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Communications

Solid-State Chemistry in a Microwave Oven: Preparation of Pd/Co Alloy from Cyanogel Coordination Polymers

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A variety of coordination polymers can be generated via a reaction of tetrachlorometalates with transition metal cyanometalates in aqueous solution.[1−3] During these reactions, some of the cyanide ligands of the cyanometalate form bridges between the two metal centers, forming a 3D polymer network. This polymer undergoes a sol−gel transition, during which it encloses water within its network. This bicontinuous system eventually spans the reaction vessel to form a hydrogel. Since the ability of these systems to gel is related to the bridging capabilities of the cyanide ligand, these coordination polymers have been named “cyanogels”.[1] The dehydration of a cyanogel leads to a xerogel, an amorphous Prussian Blue-like structure in which the pore structure of the hydrogel has collapsed.

From the viewpoint of materials chemistry, the beauty of these materials lies in the ability of the cyanide ligand to act as a reducing agent at elevated temperatures. Above 350 °C, the cyanide groups reduce the metal centers, while they are oxidized to cyanogen, $(CN)_2$. Under inert atmosphere, the elevated temperature processing of cyanogels leads to metal alloys; under oxygen, metal oxides are formed.[2,4] Similar to traditional solid-state synthesis, the high-temperature processing is accomplished in a furnace and requires 1 or more h for complete conversion, although the temperatures utilized are well-below those typically required to form solid-state systems.

In this work, we explored the possibility of carrying out the solid-state transformation of cyanogels to metal alloys with the aid of microwave radiation. Recent reports have shown that microwave radiation can facilitate the synthesis of some inorganic solid-state materials.[5−11] Typically this work has relied on the heating, which a microwave field induces in a metallic or semiconducting substrate. This Communication describes our findings about the solid-state conversion of dehydrated Pd/Co cyanogel to Pd/Co alloy using a conventional kitchen microwave oven to supply the necessary energy. In contrast to prior reports utilizing microwave energy to induce a solid-state transformation, in

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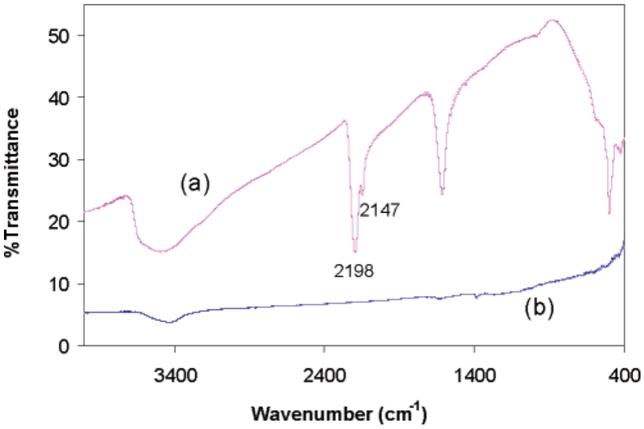

Figure 1. IR spectrum of Pd/Co cyanogel (a) showing the peaks characteristic for terminal (2147 cm^{-1}) and bridging (2198 cm^{-1}) cyanide and IR spectrum of Pd/Co gel after exposure to microwave irradiation under argon atmosphere (b).

this study the reagent cyanogel polymer is induced to undergo a redox reaction via absorption of microwave energy.

The Pd/Co cyanogel was prepared by mixing 100 mM Na_2PdCl_4 and 100 mM $K_3Co(CN)_6$ in a 2:1 ratio. The solution gelled within 1 h, and the gel was allowed to age overnight. It was then washed with water to remove NaCl and KCl products and dried at 70 °C to give a xerogel. The IR spectrum of the xerogel showed peaks at 2147 and 2198 cm^{-1} (Figure 1a), which were previously assigned to terminal and bridging cyanides, respectively.[2]

The dry xerogel was placed under an argon atmosphere in a 40 cm long Shlenk-style Pyrex tube connected to a bubbler. The sample tube was placed vertically through a hole drilled in the center of the top of an 1100 W domestic Sharp microwave oven.[12] The sample, held 4 cm from the floor of the oven, was then irradiated with the full output of the oven for up to three 2-min periods. For a 1.0-g sample, approximately 30 s were required before any signs of reaction were observed. After this time elapsed, a dark blue powdery smoke evolved from the gel; some of this material deposited on the walls of the Pyrex tube. The IR spectra of this powder showed a sharp peak at 2192 cm^{-1}, two broad peaks at 2235 and 2221 cm^{-1}, a sharp peak at 1402 cm^{-1}, and two peaks around 3150 and 3050 cm^{-1}. The three IR absorptions in the ~2200 cm^{-1} region agree with the IR spectra of Pd/Co gel taken at different stages of thermal conversion using a standard tube furnace.[2] This suggests that the microwave-assisted conversion of cyanogel to metal alloy occurs by a mechanism similar to the classical thermal mechanism, albeit on a much faster time scale. The species responsible for the peaks at 1402, 3150, and 3050 cm^{-1} are yet to be determined.

