

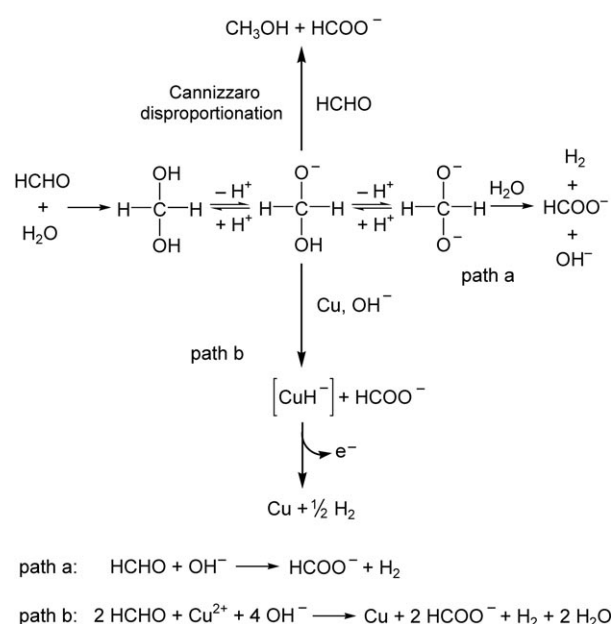
Aerobic, Copper-Mediated Oxidation of Alkaline Formaldehyde to Fuel-Cell Grade Hydrogen and Formate: Mechanism and Applications**

Debora Preti, Sergio Squarzialupi, and Giuseppe Fachinetti*

Hydrogen economy (yet hypothetical) is based upon proton exchange membrane fuel cell (PEMFC) technology and depends on the supply of fuel cell grade hydrogen (FCH), which contains no CO and is undiluted. Unfortunately, the methods available to produce FCH do not meet the required purity, size, and cost standards. Since still-abundant fossil carbon reserves are the main source of primary energy, FCH is to be ultimately produced from these reserves on a large scale. By means of oxidative and steam reforming, natural gas, coal, heavy crude oil, tar sands, and shale oil can be converted into H₂ along with CO and CO₂ (synthesis gas, syngas).^[1] The H₂ content can be enhanced in the gaseous mixture by the water–gas shift reaction; however, the complete removal of CO requires the energy-costly pressure swing adsorption (PSA) or palladium membrane technologies. Some well-established C₁ chemistry suggests an alternative pathway based on the conversion of syngas into methanol: While standard oxidative/steam reforming of methanol produces synthesis gas, its selective conversion into FCH and CO₂ is conceivable by a process in three steps, each of which produces FCH: I) methanol dehydrogenation to HCHO, a reaction which can also result in FCH formation,^[2] II) HCHO oxidation to formic acid, and III) the catalytic decomposition of formic acid into FCH and easily removable CO₂.^[3] We report herein an aerobic, copper-based chemical-looping oxidation of alkaline HCHO to formate and FCH: a transformation that fulfills step II.

It is known that the formation of FCH accompanies the conversion of alkaline HCHO into formate under two distinct sets of circumstances: a) Small amounts of FCH are self-generated slowly from an alkaline HCHO solution;^[4] b) hydrogen, presumably FCH, is evolved at a potential as low as 0.1 V (normal hydrogen electrode; NHE) by the electrochemical oxidation of alkaline HCHO at a copper electrode.^[5] A chemical counterpart of copper electrocatalysis of this type is autocatalytic electroless copper plating, in

which the oxidation of alkaline HCHO by copper(II)–ethylenediaminetetraacetic acid occurs on the copper surface and is accompanied by FCH production.^[6] A common hydroxymethanolate intermediate is believed to be involved in both FCH self-generation and the copper-catalyzed generation of FCH by electrochemical or chemical oxidation (Scheme 1).



Scheme 1. Reactions of the hydroxymethanolate intermediate.

