

## Evidence for the Photodeposition of Elemental Iron in Porous Vycor Glass

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The photochemistry of metal carbonyls adsorbed onto high surface area supports, at least initially, is similar to that found in fluid solution. However, the catalytic activity of photoactivated hybrid systems differs from that found in homogeneous solution. In some cases, differences in efficiency and selectivity, relative to fluid media, are thought to reflect constraints imposed by the support.<sup>1–3</sup> In other cases, the chemistry itself differs significantly from that found in fluid solution. For example, photoactivation of tungsten and molybdenum hexacarbonyls physisorbed onto porous Vycor glass (PVG) leads to intermediates that catalyze the conversion of CO<sub>2</sub> to CH<sub>4</sub>.<sup>4,5</sup> A similar chemistry occurs with Fe(CO)<sub>5</sub> although, in this case, the observed reactivity is dependent on initial loading. At low loadings, photoactivation leads to intermediates that exhibit a catalytic chemistry similar to that observed in fluid media.<sup>3,6</sup> With higher loadings,  $\geq 10^{-4}$  mol of Fe(CO)<sub>5</sub>/g, photolysis leads to Fe<sub>3</sub>(CO)<sub>12</sub>, and continued photolysis of the trimer leads to species that catalyze CH<sub>4</sub> evolution.<sup>7</sup> Whether the goal is characterizing catalytic activity, photodepositing nanocomposites, or patterning transparent magnetic phases in glass,<sup>8–11</sup> the nature of the species deposited, their oxidation states, and, in a porous support, levels of aggregation are crucial. Recent experiments in this laboratory have focused on characterizing the photodeposited metals. Data presented here show that, although the photolyses are carried out in air, ca. 50% of the deposited iron is present as zerovalent Fe aggregates, with the remainder present as an Fe<sup>3+</sup> oxide.

PVG samples containing  $100 \pm 10$  Å diameter cavities<sup>10</sup> were extracted and calcined<sup>6,10</sup> and then impregnated with vacuum-distilled Fe(CO)<sub>5</sub> by previously described vapor deposition procedures.<sup>6</sup> UV-visible and diffuse reflectance FTIR (DRIFT) spectra show that the complex physisorbs onto PVG without disruption of its primary coordination sphere.<sup>6</sup> UV photolyses ( $\leq 350$  nm, ca.  $2 \times 10^{-9}$  einstein/(s cm<sup>2</sup>)) reduces the near-UV absorption and corresponding 2026- and 2004-cm<sup>-1</sup> carbonyl bands of the adsorbed complex, designated Fe(CO)<sub>5</sub>(ads), within minutes. The quantum efficiency of decomposition,  $\Phi_d$ , is  $0.96 \pm 0.04$  with 350-nm excitation, and UV and DRIFT spectra recorded during and after photolysis in air give no indication of the formation of dimeric, Fe<sub>2</sub>(CO)<sub>9</sub>, or trimeric, Fe<sub>3</sub>(CO)<sub>12</sub>, intermediates. Nevertheless, photolysis causes a marked change

