Sonochemical synthesis of amorphous iron

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AMORPHOUS metallic alloys ('metallic glasses') lack long-range crystalline order and have unique electronic, magnetic and corrosion-resistant properties[1–3]. Their applications include use in power-transformer cores, magnetic storage media, cryothermometry and corrosion-resistant coatings. The production of metallic glasses is made difficult, however, by the extremely rapid cooling from the melt that is necessary to prevent crystallization. Cooling rates of about 10^5 to 10' K s^{-1} are generally required; for comparison, plunging red-hot steel into water produces cooling rates of only about 2,500 K s^{-1}. Metallic glasses can be formed by splattering molten metal on a cold surface using techniques such as gun, roller or splat quenching[4,5]. Acoustic cavitation is known to induce extreme local heatin in otherwise cold liquids, and to provide very rapid cooling rates. Here we describe the synthesis of metallic-glass powders using the microscopically extreme (yet macroscopically mild) conditions induced by high-intensity ultrasound. The sonolysis of iron pentacarbonyl, a volatile organometallit compound, produces nearly pure amorphous iron. This amorphous iron powder is a highly active catalyst for the Fischer-Tropsch hydrogenation of carbon monoxide and for hydrogenolysis and dehydrogenation of saturated hydrocarbons.

The chemical effects of ultrasound derive primarily from hot spots formed during acoustic cavitation (that is, the formation, growth and collapse of bubbles in a liquid)'-". This process serves to concentrate dramatically the low energy density of a sound field. Our previous experiments have established'z-'4 that the effective temperature reached during bubble collapse is -5,200 K, with a calculated hot-spot lifetime of <2 us. More recent sonoluminescence experiments suggest" possible lifetimes of <1 ns. Thus, we expect that heating and cooling rates during cavitational collapse are greater than 2×10^9 K s^{-1} and may be as large as 10^{13} K s^{-1}.

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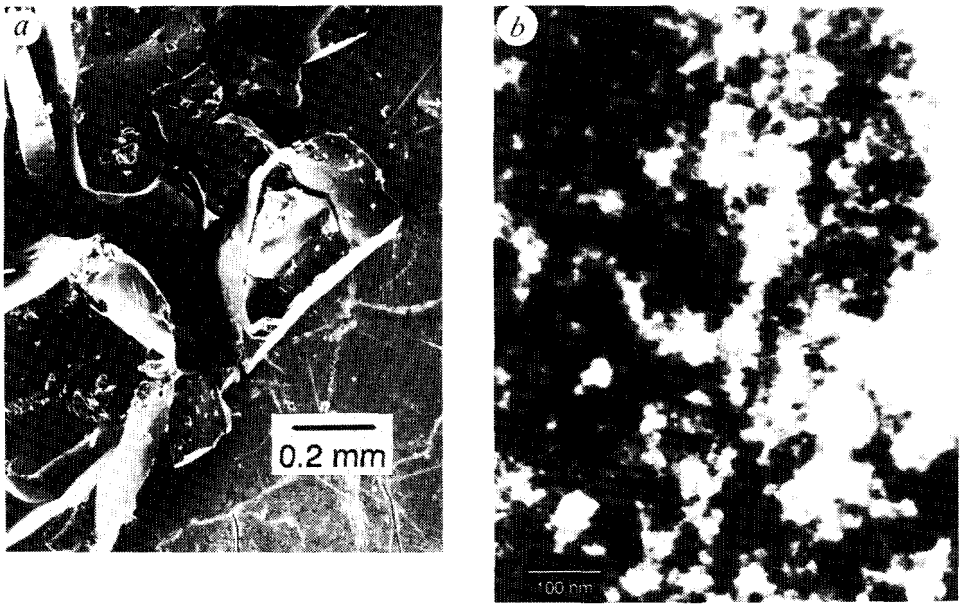

FIG. 1 a, Scanning electron micrograph of amorphous iron powder, obtained on a Hitachi S800 electron microscope. *b*, Transmission electron micrograph of amorphous iron powder, obtained on a Phillips EM 400T electron microscope.

Ultrasonic irradiation of iron pentacarbonyl, $Fe(CO)_5$, yields a dull black powder. A scanning electron micrograph of the powder is shown in Fig. la. Pure $Fe(CO)_5$ or 4.0 M solutions in decane were irradiated at 0 °C with a high-intensity ultrasonic probe (Sonics and Materials, model VC-600, 0.5 in. Ti horn, 20 kHz, 100 W cm^{-2}) for 3 h under argon. After irradiation, the iron powder produced was filtered and washed with dry pentane in an inert atmosphere box (Vacuum Atmospheres, <1 p.p.m. 0,). Gram quantities of material were isolated. Elemental analysis of the amorphous iron powder shows it to be >96% iron by weight, with trace amounts of carbon (3%) and oxygen (1%), presumably from the decomposition of alkane solvent or carbon monoxide during ultrasonic irradiation[16–18]. The applications of ultrasound to chemical synthesis[11,19–21] and useful experimental apparatus[22] are described in detail elsewhere.

