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CONTENTS

SYNTHESIS

STRUCTURE DETERMINATION

TECHNOLOGY AND APPLICATION

B. Držaj, S. Hočevar and S. Pejovnik (Editors), *Zeolites*

PREPARATION OF IRON(0) MODEL CATALYSTS WITH IRON CLUSTERS OF SUB-NM DIMENSIONS BY DECOMPOSITION OF Y-ZEOLITE ADSORBED IRON PENTACARBONYL

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ABSTRACT

Thermal decomposition in a shallow bed of iron pentacarbonyl adsorbed on NaY-zeolite is achieved under vacuum already at 370 K with low heating rates. Decomposition under fast heating in inert gas and fluidized shallow bed conditions can be completed within a few minutes at ca. 500 K. Zeolite supported iron clusters obtained by these techniques are characterized via evaluation of the respective magnetic isotherms taken with a Foner magnetometer at 4.2 K. Low temperature/vacuum as well as high temperature/inert gas thermolysis gives iron cluster systems with at least 70 to 90 wt-% smaller than 1 nm.

INTRODUCTION

Several efforts have been made in order to investigate particle size effects in catalysis[1,2,3]. In particular, iron systems used in ammonia synthesis[4] and CO-hydrogenation reactions[5] are of industrial interest.

Since zeolites are crystalline and have well defined pore structure, variable electronic[6] and solvolytic properties, they are suitable supports for model catalysts.

In attempt to overcome difficulties in the preparation of iron zeolites by classical reduction techniques such as decreased reducibility of iron exchanged samples or contamination of the metal phase using alkali metals as reductants, the decomposition of preadsorbed iron pentacarbonyl was studied in detail[7]. The aim of these investigations is to dispose of iron model catalysts with defined, narrow particle size distribution.

Adsorption equilibrium between $Fe(CO)_5$ and different large pore zeolites was studied by gravimetric and IR-spectroscopic techniques[8,9], whereas thermal decomposition was followed by thermogravimetric and IR-spectroscopic[10] methods. The effect of preparation conditions on iron particle size[11] will be reported in the present study in greater detail. The influence of different heating rates in a fluidized shallow bed reactor on iron particle size was studied by magnetic methods.

EXPERIMENTAL

Materials

Synthetic NaY(FAU) with Si/Al = 2.46 from Strem Chemicals was treated with 0.1 M NaCl solution, washed, air-dried and stored over saturated NH_4Cl solution to ensure constant humidity. Before loading with $Fe(CO)_5$, the zeolite was degassed in the reactor at 670 K for 36 ks at 10^{-3} Pa, with a heating rate of 0.033 Ks^{-1}. Iron pentacarbonyl from Ventron (99.5%) was coldly distilled in the dark and stored in a stainless steel tube over molecular sieve 5A.

Gas dosing system and reactor

A stainless steel gas dosing system with metal/viton valves, connected to a quartz reactor, allowed[7] controlled degassing of the hydrated zeolites under high vacuum (10^{-3} Pa), loading of the zeolites with purified dry vapor of $Fe(CO)_5$, thermal and photochemical decomposition of the adducts in a shallow fluidized bed and sample preparation in inert atmosphere for magnetic measurements and Mössbauer spectroscopy.

After cooling 180 - 450 mg of dehydrated zeolite in the quartz reactor with a 20 x 50 mm horizontal bed section, iron carbonyl was frozen in liquid air, degassed and allowed to warm up to 273 K, and finally contacted with the zeolite sample. An equilibrium pressure of 870 Pa saturated the zeolite pore system[9]. After 14 ks, the system was evacuated for one hour. Subsequently, the adducts were decomposed thermally under vacuum or in helium gas, using a very fast heating procedure ("shock" heating). The latter was achieved by dipping the frozen reactor into a metal bath at 490 K.

The fluidized bed was generated by a horizontal vibration of the reactor with ν = 50 Hz and about 1 mm amplitude.