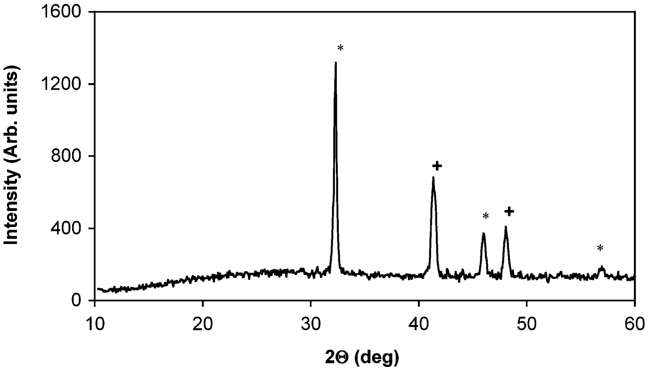

Figure 2. X-ray powder diffraction pattern of the Pd/Co alloy formed by irradiation of Pd/Co cyanogel by microwaves for three two-minute periods. The peaks marked by (+) belong to the alloy. The peaks marked (∗) belong to the internal standard NaCl. The Pd:Co ratio estimated from the powder pattern is 4:1.

As soon as the dark blue smoke appeared, the flow rate through the bubbler significantly increased. In one experiment, the evolved gases were collected in a glass coil immersed in a dry ice/ethanol bath. Subsequent mass spectra analysis indicated the presence of species with mass 52, consistent with cyanogen $(CN)_2$, along with trace amounts of species with mass 18 and 27, corresponding to water and HCN; all three species were previously observed to accompany the cyanogel to metal conversion in a tube furnace.[2,3] Between 30 s and 1 min of the reaction, blue and white smoke was observed in the tube, some of which condensed on the walls of the Pyrex tube as $CoCl_2$ and KCl. During the second minute of the reaction, the bubble rate slowed. At this time, small white "sparks" were observed in the sample. Subsequently, the entire sample began to glow orange (blackbody radiation). When microwave irradiation continued for a prolonged time during this phase of the reaction, the Pyrex reactor started to melt in the region near the sample. A control experiment in which an empty Pyrex reaction tube was irradiated with microwaves resulted in only slight heating of the glass. Likewise, microwave irradiation of the gel precursor species, $NaPdCl_4$ and $K_3Co(CN)_6$, did not lead to significant heating, indicating that it is the cyanogel polymer that directly absorbs and thermalizes the microwave energy.

The X-ray powder diffraction of the product showed a Pd/Co alloy with an FCC structure (Figure 2) and a 4:1 Pd:Co ratio as determined by interpolation between pure Pd and pure Co powder patterns. The powder pattern of the product was identical to the powder pattern of the alloy prepared thermally from the same cyanogel by slow heating to 900 °C in a furnace. The 4:1 Pd:Co ratio was supported by electron microprobe analysis and is consistent with the original 2:1 mixing ratio and the proposed stoichiometry of the autoreduction reaction 1:

$$[\mathrm{K_3Co(CN)_6(PdCl_2)_2{\cdot}}x\mathrm{H_2O}]_n \rightarrow n\left(2\mathrm{Pd} + \frac{1}{2}\mathrm{Co} + \frac{1}{2}\mathrm{CoCl_2} + 3(\mathrm{CN})_2 + 3\mathrm{KCl} + x\mathrm{H_2O}\right) \quad (1)$$

where $[K_3Co(CN)_6(PdCl_2)_2{\cdot}xH_2O]_n$ is the formula of the cyanogel polymer.

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(12) Microwave leak detector was used to ensure that there was no microwave leakage.

Magnetization measurements as a function of applied magnetic field (M vs H loop) of the product at 5 K indicated a ferromagnetic state, as expected from the phase diagram.[13] The measured saturation magnetization was 4100 emu/mol. This value corresponds to 0.74 Bohr magnetons and agrees with the value reported in the literature for a $Pd_{0.8}Co_{0.2}$ alloy.[14] As the saturation magnetization in this system has been shown to be fairly sensitive to the Co content in the alloy, the magnetization measurement supports the 4:1 Pd:Co stoichiometry of our product.

No cyanide stretches were visible in the IR spectrum of a gel subjected to 3 or more min of microwave irradiation (Figure 1b), indicating a complete conversion of the cyanogel to metal alloy. When the gel was irradiated for a shorter time, the features in the IR spectra were similar to the spectrum of the “blue smoke” that evolves at the beginning of the reaction. They showed a sharp peak at 2192 cm^{-1}, two broad peaks at 2235 and 2221 cm^{-1}, a peak of variable intensity and breadth (for different samples) around 1400 cm^{-1}, and shoulders near the broad water peak (~3200−3600 cm^{-1}) around 3100 cm^{-1}. This suggest that heating times shorter than three minutes lead to incomplete conversion of cyanogel to metal, leading to a mixture of alloy and cyanide-containing intermediates.

In summary, by using a conventional kitchen microwave oven, we have achieved a solid-state transformation of Pd/Co cyanogel to Pd/Co alloy in a fraction of the time required by traditional thermal methods. This observation is even more impressive if it is considered that the traditional synthesis of Pd/Co alloys from the two metals is carried out by heating at 1800 °C for an extended period.[14] Our data suggest that the cyanogel directly absorbs microwave radiation, which leads to a significant heating of the polymer network and causes the reduction of the metal centers in a similar way as, but much faster than, furnace heating. Similar conversion observed with the Pd/Fe system suggests that this microwave technique can be extended to other cyanogels[1,3,4] and therefore can be used to prepare a variety of metal alloys. As this fast conversion of cyanogel to metal happens on a similar time scale as, for example, solid-state reactions initiated by arc melting, it might open a new route to thermodynamically metastable bi- and possibly trimetallic phases. Further experiments to identify the mechanism of microwave absorption by the cyanogel and its conversion to alloy are underway.

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