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Highly Dispersed Supported Iron Particles from the Decomposition of Iron Carbonyl on HY Zeolite

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^{13}C-NMR spectroscopy has been applied to the investigation of the adsorption, binding, and behavior of $Fe(CO)_5$ on HY zeolite (activated at 400°C). Photochemical and thermal decompositions were followed and led to the identification of different interactions with the surface. A stronger interaction, characterized by a larger charge transfer, is observed for the various $Fe(CO)_{x<5}$ moieties present in the course of the photochemical decomposition as compared to the thermally induced process. Highly dispersed and pyrophoric iron can be prepared in this manner.

INTRODUCTION

The search for means of preparing small iron particles on various supports has been motivated, for many years, by both practical and theoretical interests. Indeed, from a practical viewpoint, one searches for catalysts with a high surface area which would naturally be of great interest as ammonia or Fischer-Tropsch catalysts. Theoretically, small particles are also of great current interest in view of the possibility that they could show different catalytic behaviors. Of course, the support may play a major role because the adherence of the metal particles to the support determines the mobility and the shape of the small particles (and then the thermostability of the catalysts) and because a strong interaction with the support can, eventually, lead to a (partially) oxidized metal-support interface which can result, in turn, in modifications in the electronic properties of the metal particles. Such an effect has been recently reported for Ni supported on alumina (*1*).

Quite a strong interaction has been shown to be present in systems where reactive small iron particles were present, as prepared by exchange of magnesium cations at the surface of magnesium hydroxy carbonate powders of high surface area followed by drying and direct reduction in hydrogen (*2*) of the Fe(III) ions introduced in this manner.

Following the early suggestion by Parkyns (*3*) (for Ni), a possibility for preparing small metal particles also exists in the use of metal carbonyls as precursors and in achieving their controlled decomposition. Recent work in this area has been reported by Anderson *et al.* (*4-6*), Robertson and Webb (*7*), Smith *et al.* (*8*), and Coudourier *et al.* (*9*). In these studies, the various stages in the decomposition of the metal carbonyl(s) and the interaction with the support were monitored by ir spectroscopy. In a recent report on the decomposi-

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tion of $Ni(CO)_4$ on various oxidic supports, we have shown that ^{13}C-NMR could provide interesting information and a deeper insight into the interaction between the precursor and the support (*10*).

The present paper reports on the thermal and photochemical decompositions of $Fe(CO)_5$ interacting with HY zeolite, obtained by decomposition and evacuation at 400°C of NH_4Y zeolite. As will be shown, both methods lead to highly dispersed iron particles although important differences are noted for the interaction (by charge transfer) between the intermediates and the surface when comparing both treatments. Attention is also paid to the reversibility of the various decomposition steps. The present work is also in line with the previous proposal that studying the decomposition of metal carbonyls could bring relevant information on the understanding of metal–CO bonding (*11*).

EXPERIMENTAL

Material. $Fe(CO)_5$ (from Alpha Ventron Co.) was carefully degassed and kept in the dark. The NH_4Y zeolite was evacuated at 110°C and decomposed at 400°C in a vacuum of about 10^{-5} Torr. Next, 0.2 to 0.3 ml of $Fe(CO)_5$ were distilled onto the activated support. Assuming an active surface of about 400 $m^2\ g^{-1}$ for the zeolite and considering the cross section of the $Fe(CO)_5$ molecule (about 30 Å), the approximate coverage is then 0.8.

Magnetic resonance measurements. ^{13}C-NMR spectra were recorded on a Bruker WP-60 spectrometer operating in the Fourier transform mode and using D_2O as external reference and lock. Calibration of the chemical shift scale was carried out by referring the shifts to benzene and/or ethanol through the difference between the spectrometer carrier frequency and the peak considered (*16*). The chemical shifts are finally expressed with respect to TMS $[(CH_3)_4Si]$. The average error on the chemical shifts is about 0.3 ppm. No bulk magnetic susceptibility corrections were made.

Ferromagnetic resonance signals from the dispersed Fe particles were observed at room temperature using a Bruker BER-420 spectrometer.

Analysis of the samples. The Fe content of the sample was measured by X-ray fluorescence induced by proton bombardment (1.8 MeV). The $K\alpha$ lines of Fe referred to the $K\alpha$ lines of Ag were used for counting. The iron contents determined in the samples decomposed thermally were 7.7% (±0.3) for sample A and 5.9% (±0.2) for sample B, respectively, and 10.2% (±0.4) for sample C which was decomposed photochemically, all values being quoted in weight percent Fe.

