Catalysis Letters 2 (1989) 323–328

MÖSSBAUER AND uv-VISIBLE SPECTROSCOPIC STUDY OF THE INTERACTION OF BIS(TOLUENE)IRON(0) WITH SURFACE HYDROXYL GROUPS OF SILICA

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Received 26 September 1988; accepted 14 April 1989

Mössbauer and in-situ uv-visible spectroscopy to probe the interaction of toluene solutions of solvated iron atoms with silica gel having different concentrations of surface hydroxyl groups. Surface hydroxyl groups on silica are found to facilitate the decomposition of bis(toluene)iron(0) well below its "normal" solution phase decomposition temperature of −30 ° C. The silica supported iron clusters formed in this way are found to be finely divided crystallites of α-Fe_2O_3 with diameters less than 50 Å.

1. Introduction

Solution phase metal atom impregnation techniques provide a novel method of preparing zeolite, oxide, carbon and polymer supported metal catalysts [1–4]. This approach can offer certain advantages over traditional catalyst preparation methods. These include the ability to form very small metal clusters with narrow particle size distributions in an extremely mild-one-step-process, without having to resort to high temperature reduction steps which often leads to undesirable sintering of the supported metal clusters. In this study the effect of the silica surface hydroxyl group concentration on the crucial stage of the birth and growth of iron clusters from toluene solvated iron atoms is investigated by Mössbauer and in situ uv-visible (microsolution) spectroscopy. Briefly, we have found that the surface hydroxyl groups of silica gel facilitate the decomposition of bis(toluene)iron(0) below its "normal" solution phase decomposition temperature of −30 ° C. Moreover, for iron atom loadings below that of the surface hydroxyl group concentration of silica, the resulting materials comprise finely dispersed supported α-Fe_2O_3.

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2. Experimental

For the Mössbauer experiments, $^{57}Fe/^{56}Fe = 1/1$ powder was vaporized into liquid toluene held at about $-105\,^{\circ}C$ in a rotary metal vapor reactor [5]. The resulting solution of bis(toluene)iron(0) was impregnated into silica gels dehydroxylated at 200 °C and 600 °C, containing 5 and 1 OH group per 100 $(Å)^2$ respectively [6], to form two kinds of supported iron clusters, namely, Fe/SIL-200 and Fe/SIL-600 using techniques similar to those described previously [5]. The detailed procedures for the Mössbauer experiments, uv-vis spectroscopy and FMR experiments are described in ref. [1], ref. [7] and ref. [8], respectively.

3. Results and discussion

The Mössbauer spectra of Fe/SIL-200 and Fe/SIL-600 are displayed in fig. 1 and their corresponding parameters from computer simulation are listed in table 1. Isomer shifts were calculated based on the hyperfine splitting of Fe NBS standard foil. The best fit isomer shifts (0.33 and 0.347 mm/sec) and quadrupole splittings (1.00 and 0.99 mm/sec) so obtained confirm that the iron in these samples is no longer present in form of bis(toluene)iron(0), which has Mössbauer parameters of $\delta = 0.39$ mm/sec and $\Delta = 0.50$ mm/sec. The observed values are however, in perfect agreement with those of Kundig et al. ($\delta = 0.32 + 0.02$; $\Delta = 0.98 + 0.01$) for α-Fe_2O_3 particles of diameter less than 50 Å [9]. However, ferric cations supported on silica give Mössbauer parameters similar to α-Fe_2O_3. In order to provide an evidence of the formation of α-Fe_2O_3 clusters, a FMR(ferromagnetic resonance) spectrum of Fe/SIL-600 as recorded. The temperature dependence of the g-value and band width of FMR band is shown in table 2. As the recording temperature of FMR spectrum increased, g-value and band width decreased, indicating that iron is present not as an isolate Fe^{3+} ion but as a cluster. The ESCA spectrum of Fe/SIL-600 suggests the presence of Fe_2O_3 indicated by the main band of B.E. at 710.7 eV and a satellite band at 725 eV. Hence, the complication in the assignment of the Mössbauer band arising from the presence of a small amount of Fe^{3+} ion and Fe(0) can be eliminated. Thus, when the total number of iron atoms per gram of silica gel is less than the total number of surface hydroxyl groups per gram of SIL-600 and SIL-200 (e.g., SIL-600 has 5.5×10^{20} OH per g of silica; 0.1 wt% Fe corresponds to 1.07×10^{19} atoms per g of silica), all iron atoms appear to be oxidized to α-Fe_2O_3, presumably via reaction of surface hydroxyl groups with bis(toluene)Fe(0). The asymmetric doublets of fig. 1 for Fe/SIL-200 and Fe/SIL-600, as discussed by Garten [10] can arise from one, or a combination of a Goldanskii-Karyagin effect [11], a relaxation phenomenon [12], or a broad particle size distribution (recall that the isomer shift has been shown to be a strongly varying function of the particle size for very small iron clusters [13] and probably holds true for iron oxide clusters).

