

## SUBSTRATE EFFECT ON THE GROWTH OF IRON CLUSTERS IN Y ZEOLITE

Th. BEIN, F. SCHMIDT \* and W. GUNSSER

*Institut für Physikalische Chemie der Universität Hamburg, Laufgraben 24, D-2000 Hamburg 13, Fed. Rep. of Germany*

and

G. SCHMIESTER

*Institut für Atom- und Festkörperphysik der Freien Universität Berlin, Arnimallee 14, D-1000 Berlin 33, Germany*

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Investigation of the decomposition process and of the thermolytic products obtained from  $\text{Fe}(\text{CO})_5$ /faujasite adducts by thermogravimetric, IR-spectroscopic, Mössbauer spectroscopic and X-ray absorption measurements (EXAFS) provides evidence for a substrate effect on the growth process of iron clusters. CsY substrate increases the Fe-CO bond strength. The stabilized intermediates generated by this effect upon thermolysis at 500 K are easily oxidized to small iron(III) oxide clusters, whereas with NaY substrate to a large extent iron(0) particles are generated. The latter show Mössbauer effect and EXAFS spectra comparable to those obtained from bulk iron. An inner oxidation process is assumed to be involved in the generation of the zeolite-supported iron oxide.

### 1. Introduction

The interaction between catalytically active metals and several supports has been subject to an increasing number of investigations [1]. In particular, adjustment of electron transfer between small metal particles and supports is important for the development of selective catalysts. Interpretation of experimental data is difficult if supports with different surface geometry are compared [2].

We have reported evidence that variable electron transfer occurs within the homologous series of Y zeolite supports – with similar surface geometry – on

\* Author to whom correspondence should be mailed.

encaged iron carbonyl clusters [3–5]. Geometric substrate effects are expected to play a minor role if only the charge-compensating cations differ. The adsorption equilibrium between  $\text{Fe}(\text{CO})_5$  and various large-pore zeolites has been studied by gravimetric and IR-spectroscopic techniques [3,4], whereas thermal decomposition was followed by thermogravimetric and in situ IR-spectroscopic methods [5]. The iron particle size distribution obtained after complete decarbonylation of  $\text{Fe}(\text{CO})_5/\text{NaY}$ -zeolite adducts depends on the preparation conditions [6,7]. The substrate effect of Y zeolites with different alkali cations on the growth of iron clusters will be reported in the present study.

Chemical state as well as the size of the iron clusters are studied by means of EXAFS and Mössbauer effect measurements.

## 2. Experimental

### 2.1. Materials

Synthetic NaY (Na-FAU;  $\text{Na}_{55.5}\text{Al}_{55.5}\text{Si}_{136.5}\text{O}_{384}$ ) from Strem Chemicals was treated with 0.1 M NaCl solution, washed, air-dried and stored over saturated  $\text{NH}_4\text{Cl}$  solution.

CsY (Cs-FAU) with the unit cell composition  $\text{Cs}_{37}\text{Na}_{18.5}\text{Al}_{55.5}\text{Si}_{136.5}\text{O}_{384}$  was prepared by ion exchange of NaY with 0.1 M CsCl solution at 293 K, washed and then dried. Before loading with  $\text{Fe}(\text{CO})_5$ , the zeolite was degassed in the reactor at 670 K for 36 ks at  $10^{-3}$  Pa, with a heating rate of  $0.033 \text{ K s}^{-1}$ .

Iron pentacarbonyl from Ventron (99.5%) was coldly distilled in the dark and stored in a stainless steel tube over molecular sieve 5A.

### 2.2. Methods

Details of thermogravimetric and in situ IR measurements are given elsewhere [5]. A stainless-steel gas-dosing system [7], connected to a quartz reactor, allowed degassing and loading of the zeolite samples with vapor of  $\text{Fe}(\text{CO})_5$  [8]. The saturated  $\text{Fe}(\text{CO})_5$ /zeolite adducts were thermolyzed under inert gas in the  $20 \times 50$  mm horizontal bed section of the quartz reactor by dipping the deeply frozen (77 K) reactor into a metal bath. Fluidized bed conditions were achieved by a horizontal vibration of the reactor with  $\nu = 50$  Hz and about 1 mm amplitude.