Particle size measurements. Particle size distributions were obtained by transmission electron microscopy using a Philips EP-301 instrument operating at 100 kV. The powdered sample was suspended in butanol and ultrasonically dispersed for about 15 min, and drops from the solution were laid onto a grid covered by a Formvar film.

Photolysis. An iodine lamp of variable power was used. In the high frequency region (uv) the NMR Pyrex tube limited the useful wavelength to 300 nm. $Fe(CO)_5$ absorbs in this region with an extinction coefficient, ϵ (300 nm), of about 2000 which characterizes the allowed d–d band corresponding to the 5 e′–5 e_1' transition (*17*).

RESULTS AND DISCUSSION

Interaction of $Fe(CO)_5$ with HY Zeolite

The *^{13}C chemical shift* of the carbonyl group (vs TMS, as external reference) in the adsorbed compound varies little with coverage. It is 209.9 ppm (at 293 K) as compared to the tabulated value of 209.0 ppm (*12*) which characterizes pure liquid $Fe(CO)_5$. The reason for this can be that the interaction of $Fe(CO)_5$ with the zeolite surface is rather small and comparable to weak solvent effects (δ_{CO} = 210.9 ppm for

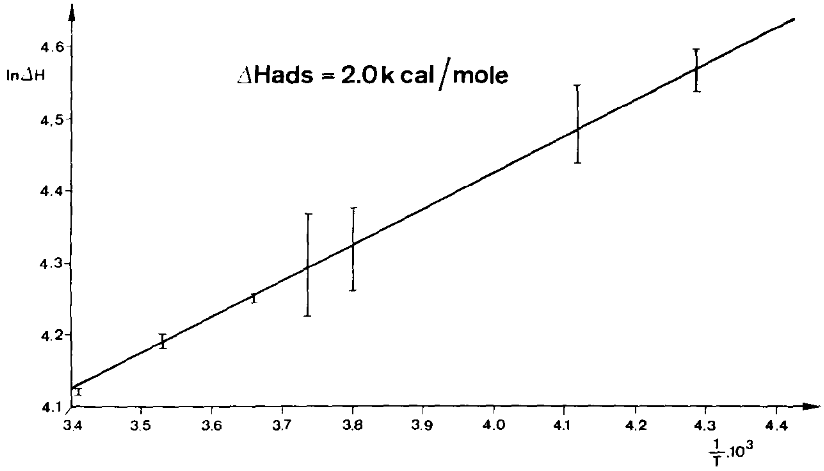

FIG. 1. Dependence of the logarithm of the linewidth for the ^{13}C resonance signal from $Fe(CO)_5$ as a function of reciprocal temperature.

30% $Fe(CO)_5$ in $CDCl_3$ (at 304 K) and δ_{CO} = 213.6 ppm in C_6H_6 (*12*)). Hence, this would suggest that the $Fe(CO)_5$ framework remains essentially unchanged in the adsorbed form. Another possibility could be a fortuitous compensation between diamagnetic (high field) and paramagnetic (low field) shifts (*13*). We will show, however, that the paramagnetic contribution is predominant for the decomposition intermediates and therefore, we favor the first interpretation.

Let us recall, at this point, the rather large chemical shifts observed for $Ni(CO)_4$ (about 10 ppm) which reflect the greater deformation of the $Ni(CO)_4$ molecule upon chemisorption, possibly because the fourfold coordination is more easily rearranged (for example, from tetrahedral to square planar) than the fivefold coordination. Such a rearrangement was indeed proposed for $Ni(CO)_4$ interacting with a surface acidic hydroxyl group (*10*).

Nevertheless, as shown by the linewidth, the mobility of the $Fe(CO)_5$ molecule is quite restricted. $\Delta H = 50 \pm 5$ Hz in the adsorbed state as compared to 20 Hz in $CDCl_3$ solution and a similar value of about 50 Hz for adsorbed $Ni(CO)_4$. From the temperature dependence of the linewidth, as shown in Fig. 1, and assuming a statistical distribution of barrier heights for diffusion as well the validity of the localized adsorption model, Resing (*14*) has proposed that the heat of adsorption can be estimated as it should be twice the height of the barrier to diffusion, $\Delta H_{ads} = 2\Delta H_d$, the relationship between ΔH_d and the linewidth, ΔH being:

$$\Delta H(\mathrm{Hz}) = C \cdot \exp(\Delta H_d/RT) \qquad (1)$$

in the temperature domain in which the relaxation times are dominated by the diffusional motion of the molecule. The activation energy for diffusion is estimated to be about 1.0 kcal mol^{-1}, resulting in a heat of adsorption on this basis of about 2.0 kcal mol^{-1}. This is a surprisingly low value, and may not have absolute significance, but we do believe that it indicates a genuinely weak interaction of the $Fe(CO)_5$ molecules with the zeolite surface.