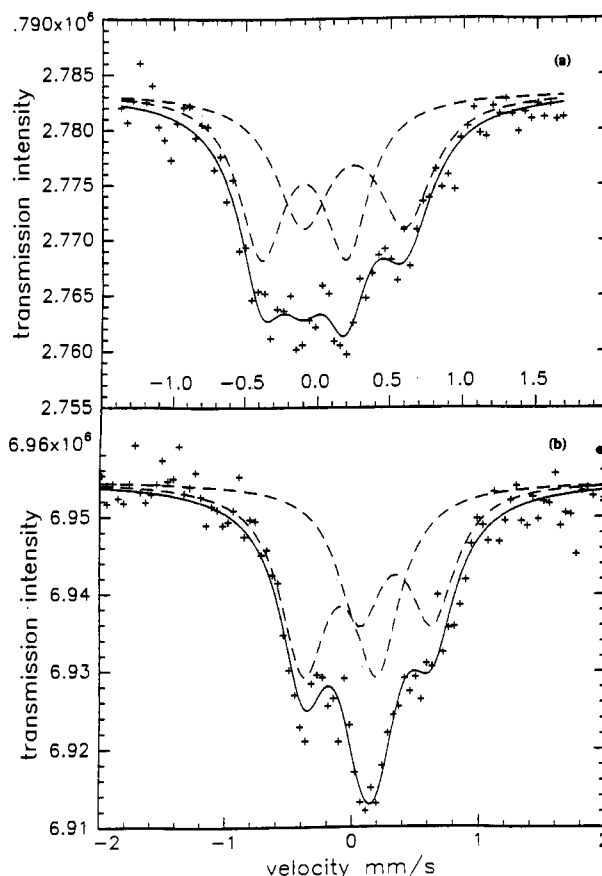


Figure 1. Mossbauer spectra recorded (a) after 300-nm photolysis of a PVG sample containing  $10^{-4}$  mol/g of Fe(CO)<sub>5</sub>(ads) in air and (b) after heating to 650 °C in air.

in adsorbate distribution within the substrate. Initially, Fe(CO)<sub>5</sub>(ads) uniformly impregnates the sample to at least a depth of 2000 μm. However, X-ray microprobe analyses and time-resolved DRIFT spectra show that, as photolysis consumes Fe(CO)<sub>5</sub>(ads) near the surface, unreacted Fe(CO)<sub>5</sub>(ads) diffuses from the interior of the sample into the photodepleted regions, where it undergoes photodecomposition, leading to aggregate formation.<sup>12</sup> Aggregate size depends on initial loading, but current SEM data show that, with Fe(CO)<sub>5</sub>(ads) loadings of  $10^{-5}$ – $10^{-4}$  mol/g, particle sizes range from hundreds of angstroms to ca. 1 μm in diameter.

Exposing the photoproduct to CO (1 atm) leads to spectral changes indicating  $\leq 20\%$  recovery of Fe(CO)<sub>5</sub>.<sup>6</sup> As expected, photolysis in air appears to lead to an irreversible oxidation of the iron. However, best fits of Mossbauer spectra recorded immediately after photolysis occur with two Lorentzian doublets (Figure 1), indicating two forms of iron in the glass. One form exhibits an isomer shift of  $0.52 \pm 0.05$  mm/s and a quadrupole splitting of  $0.64 \pm 0.06$  mm/s. Comparisons with published data indicate that this form corresponds to octahedrally coordinated

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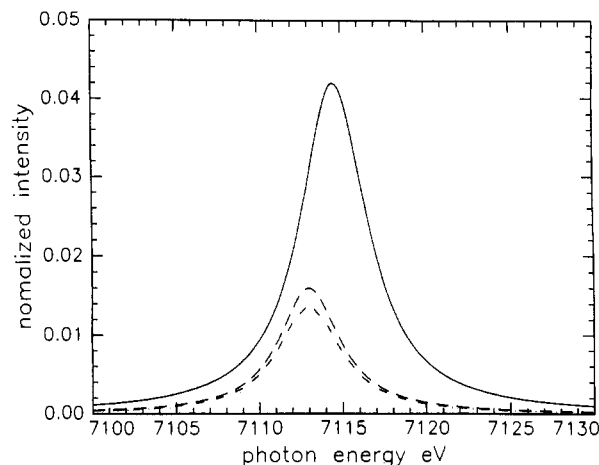
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$\text{Fe}^{3+}$  ions, like that found in  $\text{Fe}_2\text{O}_3$ .<sup>13</sup> The other doublet exhibits a very small isomer shift,  $0.13 \pm 0.01$  mm/s, and a quadrupole splitting of  $0.57 \pm 0.01$  mm/s. Since the photolyses were carried out in air, the immediate thought was to assign the latter species to tetrahedrally coordinated  $\text{Fe}^{3+}$ . However, tetrahedrally coordinated  $\text{Fe}^{3+}$  generally exhibits isomer shifts of ca. 0.2 mm/s and quadrupole splittings significantly larger than those found for octahedrally coordinated  $\text{Fe}^{3+}$ , while tetrahedrally coordinated  $\text{Fe}^{2+}$  exhibits isomer shifts of  $\geq 0.8$  mm/s.<sup>13</sup> Instead, the small isomer shift and quadrupole splitting are assigned to zerovalent iron, which would exhibit a vanishingly small isomer shift relative to the source.