The amorphous nature of these powders has been confirmed by several different techniques, including scanning and transmission electron microscopy, differential scanning calorimetry, X-ray powder diffraction and electron-beam microdiffraction. Scanning electron micrographs of iron powder from ultrasonic irradiation of $Fe(CO)_5$ show conchoidal fractures, typical of a non-crystalline material (Fig. 1 a). Transmission electron microscopy show no evidence for crystallite formation to a resolution of below 4 nm (Fig. 1 b). Differential scanning calorimetry shows one large exothermic transition at 308 °C corresponding to a disorder-order transition (crystallization) of the amorphous iron (Fig. 2).

Initial X-ray powder diffraction shows no diffraction peaks; after heat treatment under N_2 at 350°C (sufficient to induce crystallization), the lines characteristic of α-iron metal (*d* spacings of 2.03, 1.43, 1.17 and 1.04 Å) are observed (Fig. 3). After crystallization, the X-ray powder diffraction pattern contains no peaks attributable to iron carbide or other iron-based phases, thus confirming the formation of essentially pure iron glass from ultrasonic irradiation of $Fe(CO)_5$. This is especially noteworthy because all iron-containing metallic glasses prepared previously contain large amounts of other alloying elements (typically >20%)[1–3,23,24]. Electron microdiffraction with a transmission electron microscope confirms these observations and shows only a diffuse ring characteristic of an amorphous material. After continued sample exposure to the electron beam and its consequent heating, the iron powder crystallizes in *situ* and the diffraction rings from a-Fe are observed.

Transmission electron micrographs reveal the microstructure of the powder (Fig. 16). The large particles shown in the scanning electron micrograph are composites of very small particles (-10 nm) with significant void volume. Surface areas, determined by Brunauer-Emmett-Teller gas adsorption isotherms, were found to be 120 $m^2 g^{-1}$, which is about 150 times greater than the 5-μm-diameter iron powder commercially available (Aldrich Chemicals). The sonochemically produced amorphous iron powder sinters at unusually low temperatures. At 350 °C, the amorphous powder acquires a metallic lustre and the transmission electron micrographs show loss of porosity and growth of ~50-nm crystallites. After heating, the surface area decreases by roughly one hundredfold and becomes comparable to that of the commercial crystalline powder.

We probed the catalytic activity of the amorphous iron powder for two commercially important reactions: the Fischer-Tropsch process (hydrogenation of CO) and the hydrogenolysis and dehydrogenation of saturated hydrocarbons. Catalytic studies were carried out in a continuous flow microreactor. The iron catalyst was loaded in the reaction chamber under an inert atmosphere and placed on the flow microreactor without exposure to air. The reaction products were monitored using

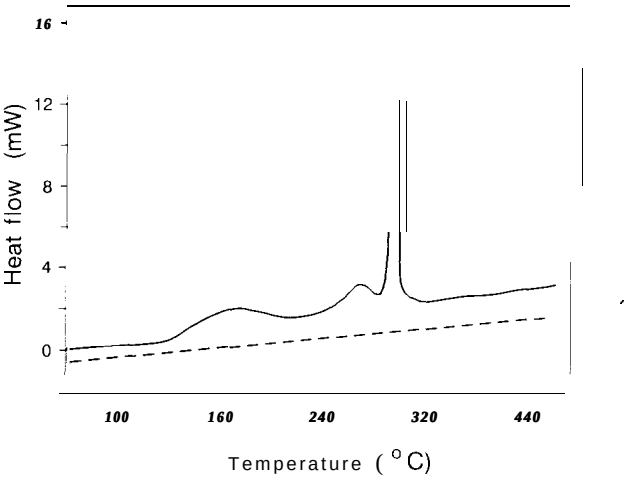

FIG. 2 Differential scanning calorimetry of amorphous (solid line) and crystalline (dashed line) iron powders, obtained at 10 °C min^{-1} on a DuPont 1090 calorimeter.

