

Crystallization of hydroxide cobalt carbonate $\text{Co}_2\text{CO}_3(\text{OH})_2$, precursor of Co_3O_4 , at room temperature

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The crystallization of cobalt carbonate CoCO_3 , cobalt hydroxide carbonate $\text{Co}_2\text{CO}_3(\text{OH})_2$ and its hydrated phases $\text{Co}_2\text{CO}_3(\text{OH})_2 \cdot n\text{H}_2\text{O}$ have been subject of interest in the scientific literature because they can be precursors of the so-called low-dimensional cobalt oxide-based nanomaterials. Various cobalt salts can be precursors of Co_3O_4 , but carbonates and hydroxide carbonates are the most desirable because they are readily available and because no toxic product gases are produced during their calcination. In most cases, the physical properties and applications of the oxide-based nanomaterials are in linked with specific morphologies and hence, a number of works are focused on different experimental methods to achieve these morphologies. In most of the reported experimental works the cobalt carbonate phases have been synthesized by hydrothermal methods and their transformation into cobalt oxides occurs by calcination.

At room temperature, the crystallization behaviour of Co-carbonates seems to be complex and needs to be studied in depth. Under these conditions, the precipitation of crystalline cobalt carbonates or hydroxycarbonates from soluble salt of Co^{2+} and CO_3^{2-} is prevented by the formation of Co^{2+} aqueous complexes. Therefore the obtained phases by direct precipitation in aqueous solution are amorphous. In this experimental work we have aged this amorphous phase in the remaining aqueous solution for two months. We have observed its progressive transformation into a crystalline phase with roasite-type crystal structure $\text{Co}_2\text{CO}_3(\text{OH})_2$. The evolution of the morphology and chemical composition of the solids with aging time, have been examined by X-ray Powder diffraction, scanning electron microscopy, transmission electron microscopy and infra-red spectroscopy.

The final $\text{Co}_2\text{CO}_3(\text{OH})_2$ crystals grown by aging at room temperature show platelet morphology and are transformed into Co_3O_4 by calcination in a similar way as the crystals of this substance grown by hydrothermal methods do. Moreover, the layered crystal structure of the precursor $\text{Ca}_2\text{CO}_3(\text{OH})_2$ favors the development of lamellar morphology that, after a topotactic transformation, is approximately maintained in the cobalt oxide new phase.

Nano iron sulfides for carbon dioxide reduction

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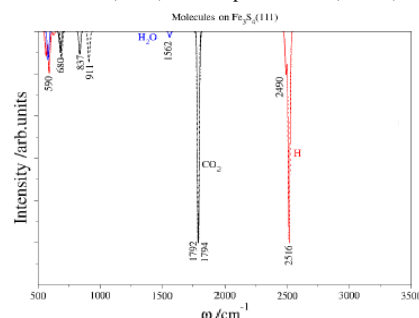
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Despite the high thermodynamic stability of CO_2 , biological systems are capable of converting it into a range of organic molecules, under moderate conditions. Iron sulfide membranes formed in the warm, alkaline springs on the ocean floor are increasingly considered to be early catalysts involved in the emergence of life. These anaerobic reactions are thought to have been catalyzed by small (Fe,Ni)S clusters similar to the surfaces of present day sulfide minerals.^[1]

We have synthesised iron sulfide nanomaterials using a novel methods based on continuous hydrothermal synthesis, where aqueous flows of iron and sulfide ions are brought into contact with a flow of superheated water (at 450 °C). The conditions and processes occurring during synthesis can be compared to those that might occur in hydrothermal vents.^[2,3] The electrochemical properties of these materials and their stability and activity towards CO_2 and their selectivity to products can be evaluated.

Figure 1: Simulated (solid) and experimental (dotted) IR spectra of



Greigite nanoparticles after CO_2 has been bubbled over the surface

Based on comprehensive computational investigations, a number of iron and iron-nickel sulphide nanoparticles have been designed, synthesised, tested, characterised, and evaluated for the activation and chemical modification of CO_2 at low voltages (obtainable from solar energy) and ambient conditions. Structures including greigite show evidence of interacting with CO_2 (figure 1). The electroreduction of CO_2 on iron sulfide surface has been shown to produce small organic molecules including formic acid

- [1] Russell (2005) *Economic Geology* **100**, 419-438.
 [2] Crabtree (1997) *Science* **276**, 222-222. [3] Middelkoop (2009) *Chemistry of Materials* **21**, 2430-2435