This is a rather surprising assignment, since the photolyses were carried out in air and Mossbauer spectra recorded after heating the samples in air to 650 °C (Figure 1) continue to exhibit two quadrupole doublets. Nevertheless, analyses of the X-ray absorption pre-edge feature are consistent with the formation of  $\text{Fe}^0$ . The pre-edge feature corresponds to an Fe 1s–3d transition and, being forbidden by dipole selection rules, occurs only when the Fe 3d orbitals hybridize with the orbitals of the surrounding coordinating atom.<sup>14</sup> In this case, where Mossbauer indicates  $\text{Fe}^{3+}$  octahedrally coordinated to oxygen and  $\text{Fe}^0$ , only the iron in the oxide contributes to the intensity of the transition. Consequently, the relative amounts of  $\text{Fe}^{3+}$  and  $\text{Fe}^0$  present in the sample are accessible by resolving the pre-edge feature and normalizing its height to that of the edge crest of the photodeposited sample and a PVG sample impregnated with a known amount of  $\text{Fe}_2\text{O}_3$ . The normalized pre-edge features (Figure 2) show that, after photolysis, 53–65% of the iron deposited in these samples is present as  $\text{Fe}^0$  while the remainder is present as an oxide, principally  $\text{Fe}_2\text{O}_3$ . These results are in excellent agreement with the Mossbauer data. The ratio of areas of the two doublets, which is proportional to the number of Fe atoms of each type, indicates that  $56 \pm 5\%$  of the iron present is zerovalent Fe, while the remaining  $44 \pm 5\%$  corresponds to octahedrally coordinated  $\text{Fe}^{3+}$ . Current data are limited to initial loadings of  $10^{-5}$ – $10^{-4}$  mol of  $\text{Fe}(\text{CO})_5/\text{g}$ , and within this range, the  $\text{Fe}^0/\text{Fe}^{3+}$  ratio is independent of initial loading. The increase in intensity of the pre-edge feature (Figure 2) shows that heating in air to 650 °C reduces the amount of  $\text{Fe}^0$  by 15%, while consolidation reduces the amount of  $\text{Fe}^0$  by 25% relative to that present immediately after photolysis.

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**Figure 2.** Resolved X-ray absorption pre-edge feature after photolysis (—·—), after heating in air to 650 °C (---), and after consolidation of the matrix at 1200 °C (···) and pre-edge (—) feature of a reference sample impregnated with  $\text{Fe}_2\text{O}_3$ .

The occurrence of zerovalent Fe in these porous glasses may reflect an inability of  $\text{O}_2$  to diffuse throughout the entire pore structure. Although not exactly analogous to this system,  $\text{Ru}(\text{bpy})_3^{2+}$  also impregnates the interior of the matrix, and  $22 \pm 2\%$  of the adsorbed complex is not quenched by  $\text{O}_2$ .<sup>15</sup> Photoproduct aggregation in the outer regions of glass during photolysis may further impede  $\text{O}_2$  diffusion into the matrix. Water would also be expected to oxidize small zerovalent iron aggregates, yet consolidation of the matrix, which leads to water evolution, does not result in complete oxidation. Possibly, oxidation of the surfaces of these  $\text{Fe}^0$  aggregates by either  $\text{O}_2$  or evolved  $\text{H}_2\text{O}$  prevents further oxidation of the aggregate interior.

In summary, Mossbauer and X-ray absorption data establish that, although the photolysis of  $\text{Fe}(\text{CO})_5$  physisorbed on PVG is carried out in air, the result is a mixture of iron oxide and  $\text{Fe}^0$  aggregates. Within the limits of these experiments, the relative  $\text{Fe}^0/\text{Fe}^{3+}$  ratio,  $(1.25 \pm 0.02)/1$ , is independent of initial loading. Heating in air or consolidation of the matrix reduces the  $\text{Fe}^0/\text{Fe}^{3+}$  ratio but does not result in complete oxidation.

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