While the linewidth is closely associated with the transversal (spin–spin) relaxation, interesting information is also obtained by the consideration of the *longitudinal relaxation behavior*, as obtained from T_1 (spin–lattice) relaxation data. Using different repetition times during the accumulation of the data (therefore allowing for various

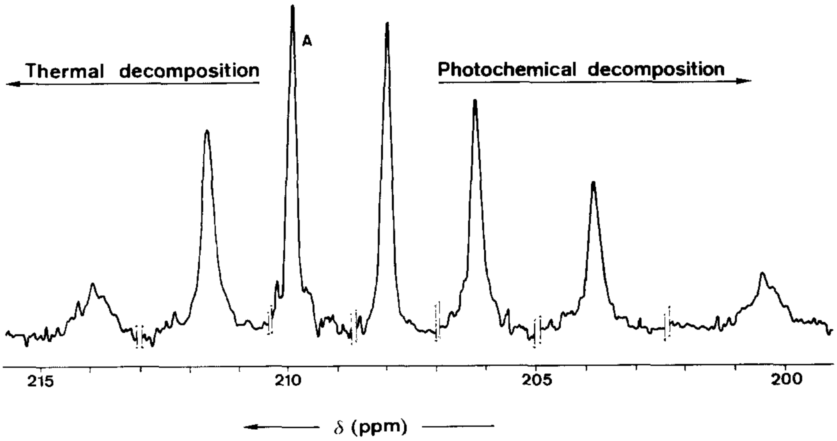

FIG. 2. ^{13}C-NMR spectra as observed during the progressive thermal and photochemical decompositions of $Fe(CO)_5$. (A) indicates pure $Fe(CO)_5$.

time lags between individually accumulated spectra), the longitudinal relaxation time, T_1, has an estimated value of about 10 s which must be compared to the pure liquid value of 50 s (*15*). The rather long relaxation time observed in the adsorbed state results from poor relaxation mechanisms of the spin rotation or chemical shift anisotropy types. Although weak, the interaction with the surface can nevertheless be observed in the decrease by a factor of 5 of the T_1 value.

As a conclusion, we also feel in line with recent suggestions (*13*) that in the case of rather weak interactions with the surface, the best information on the nature of the adsorbed state is obtained from estimations of relaxation times.

Decomposition of $Fe(CO)_5$ on the HY Zeolite

As previously proposed for the photolysis of $Fe(CO)_5$ in low-temperature matrices, the decomposition of $Fe(CO)_5$ occurs stepwise leading to atomically dispersed Fe particles (*19*):

$$Fe(CO)_5 \overset{(a)}{\rightleftarrows} Fe(CO)_4 \overset{(b)}{\rightleftarrows} Fe(CO)_3 \overset{(c)}{\rightleftarrows} Fe(CO)_2 \overset{(d)}{\rightleftarrows} Fe(CO) \overset{(e)}{\rightleftarrows} Fe \quad (2)$$

When considering the decomposition of the adsorbed molecule, several questions arise, namely: (a) the reversibility of the decomposition steps; (b) the nature of the interaction of the various intermediates with the surface; and (c) the possibility of clustering for Fe. These are the main points which will be dealt with in the following discussion. The qualitative behavior of the ^{13}C-NMR resonance of the carbonyl group, for both the thermal and the photochemical decompositions, is illustrated in Fig. 2.

Thermal Decomposition

When the temperature is progressively raised from 20 to 70°C, the sample being heated by 5°C steps of 30 min, the intensity of the ^{13}C-NMR line attributed to the CO groups decreases monotonically until a ratio CO/Fe slightly less than unity is observed. In parallel, the linewidth progressively increases from the initial 50-Hz value to about 140 Hz. In addition, the resonance progressively shifts downfield (to higher chemical shifts), from 209.9 ppm at 20°C up to 214 ppm after decomposition at 70°C (see Fig. 2).