The anionic intermediate formed by deprotonation of hydrated HCHO^[7] is hydridic in character and participates in the Cannizzaro disproportionation. Depending on the concentration of the base, a doubly deprotonated methanediolate can be formed. Hydride transfer from this intermediate to H₂O results in FCH self-generation (path a). In the presence of Cu, hydride transfer from the hydroxymethanolate to the metal surface can occur; electrons are then drawn from the metal, either electrochemically or chemically by Cu²⁺, to generate FCH and formate (path b).

In the chemical literature, path a and path b are not distinguished adequately. It was reported recently that nanocrystalline Cu (nano-Cu) catalyzes path a,^[8] a rather unlikely accelerating effect, since the rate of FCH self-generation appears to be controlled by the methanediolate, that is, by the concentration of the base, and not to be affected by Cu, regardless of its particle size. However, such a catalytic effect

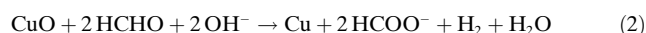
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was observed by us only when the alkaline HCHO solution was stirred vigorously in air, but did not occur under an inert atmosphere (see the Supporting Information). In a closed vessel, a quantity of 0.5 mol of O₂ was consumed per mol of FCH produced. (**CAUTION:** Potentially explosive gas mixtures can be produced at intermediate stages.) These results suggest that nano-Cu reacts with oxygen to give CuO [Eq. (1)], which oxidizes alkaline HCHO to produce formate and FCH according to path b [Eq. (2)].



Thus, a chemical loop resulting in aerobic copper-mediated alkaline HCHO oxidation to FCH and formate is suggested. However, the use of nano-Cu hampers practical applications, since these particles generate noxious dust, agglomerate, and react slowly and partially with air. To overcome these limitations, we sought to identify a more suitable form of Cu.

We found that a suitable Cu/CuO couple is obtained when CuO is formed by the thermal decomposition of Cu(NO₃)₂. The heterogeneous reduction by alkaline HCHO of CuO prepared in this way is autocatalytic, fast, and exothermic ($\Delta H_{298}^\circ = -180 \text{ kJ}(\text{mol Cu})^{-1}$, as determined calorimetrically); formate and FCH, the quality of which was ascertained by gas chromatography and nondispersive IR (NDIR) spectroscopy (see the Supporting Information), are produced selectively. Gas-volume measurements of evolved FCH, quantitative determination of the amount of CuO, NaOH, and HCHO consumed, and quantitative determination of the amount of the formate product confirmed the stoichiometry of Equation (2). Only traces of methanol, from a slower Cannizzaro disproportionation of HCHO, were detected.

Remarkably, Cu formed in this way reacts with air almost quantitatively and so fast that it can ignite. To avoid the melting of Cu, the air flow must be limited, or Cu diluted with an inert material, such as sand (see the Supporting Information). This form of Cu is superior to nano-Cu (<100 nm), which is only slowly and superficially oxidized by air. An explanation for this exceptional reactivity is given below.

We examined CuO and Cu by scanning electron microscopy (SEM) after their repeated use in the chemical loop described by Equations (1) and (2). Surprisingly, the oxide and the metal appeared to have the same morphology, and the morphology of the original CuO derived from Cu(NO₃)₂ was preserved in the CuO restored by the exposure of Cu to air: namely, tennis-ball-like aggregates of microleaflets (Figure 1).

