters.

Under the assumptions mentioned in the experimental section, the results allow us to conclude the following:

(i) Thermolysis of the Fe(CO)₅/FAU adduct gives superparamagnetic iron particle systems. Within the error of the iron content, the superparamagnetic fraction represents 100% of the iron present. This is derived from the *q*-value, $M_{\infty, \text{exp}}/M_{\infty}(4.2 \text{ K})$ being equal to 119%.

(ii) The main fraction of the particles shows magnetic moments corresponding to clusters with linear dimensions smaller than 1 nm. Fast heating under inert gas and fluidized bed conditions seems to prevent the sample effectively from sintering despite the high temperature (470 K) which is reached during the decomposition procedure.

(iii) A certain amount of larger particles is present as evidenced by the Brillouin fit. The exact size of this fraction can, however, not be determined from the magnetic isotherm at $T = 4.2$ K, since the particles are magnetically blocked at this temperature. Greater particles could be detected independently by X-ray diffraction methods.

A weak, broad line was found with the *d*-value of the α -Fe d_{110} line. Line broadening allowed estimation of the mean particle size of this fraction to be $d = 30 \pm 20$ nm. Transmission electron micrographs of comparable samples indicate that the greater particles stick at the outer surface of the zeolite crystals²⁷.

In a recent Mössbauer spectroscopic study²⁸ with comparable samples, typical bulk iron hyperfine splitting at room temperature was found. This shows that spin equilibrium is not attained in the time domain of the Mössbauer effect. (The time scale of the Mössbauer experiment is about 10^{-9} s, compared to 10^2 s in static measurements of magnetization.)

(iv) The final iron content, corresponding to about 3 wt% of the thermolysed Fe(CO)₅/FAU adduct, exceeds by far that obtained on γ -Al₂O₃²⁹ or graphite³⁰ by thermolysis of preadsorbed Fe(CO)₅. Even with large pore zeolites, however, an iron loss of more than 50% occurs with respect to the original iron carbonyl loading.

2. Photolysis of faujasite adsorbed iron pentacarbonyl

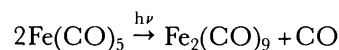
Carbonyl-loaded FAU was irradiated with the u.v.-light of a Hg-lamp under fluidized bed conditions. In order to prevent thermal decomposition, the reactor was cooled with water to 290 K during photolysis.

Due to their small size around 1 μm , zeolite crystals should allow sufficient light transmission in the near ultra-violet range, multiple surface scattering in the zeolite powder, however, decreases considerably the available light intensity. To overcome this difficulty, the adduct was irradiated for several hours in a very shallow bed (1 mm thick) under fluidized bed conditions.

Preparation conditions of the photolysed Fe(CO)₅/FAU adduct are given in Table 2. The magnetization curve at $T = 4.2$ K of a representative sample (F/UV) is shown in Figure 3. A Brillouin fit is given for a cluster spin quantum number $l = 3$. Additional results are listed in Table 2. During the first hour, the colour of the sample turned to redbrown and subsequently remained unchanged. Therefore, photolysis is assumed to be complete after 15 h (54 ks) of irradiation. Following the photolysis volumetrically, no significant rise of the pressure above 10 Pa could be detected within one hour. This indicates that only a small amount of CO is split off during the course of the reaction.

Sample colour as well as magnetic properties indicate that photolysis of Fe(CO)₅/FAU adducts generates products quite distinct from those obtained after thermal decomposition: mean cluster moment and superparamagnetic fraction (*q*-value) are found to be about ten times smaller compared to the latter samples. Possible reaction paths are the following.

The photo-reaction of liquid or gaseous Fe(CO)₅ was found to give mainly the dimer³¹



This reaction seems to be quenched at temperatures above 330 K. Interpretation of the poorly structured u.v. spectrum^{22,32} as well as of matrix isolation

Table 2 Photolytic decomposition conditions of saturated Fe(CO)₅/FAU adduct^a F/UV and magnetic characterization of the product^b

Irradiation time (ks)	Colour	Iron content (wt%)	Cluster spin quantum number <i>l</i>	Fraction (%)	<i>q</i> -value (%)
54	redbrown	4.8	3	100	9.8

^a Under fluidized bed conditions, static bed, thickness 1 mm, irradiation intensity ($\lambda_{\text{max}} = 254 \text{ nm}$) 40 Wm^{-2} , under a dynamic vacuum of 10^{-2} Pa, cooled down to $T = 290 \text{ K}$

^b Characterized by means of a Brillouin fit to the magnetization curve at $T = 4.2 \text{ K}$ — for fit parameters see Table 1