In addition, interesting information is also obtained if CO is tentatively readsorbed. If the decomposition of the $Fe(CO)_5$ is stopped at CO/Fe values slightly less than unity, CO can be readsorbed, independently of the CO pressure, until the final CO peak intensity corresponds to one-fifth of the initial spectral intensity, hence corresponding to a CO/Fe ratio of 1, and the linewidth decreases from 140 to 80 Hz. If, however, $Fe(CO)_5$ is decomposed to completion, no uptake of CO is detected by ^{13}C-NMR. Ferromagnetic resonance signals are observed in both cases, and therefore, the ferromagnetism of the sample (due to small Fe particles) cannot be made responsible for this difference in behaviors.

The variation of the NMR parameters is easily interpreted as follows. For the chemical shift, let us focus our attention on the paramagnetic contribution to the shielding parameter. It is essentially determined by variations in the energy of the excited state corresponding to the π^* antibonding orbital(s) of the CO group(s), neglecting the average C 2p radius and the bond order variations for the C atoms (*10, 12*). If the electron back-donation from the metal (Fe) to CO is favored, the excited π^* state is more stabilized, and this raises the paramagnetic contribution to the chemical shift (note that this contribution parallels the well-known effect of Van Vleck orbital paramagnetism). During the thermal decomposition, $Fe(CO)_5$ is progressively stripped, progressively and statistically releasing the CO molecules. As CO is evolved, the electronic charge density on Fe increases, and more extensive back-donation to the CO groups that are left occurs. Therefore, however, the charge transfer between the $Fe(CO)_x$ residues and the surface must remain rather small, confirming the weak interaction between these residues and the surface. The progressive decrease in spectral intensity of course reflects the progressive loss of CO while the increase in linewidth shows an increasing (although still weak) interaction with the surface.

As CO can be readsorbed to reach CO/Fe = 1 when the carbonyl is not decomposed to completion, one can conclude that the decomposition of $Fe(CO)_5$ in such conditions initially results in 100% dispersed Fe. The absence of an NMR signal when the decomposition has been fully completed before readsorption is interpreted as due to clustering of the Fe, leading to lower dispersion.

Photochemical Decomposition

The variations in linewidth and signal intensity follow patterns similar to those observed in the course of the thermal decomposition as shown in Fig. 2. The intensity of the resonance signal decreases with increasing exposure time or power of irradiation. Results from CO readsorption experiments also confirm the former observation: The intensity of the CO resonance is restored to one-fifth of its original value when the decomposition of $Fe(CO)_5$ is not fully completed, while fully decomposed $Fe(CO)_5$ does not lead to any observable CO NMR signal. The initial linewidth (50 Hz) rises to 300 Hz (higher than the thermal decomposition value, for CO/Fe slightly smaller than unity) and decreases to 200 Hz after CO readsorption (CO/Fe = 1).

Surprisingly enough, the CO resonance now moves highfield (toward lower chemical shift values, as shown in Fig. 2). As discussed formerly, this corresponds to a smaller back-donation of electrons from Fe to the π^* orbitals from the CO groups that are left, as CO is progressively removed, hence resulting in a decrease of the paramagnetic contribution. It must therefore be concluded that the charge transfer from the Fe carbonyl residues to the surface increases with increasing stripping of the precursor and is much higher than in the thermal decomposition.

During photolysis, d–d transitions, such as the $d_{x^2-y^2}$, $d_{xy} \rightarrow d_{z^2}$ excitations, are stimulated, thereby populating the d_{z^2} orbital and resulting in a weakening of the Fe–axial CO bond (*17*). The departure of CO is therefore facilitated, and in the meantime the Fe excited state can interact more efficiently with the surface resulting from a net charge transfer from the Fe moiety to the surface. This charge transfer remains in the ground state of the Fe–surface bond which explains our observations.

It is then concluded that photochemical decomposition leads initially to 100% dispersed Fe which interacts with the surface more effectively than the corresponding system prepared thermally. That is confirmed by the higher NMR linewidth. Clustering also occurs when the decomposition is completed.

Comparison between $Fe(CO)_5$ and $Ni(CO)_4$ Interacting with the Zeolite Surface

As suggested earlier in this paper, a possible reason for the stronger interaction of $Ni(CO)_4$ (as compared to $Fe(CO)_5$) with the zeolite surface can be an easier rearrangement of the adsorbed molecule. Tetrahedral $Ni(CO)_4$ can easily adopt a square planar configuration on the basis of symmetry arguments. In this way, the central Ni atom is exposed to the surface and a strong interaction can take place.