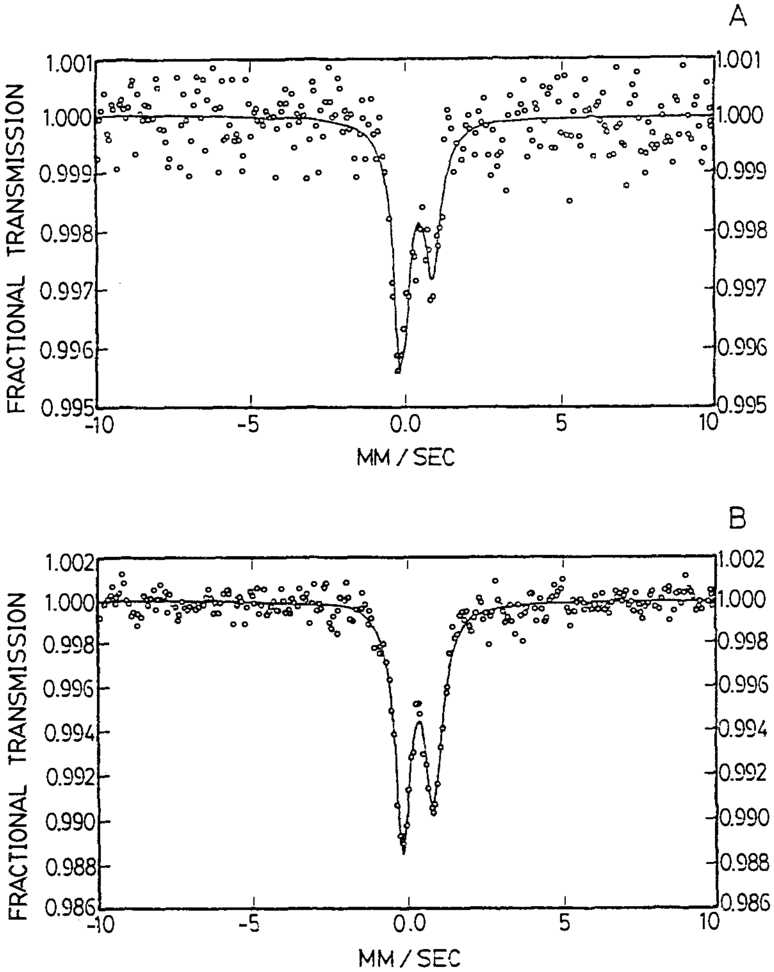

Fig. 1. Room temperature Mössbauer spectra of (A) Fe/SIL-200 and (B) Fe/SIL-600 generated by solution phase toluene solvated iron atom impregnation techniques.

Table 1
Mössbauer parameters for ^{57}Fe/SIL-200 and ^{57}Fe/SIL-600

	^{57}Fe/SIL-600	^{57}Fe/SIL-200
Loading (wt%)	0.100	0.044
Isomer shift (δ, mm/sec)	0.330	0.347
Quadrupole splitting (Δ, mm/sec)	1.00	0.99
A_2/A_1 [a]	0.934	0.681
$\Delta\nu_{1/2}(2)/\Delta\nu_{1/2}(1)$ [b]	1.09	1.12

[a] A_2 = area of high energy band; A_1 = area of low energy band.

[b] $\Delta\nu_{1/2}(2)$ = band width of the half height of the high energy band; $\Delta\nu_{1/2}(1)$ = band width of the half height of the low energy band.

Table 2
Temperature dependence of the g-value and the band-width in the FMR band of Fe/SIL-600

Recording temperature (°C)	−150	−90	25	60	100	200	260
band-width (Gauss)	no band	2200	1280	1100	940	730	640
g-value	–	3.2	2.46	2.36	2.30	2.23	2.20

The latter effect would give rise to a distribution of isomer shifts and quadrupole splittings. As the line intensities and widths of the Mössbauer doublet are somewhat different, fitting the spectra with range of isomer shifts and quadrupole splittings would probably better approximate the physical structure than G-K and relaxation effects. The Mössbauer parameters are particle size dependent. However, it is very difficult to correlate isomer shift and quadrupole splitting with cluster size. Van der Kraan reported that the quadrupole splitting was larger and the recoil-free fraction smaller for the surface atoms than for the bulk atoms in small α-Fe_2O_3 clusters ($\simeq 7$ nm) [14]. The quadrupole splitting of Fe/SIL-600 (1.00 mm/sec) is almost the same as that of Fe/SIL-200 (0.99 mm/sec). Furthermore, the band areas of the quadrupole doublet of Fe/SIL-600 and Fe/SIL-200 are 6.73×10^7 counts/(g ^{57}Fe) and 6.66×10^7 counts/(g ^{57}Fe), respectively, indicating that two samples have a similar effective Debye temperature. Hence, the G-K effect observed in the sample of Fe/SIL-200 (unequal band area but with equal widths–table 1) is not ascribed to the larger surface to volume ratio arising from the smaller particle size. Fe/SIL-200 provides the higher concentration of surface OH sites. The perturbation in the surface electric field of small Fe_2O_3 clusters arising from the interaction of small iron clusters with OH groups could be manifest as line asymmetry arising from the G-K effect [11]. Conversely, the asymmetry in the Mössbauer doublet spectrum of sample Fe/SIL-600 may be more akin to relaxation effect (equal band area but unequal widths–table 1).