The decomposition was carried out at a heating rate of about  $10 \text{ K s}^{-1}$  under helium (80 kPa). Subsequently, the adducts were degassed for 50 ks at  $T = 370 \text{ K}$  and  $p = 10^{-3}$  Pa. Sample *Na-FAU/S*: final decomposition temperature  $T_{\text{max}} = 490 \text{ K}$ ; heating at  $T_{\text{max}}$  for 0.36 ks; iron content: 3.9 wt%. Sample *Cs-FAU/S*: final decomposition temperature  $T_{\text{max}} = 500 \text{ K}$ ; heating at  $T_{\text{max}}$  for 0.42 ks; iron content: 4.3 wt%.

Mössbauer spectra of the 14.4 keV  $\gamma$ -resonance of iron in zeolite samples embedded in paraffin were taken at temperatures between 1.8 and 300 K using a Fe(Rh) source.

EXAFS measurements of the K-edge of iron were carried out at liquid-nitrogen temperature with the EXAFS II spectrometer at HASYLAB (DESY, Hamburg, FRG).

### 3. Results and discussion

#### 3.1. Substrate effect on the thermal decomposition process of iron carbonyl adsorbed on faujasites

When  $\text{Fe}(\text{CO})_5$ /faujasite adducts are decarbonylated in a thermobalance, an influence of the zeolite charge-compensating cations on thermal stability can be derived from the respective weight-loss curves. The temperature at which the respective fast, endothermic decomposition period begins ( $T_i$ ) as well as the temperature at which constant weight is reached ( $T_c$ ) is lower in the case of Na-FAU substrate compared to Cs-FAU substrate (table 1).

This effect is confirmed with infrared in situ measurements, i.e. by the higher temperatures and longer decomposition times which are necessary for complete removal of the carbonyl stretching pattern from the  $\text{Fe}(\text{CO})_5$ /Cs-FAU adduct. Additional evidence on the substrate effect is obtained when the CO-stretching frequencies of the last surviving  $\text{Fe}_x(\text{CO})_y$  intermediates are compared (table 1): the CO vibrations of  $\text{Fe}_x(\text{CO})_y$ /Cs-FAU species are found

Table 1  
Substrate effect on the thermal decomposition process of  $\text{Fe}(\text{CO})_5$ /faujasite adducts

	Substrate	
	Na-FAU	Cs-FAU
Thermal stability <sup>a)</sup>		
$T_i$ (K)	390	400
$T_c$ (K)	550	570
Last intermediates <sup>b)</sup>		
CO stretching ( $\text{cm}^{-1}$ )	1895	1713 1755 1865
Sanderson electronegativity	3.55	3.36

<sup>a)</sup> Derived from thermogravimetric measurements with 10 mg of sample, using a heating rate of 2 K per minute.  $T_i$  is the temperature at which the endothermic decomposition begins; constant weight is reached at the final temperature  $T_c$ .

<sup>b)</sup> The last decomposition intermediates are characterized by their CO-stretching frequencies, obtained during in situ IR measurements.

at around  $1700\text{ cm}^{-1}$ , whereas the  $\text{Fe}_x(\text{CO})_y/\text{Na-FAU}$  intermediate vibrates at  $1895\text{ cm}^{-1}$ .

Both the enhanced thermal stability and the lower CO-stretching frequencies with Cs-FAU substrate can be rationalized in terms of increased  $\pi$ -back-bonding in the Fe–CO bond [3,5]. The Sanderson electronegativity [10] concept allows one to calculate average substrate electronegativities which clearly correlate with the effects discussed above (table 1): the increased electron donor properties of Cs-FAU substrate compared to Na-FAU increase the stability of the Fe–CO bond via  $\pi$ -bonding and, in turn, decrease the force constant of the respective CO bonds. This results in lower CO-stretching frequencies as observed with Cs-FAU substrate.