Since the particles of CuO and Cu maintain their shape and size, neither dissolution/precipitation nor fragmentation can explain how internal Cu atoms participate in the reactions described by Equations (1) and (2). By monitoring the reduction of large leaflets of CuO (a natural tenorite mineral, Vesuvius, Italy) and by following the reduction of CuO microparticles in electrochemical devices, we established that CuO reduction does not occur at the interface with the reducing solution; rather, an electrochemical reaction

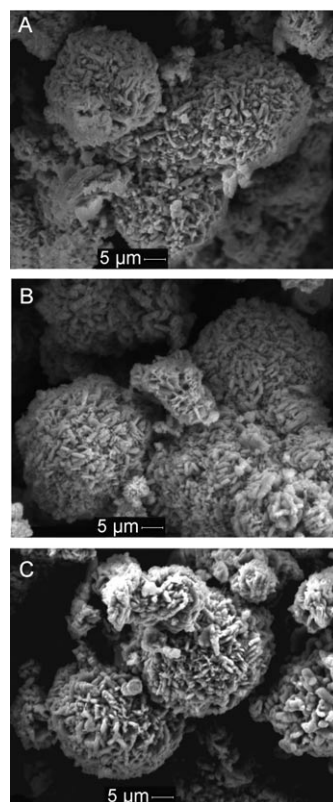
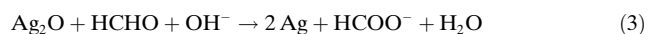


Figure 1. SEM images: A) CuO formed from Cu(NO₃)₂; B) Cu formed through the reduction of CuO by alkaline HCHO; C) CuO restored by exposure to air. Scale bars: 5 μm.

drives electrons to inner CuO. An aggregate of tenorite leaflets was immersed in alkaline HCHO and gently warmed by the reflected illumination of a stereomicroscope. At about 40 °C, bubbles formed at a copper spot that appeared on the black surface of the mineral. Then, in an autocatalytic process, both the surface of the Cu spot and hydrogen evolution increased rapidly until complete reduction had occurred (Figure 2).

The induction period and autocatalysis in tenorite reduction appear to be related to an initial copper-formation step, which presumably occurs through a higher-energy pathway. For example, in the case of Ag₂O reduction [Eq. (3)], alkaline HCHO acts as a two-electron reducing agent without hydrogen evolution.^[9]



The initially formed Cu then catalyzes the lower-energy reduction pathway, which proceeds through hydride transfer from alkaline HCHO to the metal. The following electron transfer to CuO is accompanied by FCH evolution (Scheme 1, path b). For the electron-transfer process to be effective, CuO must be in electric contact with Cu. After the initial formation of Cu, the reaction accelerates with the increase of the Cu–CuO junction, the extent of which increases with the perimeter of the Cu spot. The requirement of the Cu catalyst and of an intimate electric contact between Cu and CuO was confirmed by adopting, as model of a CuO particle, a Cu

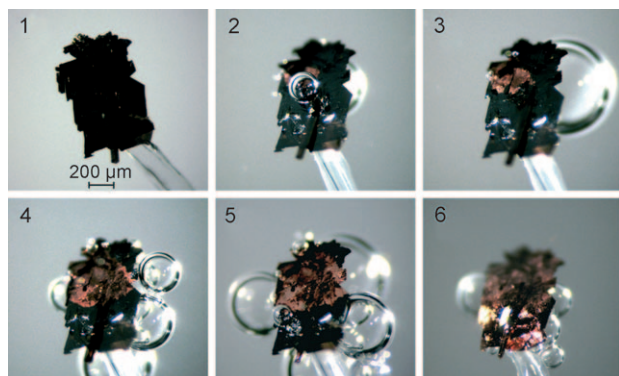


Figure 2. Reduction of an aggregate of natural tenorite leaflets by alkaline HCHO at 40°C. After the induction period, snapshots 1–6 were taken at intervals of 5 minutes.

electrode fully covered with a CuO layer and immersed in a 30% NaClO₄ electrolyte solution containing NaOH and HCHO (both 0.2M): No reaction occurred within minutes at 20°C. A second smooth Cu electrode was immersed in the same solution, and an open-circuit voltage of 0.78 V was measured. Reduction of the black CuO layer and FCH evolution from the smooth Cu electrode started as soon as an electrical connection was established. When the electric contact was discontinued, reduction persisted, and bubbles were evolved at an increasing rate from the partially reduced CuO layer (see Figure S2 in the Supporting Information). On these grounds, we concluded that the reduction described in Equation (2) is an electrochemical transformation; the source of electrons, and FCH, is the hydride transferred from the hydroxymethanolate intermediate to the Cu surface.