Magnetization measurements

About 20 mg of iron zeolite sample was pressed with a quartz rod into a quartz tube (2.5 mm diameter) under vacuum, sealed off and introduced into the helium cryostate (Janis) of a Foner vibrating sample magnetometer (P.A.R.).

The magnetization curve was taken at 4.2 K in magnetic fields up to 6 T.

The magnetometer was calibrated with a pure Ni metal sample and corrections for sample holder and quartz tube were taken into account.

Most 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 is sufficient for the attainment of spin equilibrium, particle anisotropy, particle interaction and chemically inhomogeneous phases can be neglected.

Under these assumptions, the numerical reconstruction of the magnetic isotherms by a sum of different Langevin-[12] or Brillouin-functions[13] gives appro-

ximated weight fractions of particles with different sizes or cluster spin quantum numbers, I, respectively.

The Brillouin function

$$B_I(x) = M/M_\infty = \frac{2I+1}{2I} \coth \frac{2I+1}{2I} x - \frac{1}{2I} \coth \frac{1}{2I} x ,$$

with $x = Ig\mu_B B/kT$ applies to particles with a small magnetic moment.

(M = magnetization, M_∞ = saturation magnetization, I = cluster spin quantum number, g = Landé factor, μ_B = Bohr's magneton, B = magnetic field, k = Boltzmann's constant, T = temperature)

In attempt 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 ± 15%.

RESULTS AND DISCUSSION

Different heating rates in the range between 0.0025 and about 10 Ks^{-1} were used during thermolysis of carbonyl/FAU-adducts.

The sample to which the slowest heating rate was applied (FAU/0.0025), was treated in a static bed under vacuum, because very slow heating under inert gas conditions may give an inhomogeneously distributed iron phase.

All other samples were decomposed under fluidized bed conditions in helium atmosphere. The respective decomposition parameters are given in table 1. The rate and degree of decomposition can be monitored following the gas pressure.

TABLE 1. Thermolysis of $Fe(CO)_5$/FAU-adducts under fluidized shallow bed conditions[a]

Sample	Heating rate/ Ks^{-1}	Final Temp. T_{max}/K	Heating period at T_{max}/ks	Helium-pressure /kPa	Outgassing[b] ks	Iron content /wt-%	Amount[c] CO/%
F/0.0025[d]	0.0025	373	18	10^{-2} Pa	-	5.2	-
F/0.33	0.33	490	0.24	48	50	5.3	88
F/S	ca. 10	490	0.36	80	54	3.9	88

[a] These preparations were carried out with amounts of dry zeolite ranging from 185 to 444 mg.
[b] At 373 K and 10^{-3} Pa.
[c] Amount of CO generated with respect to the theoretical amount expected for an initial loading of 30 wt-% $Fe(CO)_5$.
[d] This sample was decomposed under static bed conditions.

Representative pressure curves obtained at decomposition rates of 0.33 Ks^{-1}

(sample F/0.33) and "shock" heating (sample F/S), respectively, are shown in fig. 1.

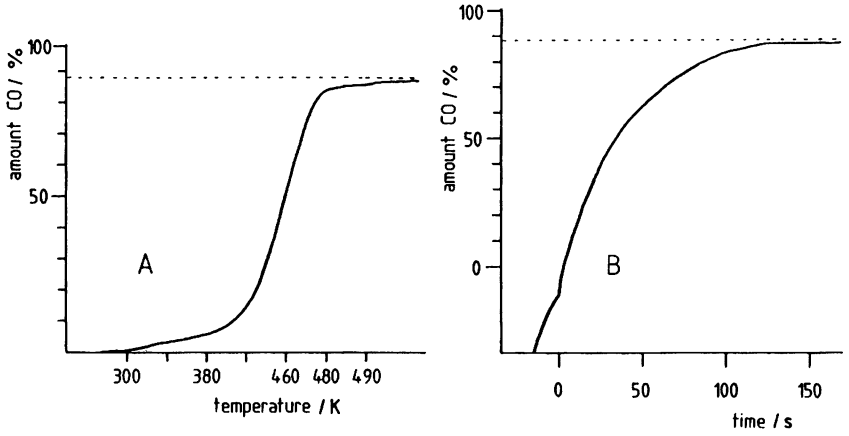

Fig. 1. Gas evolution curves during thermal decomposition of $Fe(CO)_5$/FAU-adduct under fluidized bed conditions.
A, with a heating rate of 0.33 Ks^{-1}, sample F/0.33;
B, with shock heating (sample F/S); parameters see table 1.