### 3.2. Characterization of the thermolytic products of $\text{Fe}(\text{CO})_5$ adsorbed on Na-FAU

The Mössbauer spectrum of  $\text{Fe}(\text{CO})_5$ , decomposed on Na-FAU substrate by very fast heating in the shallow bed mode, shows a sextet both at 4.2 K and 300 K with the typical hyperfine splitting of bulk iron ( $B_{\text{eff}} \approx 33\text{ T}$  at 300 K; fig. 1A). Additionally, another iron phase with a larger hyperfine splitting of  $B_{\text{eff}} \approx 48\text{ T}$  can be observed. The latter phase represents about 50% of the total absorption area and might be assigned to small iron(III) oxide species. The Fourier transform of the EXAFS spectrum (fig. 2A) of the same sample clearly resembles the pattern of the bulk iron spectrum.

### 3.3. Characterization of the thermolytic products of $\text{Fe}(\text{CO})_5$ adsorbed on Cs-FAU

The Mössbauer spectra of  $\text{Fe}(\text{CO})_5$ , decomposed on Cs-FAU substrate (sample *Cs-FAU/S*) under conditions similar to those used with the sample *Na-FAU/S*, show magnetic relaxation phenomena at temperatures below 77 K (fig. 1B). At lower temperatures, the main iron phase is represented by a sextet with a hyperfine splitting typical of iron(III) oxides such as  $\alpha\text{-Fe}_2\text{O}_3$  or  $\gamma\text{-Fe}_2\text{O}_3$  ( $B_{\text{eff}} \approx 48\text{ T}$ ) [11]. By rising the temperature, the oxide sextet relaxes to a quadrupole-split doublet with  $V_{zz} \approx 1.13\text{ mm s}^{-1}$ . The magnetic relaxation of the *Cs-FAU/S* sample indicates the formation of very small iron(III) oxide clusters. This interpretation is confirmed by evaluation of the EXAFS spectrum of sample *Cs-FAU/S*. The respective Fourier transform (fig. 2B) shows a main peak at a next neighbour distance typical of iron(III) oxides ( $d_{\text{nn}} \equiv 0.18\text{ nm}$ ).

### 3.4. Substrate effect on the formation of iron clusters

The most surprising result of the decarbonylation of  $\text{Fe}(\text{CO})_5/\text{zeolite}$  adducts is the formation of completely different products – mainly  $\alpha\text{-Fe}$  in the case of a Na-FAU matrix and small iron(III) oxide clusters in the case of a