The bipyramidal $Fe(CO)_5$ can also rather easily be transformed to a square pyramidal configuration, according to the Berry pseudorotation mechanism. Calculated and estimated (from NMR data) values for the activation energy of such a rearrangement are 1.5 and 1.0 kcal mol^{-1}, respectively (*18*). Nevertheless, *ab initio* calculations for the latter configuration show that the central Fe atom stays rather buried inside the molecule. Indeed, the axial -metal–basal ligand angle is 98° while the basal -metal–basal ligand angle is equal to 164°. Hence, the Fe atom will not interact effectively with the surface, and this explains the observed difference in the behaviors of the Fe and Ni carbonyls.

When CO is progressively removed, by either thermal decomposition or photolysis, steric effects do not play a major role any more, and the interaction with the surface depends effectively on charge transfer from the residue to the surface as discussed before.

Particle Size Analyses

Samples decomposed to completion are all pyrophoric indicating the presence of very small Fe particles. This also prevents direct observation of the small Fe particles by electron microscopy.

Figure 3 shows the particle size histogram for sample A which was decomposed thermally. The size distribution of the Fe particles was estimated from the distribution of the oxide particles as measured by electron microscopy. The smallest (observed Fe particles would have a size of about 12 Å. By contrast, the oxide particles could not be observed for the sample (C) decomposed photochemically. Therefore, these particles should have dimensions smaller than 15 Å (corresponding to Fe smaller than 9 Å), despite the sintering which occurs upon oxidation.

This is a clear demonstration of the role played by the interaction with the surface: Stronger interactions lead to smaller particles.

CONCLUSIONS

The thermal and photochemical decompositions of $Fe(CO)_5$, adsorbed in HY zeolite, lead to the formation of highly dispersed Fe particles. The photochemical decomposition results in smaller particles because of the stronger interaction between the intermediates and the zeolite surface.

The use of ^{13}C-NMR spectroscopy gives a deeper insight into the identification (nature and strength) of the interactions between the precursor and its decomposition products and the surface. While a small interaction is characteristic of $Fe(CO)_5$ and its thermal decomposition residues, a much stronger interaction characterizes the moieties obtained by photolysis because of

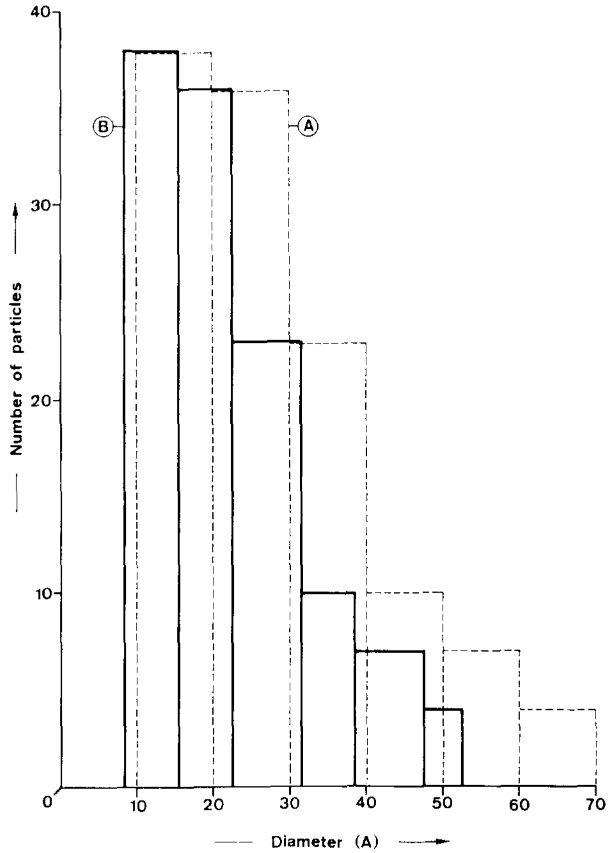

FIG. 3. Particle size distributions for sample A (thermal decomposition). The oxide particle distribution is measured from electron micrographs while the Fe particle distribution is estimated from the former one. (A) (dotted lines) corresponds to the oxide particles and (B) (solid lines) to the Fe particles.

the electronic excitation of the adsorbed molecule during the decomposition process. In addition, CO readsorption experiments show that 100% dispersion of Fe can be achieved in systems for which the CO/Fe ratio is smaller than unity, the clustering of Fe occurring only when the decomposition is fully completed.

Our results demonstrate in addition that ^{13}C-NMR can be used, at least in some cases, as successfully as infrared spectroscopy and especially draw attention to the role played by the precursor–surface interaction in determining the size of the metal particles. Better control of such interactions and their quantitative monitoring could possibly result in the preparation of systems with very high metallic dispersion.

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