In the first case, the gas evolution rate clearly allows us to divide the decarbonylation process into three distinct regions: two zones of slow gas evolution are separated by a fast reaction (fig. 1a). The latter is accompanied by the typical color change from ivory-like to black.

Obviously, this curve resembles those obtained during thermogravimetric experiments with similar $Fe(CO)_5$/zeolite adducts[8,10] and confirms independently the picture of a fast, endothermic reaction, splitting off the main carbonyl fraction to give relatively thermostable, highly unsaturated polynuclear carbonyl clusters.

If in contrast the adduct is heated by a temperature shock, the slow gas evolution prior to the main reaction is missing (fig. 1b).

Quantitative interpretation of these volumetric data shows that decarbonylation occurs in a reproducible and complete manner (table 1), irrespective of the heating rate and the amount of sample.

Characterization of the thermally decomposed samples was done via evalua-

tion of the respective magnetization curves at T = 4.2 K. A representative curve (F/0.33) is depicted in fig. 2, whereas the results for other samples are given in table 2. As can be seen from table 2, in most cases one single

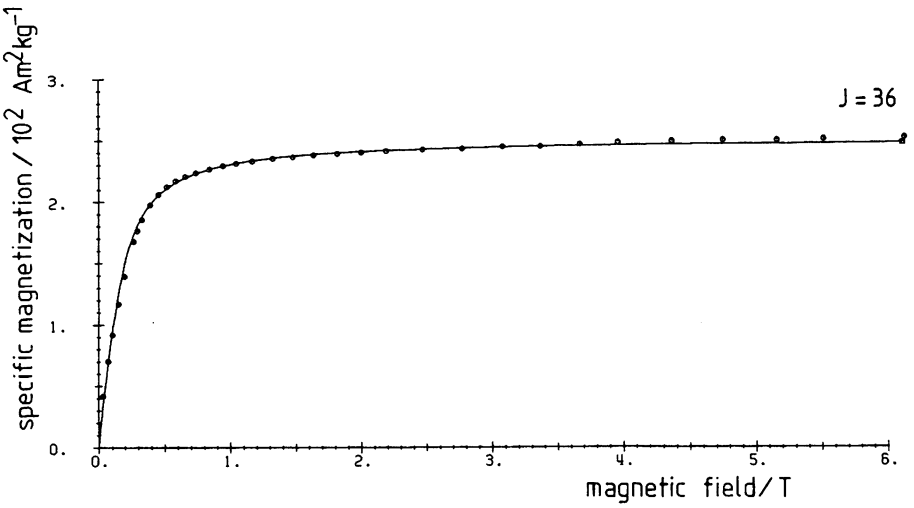

Fig. 2. Magnetization curve of sample F/0.33 at T = 4.2 K, fitted by one Brillouin function with I = 36. Parameters see table 1 and 2.

Brillouin function suffices to fit the experimental magnetization curve. Under the assumptions mentioned in the experimental section, the results allow us to conclude the following:

- Thermolysis of $Fe(CO)_5$/FAU-adducts gives iron particle systems with superparamagnetic behavior. In attempt to determine the mass fraction of the superparamagnetic particles, the experimental saturation magnetization $M_{\infty,exp}$ was related to the bulk value ($M_\infty(4.2\ K) = 1.752 \cdot 10^6\ Am^{-1}$). The superparamagnetic fraction $q = M_{\infty,exp}/M_\infty$ is found to be 100%, within the error of the iron content, for all samples.
- The main fraction of the particle system shows magnetic moments corresponding to clusters with linear dimensions below 1 nm.
- The mean cluster size seems to be nearly independent of the heating rate applied to the fluidized shallow bed (samples F/0.17, F/0.33, F/S). It can be assumed that fast heating under inert gas prevents the samples effectively from sintering - even at the considerably high final temperatures which are

used to complete the decomposition.