The uv-visible spectrum of iron vapour deposited into a 10% toluene/methylcyclohexane solution film held at 150 K shows three main absorptions at 300(m), 365(w), and 436(s) nm [7]. In order to gain an insight into the interactions of silica gel with bis(toluene)Fe(0) at low temperatures, Fe atoms were codeposited with toluene onto a cooled self supported silica gel wafer (dehydrated at 25°C under 7×10^{-7} torr for 24 hours) as a thin-quasi-liquid film and the uv-visible spectrum was recorded (fig. 2). Three bands were observed at 297(m), 350(vw), and 436(s) nm for the 150 K deposit (fig. 2(B)). The pattern of the three bands is essentially the same as that of bis(toluene)Fe(0) [7]. Cooling the sample to 50 K does not alter the spectrum (fig. 2(C)), whereas cooling the sample of iron atom deposited into a 10% toluene/methyl cyclohexane solution film to 50 K changed the spectrum [7], indicating that the transformation of bis(toluene)iron

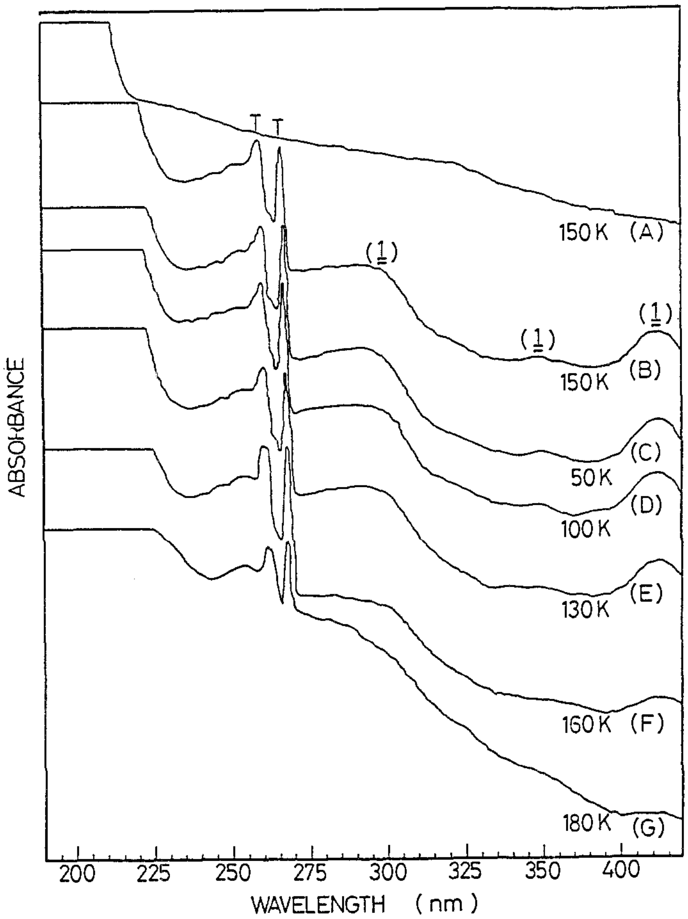

Fig. 2. uv-visible spectra of (A) a silica gel self-supporting wafer at 150 K, (B) the result of depositing iron atoms with toluene at 150 K onto (A) (Fe/toluene ≈ 1/1000), (C) the sample in (A) cooled to 50 K, (D)–(G), the sample in (C) warmed to 100 K, 130 K, 160 K and 180 K (T represents toluene absorptions and (1) denotes bis(toluene)iron(0) absorptions).

into low temperature form was inhibited by the matrix of silica gel. Warm up from 50 K to 130 K for 4 hrs also causes little change in the spectrum (fig. 2(D), 2(E)). However, the intensities of the three bands due to bis(toluene)Fe(0) do begin to decrease at 160 K with rapid disappearance setting in around 180 K. The fact that this temperature is roughly 70 K below the solution phase decomposition temperature of bis(toluene)Fe(0) in the absence of the silica support (~ 250 K) indicates that the decomposition process of bis(toluene)Fe(0) is facilitated by the surface hydroxyl groups on the silica gel, which subsequently may provide the nucleation sites for the formation of iron clusters.

The results of this study demonstrate that the interactions of the surface hydroxyl groups of silica with bis(toluene)Fe(0) appear to play a key role in the decomposition of bis(toluene)Fe(0) as well as subsequent nucleation events which lead to the genesis of the supported iron clusters.

Acknowledgements

The generous financial assistance of NSERC and Connaught Foundation of the University of Toronto is greatly appreciated. G.A.O. acknowledges 3M Co. St Paul, for financial support of his sabbatical leave of absence from U of T.

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