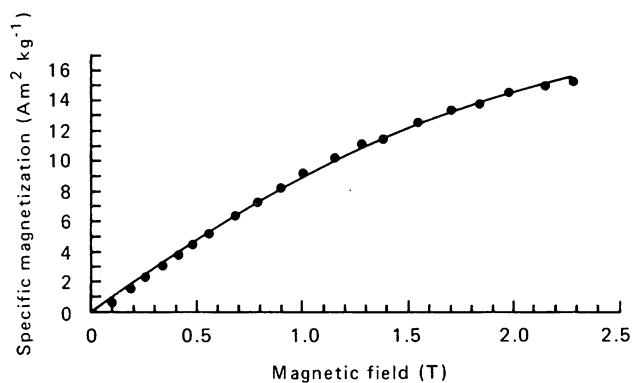


Figure 3 Magnetization curve of sample F/UV taken at $T = 4.2$ K, fitted by one Brillouin function with $l=3$. (○) measured values. Solid curve: calculated according to the Brillouin function

results³³⁻³⁵ provided evidence for the intermediate generation of the $\text{Fe}(\text{CO})_4$ radical. Subsequent photolysis under inert gas-low temperature conditions or in the gas phase splits off all carbonyl ligands in a stepwise reaction³⁶⁻³⁹.

In contrast to the above-mentioned extreme reaction conditions, room temperature photolysis in condensed phase leads to subsequent reactions of the generated intermediates, e.g. via mono- or disubstitution of CO ligands or oxidative addition, to give sixfold coordinated iron complexes¹⁹. Oxidative addition of acid hydroxyl groups of the H-FAU matrix with adsorbed $\text{Fe}(\text{CO})_5$ could explain the ^{13}C -n.m.r. line shift which was reported during irradiation of $\text{Fe}(\text{CO})_5/\text{H}-\text{FAU}$ adduct¹². A H-faujasite is a solid acid.

A complete decarbonylation of the adduct was found in the latter study, though irradiation was performed at wavelengths greater than 300 nm in a cylindrical n.m.r. pyrex tube. Due to the unfavourable reactor geometry and since temperature control was not reported, a considerable part of the carbonyl might have been decomposed thermally. The authors propose a stepwise CO-split off during photolysis until iron atoms are generated¹².

In the present study, no evidence could be found for $\text{Fe}(\text{CO})_4$: An electronic triplet state has been postulated for $\text{Fe}(\text{CO})_4$ from the results of MO-calculations⁴⁰ and matrix i.r. spectroscopic studies³⁵. The expected paramagnetism could be shown in a MCD study⁴¹.

In contrast to this, the present magnetization study provides an I value of $I=3$, which results in a magnetic moment of $|\vec{\mu}| = g \cdot \mu_B \cdot \sqrt{I(I+1)} = 7.1 \mu_B$. This value is even higher than that expected for Fe^{3+} -ions ($5.1-5.7 \mu_B$) and provides evidence for species with at least a pair of magnetically coupled iron atoms or ions.

The small q -value of about 10% can be explained by assuming the presence of a certain fraction of diamagnetic $\text{Fe}_2(\text{CO})_9$ or higher complexes. This is confirmed by the low CO evolution found during photolysis and the redbrown colour of the sample, which might be due to red $\text{Fe}_2(\text{CO})_9$ inside the zeolite cavities.

From the results discussed above, naked iron (0) clusters can be excluded to be the main photolysis product of $\text{Fe}(\text{CO})_5$ adsorbed in FAU zeolite.

CONCLUSION

The thermal and photochemical decomposition of zeolite adsorbed iron pentacarbonyl was studied under

fluidized shallow bed conditions in a quartz reactor. Evaluation of the respective magnetic isotherms at $T = 4.2$ K allows us to attribute the following features to the two different decomposition modes.

(1) *Thermal* decomposition under fast heating rates of $\text{Fe}(\text{CO})_5/\text{FAU}$ adduct is complete within a few minutes at about 500 K and gives iron(0) cluster systems of which at least 70 to 90 wt% are smaller than 1 nm. The remaining fraction of iron particles shows a mean diameter which is larger than 10 nm.

(2) In contrast to thermolysis, *photochemical* decomposition with ultraviolet light at $T = 290$ K does not show the formation of 'naked' iron(0) clusters, but gives a limited fraction of magnetically coupled $\text{Fe}_x(\text{CO})_y$ species. Photodimerization cannot be excluded to be the main reaction path.

Further investigations are under work in order to characterize the generated iron zeolites by Mössbauer spectroscopy²⁸ and catalytic testing.

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