- Iron cluster sizes obtained by very slow heating up to 373 K under vacuum (sample F/0.0025) are comparable to those of the inert gas/fast heating samples discussed above.
- Separate testing of the applied fit procedure provided estimated values for fractions of magnetically blocked particles, which still do not change significantly the sample's magnetization curve at T = 4.2 K. At this temperature, the used magnetic particle size determination is insensitive to fractions of greater particles (i.e. greater than about 3 nm) below 20 wt-%. Since these particles contain more than 10^6 atoms, their total number should be negligible.

Additional characterization of the iron/zeolite systems was obtained in a recent Mössbauer spectroscopic study[19]. A typical bulk iron hyperfine splitting of comparable samples at room temperature indicates that spin equilibrium is not attained in the time domain of the Mössbauer effect (10^{-9} s).

TABLE 2. Cluster spin quantum number distribution of thermally decomposed $Fe(CO)_5$/FAU-adducts, derived from Brillouin-fits.

Sample	I[a]	Number of atoms[b] / N	particle size[c] $V^{1/3}$/nm	weight fraction[e]/ %	q-value[d]/ %
F/0.0025	35	35	0.74	100	107
F/0.33	36	36	0.75	100	111
F/S	43	43	0.80	100	117

[a] A Landé-factor g = 2.06 was used in the argument of the Brillouin function[14].
[b] The number of atoms equals I, since the value of I=1 per atom was assumed.
[c] Particle size was calculated assuming bcc structure and atomic radius of iron to be R = 0.124 nm, according to $V^{1/3} = 0.227 \cdot N^{1/3}$ with N = number of atoms[15].
[d] The q-value indicates the ratio between experimental saturation magnetization $M_{\infty,exp}$ as derived from the Brillouin fit and the bulk value $M_\infty(4.2\ K) = 1.752 \cdot 10^6\ Am^{-1}$.
[e] Mass fraction of the respective discrete particle size fraction.

The presence of a certain amount of larger 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. Linebroadening allowed us to estimate the mean particle size of this fraction to be $\bar{d}$ = 30 nm ± 20 nm - including Gauss- and Cauchy-line profile into the calculation. Transmission electron micrographs of comparable samples indicate that the large particles stick to the outer surface of the zeolite crystals[16].

- The final iron content of the thermally decomposed $Fe(CO)_5$/FAU-adducts is in the range between 3 and 6 wt-% of dry zeolite, indicating a total iron loss

of about 50% with respect to the original iron carbonyl loading (after degassing saturated adducts at T = 295 K, an iron loading of ca. 9 wt-% remains on FAU[8,9]). This relatively high iron content exceeds by far those obtained on γ-Al_2O_3[17] or graphite[18].

CONCLUSION

The thermal decomposition of zeolite adsorbed iron pentacarbonyl was studied in a quartz reactor under fluidized shallow bed conditions.

Magnetic isotherms of the respective samples taken in a Foner magnetometer under inert conditions were evaluated using a Brillouin fit.

Thermal decomposition of the $Fe(CO)_5$/FAU-adduct is achieved under vacuum already at 370 K with low heating rates, whereas decomposition under fast heating rates can be completed within a few minutes at ca. 500 K. Low temperature/vacuum as well as high temperature/inert gas thermolysis gives iron cluster systems with at least 70 - 90 wt-% smaller than 1 nm, indicating the effective prevention from sintering by heating under fluidized bed conditions.

Additional characterization of the generated iron zeolites by Mössbauer spectroscopy[19], EXAFS and catalytic testing is under way.

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