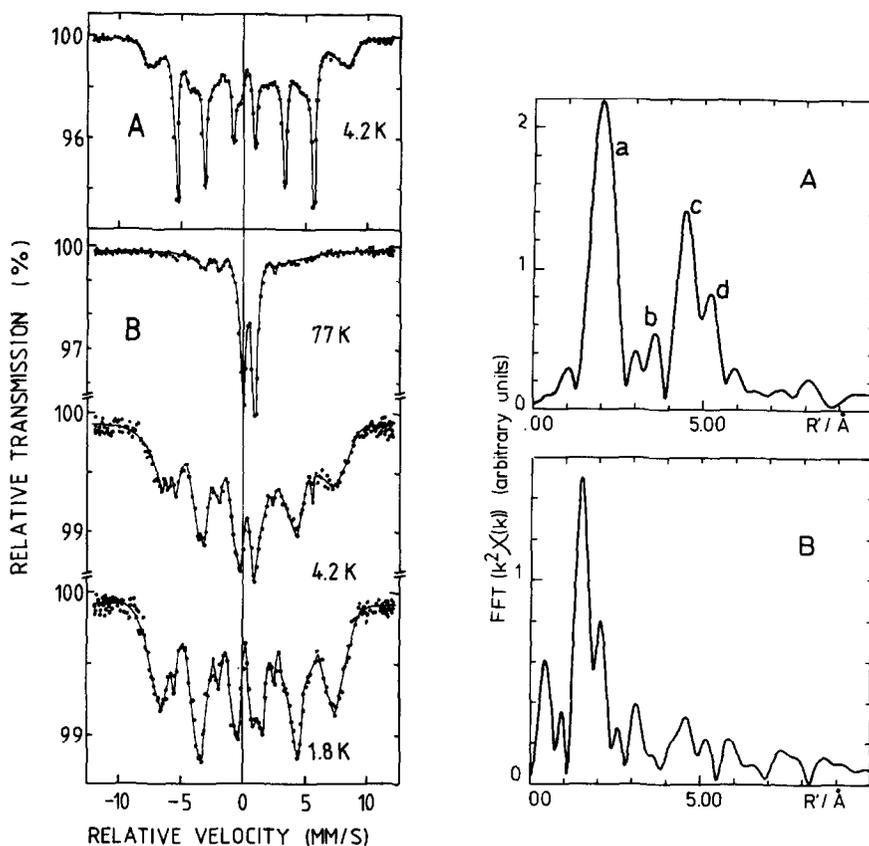


Fig. 1. (A) Mössbauer effect spectra of sample *Na-FAU/S* at  $T = 4.2$  K; (B) Mössbauer effect spectrum of sample *Cs-FAU/S* at  $T = 1.8$ , 4.2 and 77 K. The lines are given to guide the eye and do not correspond to least-square fits.

Fig. 2. (A) Fourier transform of the EXAFS spectrum of sample *Na-FAU/S*; (a) first and second nearest neighbour shells (nns) plus Fe(III) oxide; (b) third; (c) fourth and fifth; and (d), sixth nns; the peak positions  $R'$  are shifted by 0.02–0.05 nm from the actual distances due to phase shift effects [13]. (B) Fourier transform of the EXAFS spectrum of sample *Cs-FAU/S*. Peak positions: see (A).

Cs-FAU matrix – despite of the comparable experimental procedure. This substrate effect has been proved to be reproducible. It has therefore to be associated with the different alkali cations present in the zeolite.

Because hydrolysis during ion exchange can be excluded in case of Na-FAU and Cs-FAU as well, the formation of a solid acid during dehydration is improbable. Thus, after carbonyl decomposition, oxidation of the iron clusters by means of protons is unlikely. However, it is shown above that the decomposition process itself is strongly influenced by the nature of the alkali cation.

From the arguments discussed in the beginning of this section it can be concluded that the Cs-FAU substrate increases the Fe–CO bonding strength due to a decrease in the average electronegativity. This leads to *smaller* iron cluster sizes upon thermolysis because intermediates are stabilized by this effect and will not extensively diffuse.

It has been found that the ionization potential of very small aggregates is a function of the cluster size [12]. The very small clusters in Cs-FAU are expected to be more sensitive to oxidation than the larger clusters in Na-FAU substrate. An explanation for the origin of the oxygen still cannot be advanced. Since the total leak rate of the gas-dosing system ( $2 \times 10^{-3} \text{ Pa dm}^3 \text{ s}^{-1}$ ) does not suffice to oxidize the amount of iron present in the respective samples, an inner oxidation process may be involved alternatively.

#### 4. Conclusion

The combined study of the decomposition process and the final thermolytic products of iron pentacarbonyl adsorbed on Na- and Cs-faujasite provides clear evidence for a substrate effect on the respective growth of iron clusters.

Due to the higher electron donor properties of Cs-FAU substrate compared to Na-FAU, increased  $\pi$ -backbonding leads to a higher thermal stability of the Fe–CO bond. This, in turn, favours the generation of smaller cluster sizes since intermediates are stabilized by this effect and will not extensively diffuse. Small iron oxide particles are the final product in case of Cs-FAU matrix under the experimental conditions used. With Na-FAU substrate to a large extent iron(0) particles are generated. Variation of the electronic properties of the substrate will allow to adjust the charge transfer onto the clusters as well as the resulting product and size distribution.

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