Only CuO in electric contact with Cu can be reduced according to the low-energy electrochemical mechanism, as shown conclusively by a test carried out in a galvanic cell: We filled both half-cells and the salt bridge with 30% NaClO₄. In one half-cell we placed a glass pH electrode and the above-mentioned copper plate covered by a layer of CuO. We immersed a smooth copper electrode in an electrolyte containing NaOH and HCHO (both 0.2M) in the other compartment. When the two electrodes were connected to a galvanometer, the electron flow in the external circuit was from the alkaline HCHO half-cell to the copper oxide half-cell. The oxidation of HCHO was accompanied by FCH evolution; the reduction of CuO was evident and caused a sharp increase in the pH value. By comparison, when the copper-oxide-coated electrode was replaced with a smooth electrode in the same galvanic cell, and the CuO micro-particles were stirred in the solution, FCH was not evolved, nor did reduction occur. We thus confirmed the need for a direct Cu/CuO electric contact.

During CuO reduction, the Cu/CuO electric contact was retained, as evident from the metallic texture detected upon breaking a Cu leaflet derived from tenorite reduction with a needle (Figure 3). The necessary drastic reorganization of copper atoms from CuO to face-centered-cubic Cu does not cause structural collapse; rather, electric connections of Cu extend inside the structure to leave cavities of various shapes but preserve the morphology.

If these observations are applied to the case of CuO microleaflets [Eq. (2)], nanocavities are expected. Although not directly detectable, these cavities are responsible for the high reactivity with air. Since the morphology is preserved even during Cu oxidation by air, the construction of the larger CuO cell fills the cavities that arise from reduction.

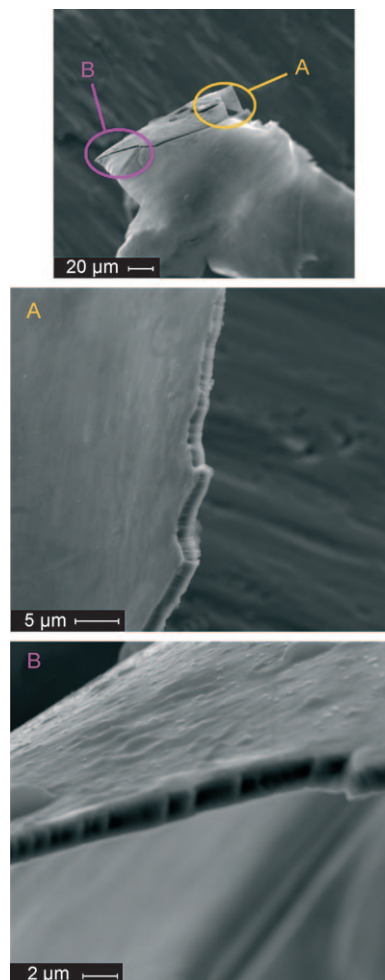


Figure 3. SEM images of internal cavities in copper metal formed through tenorite reduction by alkaline HCHO: Fractures made with a needle, and magnification of the fractures. Scale bars: top image: 20 µm; middle image: 5 µm; bottom image: 2 µm.

These findings show that a new robust, highly reactive form of copper is obtained by the reduction of CuO (formed by the thermal decomposition of Cu(NO₃)₂) with alkaline HCHO. The aerobic oxidation of alkaline HCHO to formate reported herein is selective, quantitative, and accompanied by the generation of FCH and heat. The new chemical loop should be suitable for implementation on a large scale and could therefore find application in C₁ chemistry. This process constitutes a step towards the selective oxidative reforming of methanol to FCH and CO₂ and facilitates the conversion of methanol into formate and formic acid.

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