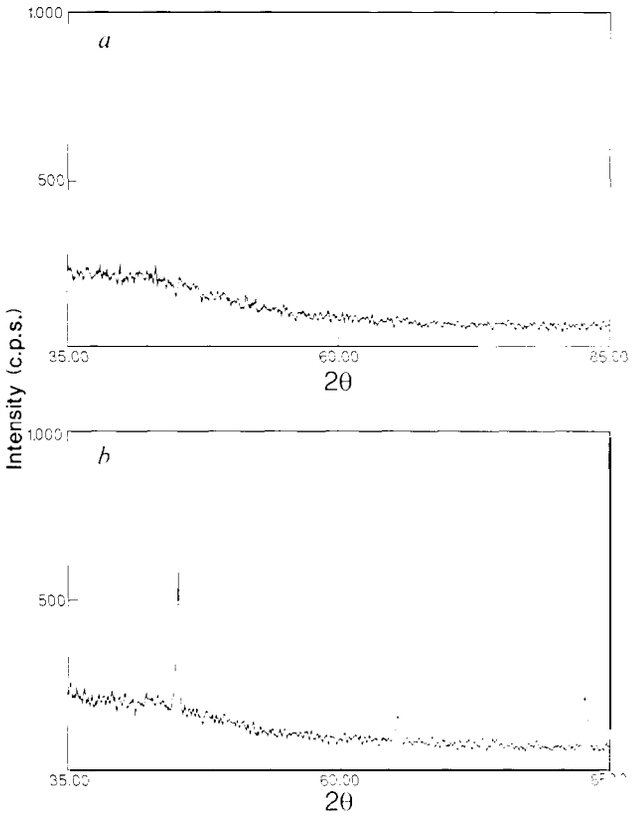

FIG. 3 X-ray diffractron powder patterns of amorphous iron powder *(a)* before heat treatment and (*b*) after crystallization at 350 °C for 6 h. Data collected on a Rigaku D-max diffractometer.

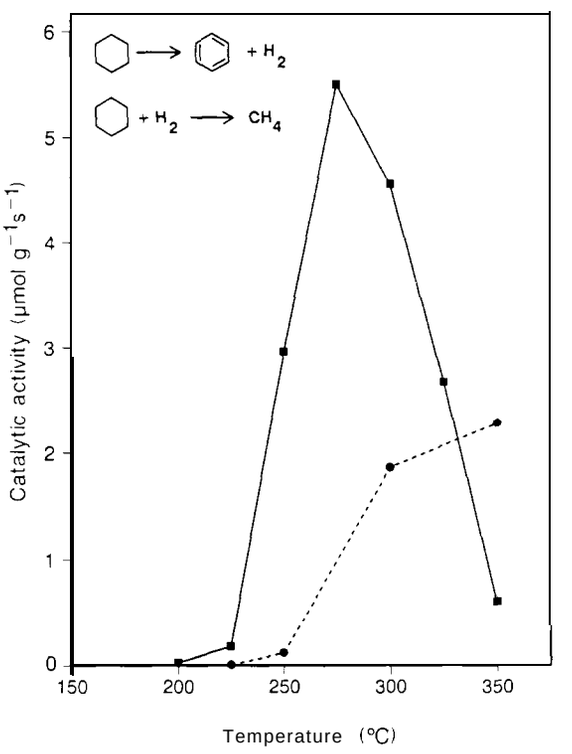

FIG. 4 The catalytic activity of amorphous and crystalline iron powder as a functron of temperature for the cyclohexane dehydrogenation and hydrogenolysis reactron. Solid line, amorphous iron powder, prepared sonochemitally from $Fe(CO)_5$; dashed line, crystalline iron powder (5-km dtameter. Aldrich Chemicals).

gas chromatography. The Fischer-Tropsch conversion of carbon monoxide and hydrogen to low-molecular-weight alkanes occurred at very low reaction temperatures (200 "C). The amorphous powder was roughly ten times more reactive per gram than 5-μm-diameter crystalline iron powder. At 250 °C, the overall activity for cyclohexane dehydrogenation (to benzene) and hydrogenolysis (predominantly to methane) was >30 times greater for the sonochemically produced amorphous iron relative to crystalline iron (Fig. 4). We believe that the high surface area of the amorphous iron accounts for much of the increase in chemical reactivity. As expected, sintering and crystallization of the metallic glass powder at >300 "C significantly decreased its catalytic activity. The ratio of cyclohexane dehydrogenation to hydrogenolysis depended on temperature and ranged from 0.3 to 1.0.

The production of metal powder is not the only possible sonochemical reaction of $Fe(CO)_5$. We have previously reportedZ5-" on sonochemical ligand substitution, cluster formation and catalytic alkene isomerization. The extent of CO loss can be controlled by the experimental parameters that affect cavitational collapse, including solvent vapour pressure, thermal conductivity of dissolved gas, and the ratio of heat capacities C,/C, of the dissolved gas. Complete ligand dissociation leading to formation of metallic glass powders occurs when the cavitational collapse is most extreme (for example, at low vapour pressure and with low gas thermal conductivity). Under such conditions, we have recently observed iron atomic emission lines in the sonoluminescence spectra (K.S.S., E. B. Flint, M.W.G. and K. A. Kemper, manuscript in preparation), confirming that iron atoms are formed during ultrasonic irradiation of Fe(CO),. C

Received 29 April: accepted 31 July 1991

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ACKNOWLEDGEMENTS This woh was supported by the hSF the loan of ultrasonic equipment from Sonics and Mater~als IS greatly appreciated We gratefdlli acknowledge receipt of the American Chemical Society Fellowship r Collold and Surface Chemistry sponsored by Procter and Gamble Co IM W G We thank Peggy Mochel and the UIUC Center for Microanalysis of Materials supported by the US Department of Energy for their ass~sfance I" the characterizationstudies