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Preliminary note

Molecular hydrogen from hydrochloric acid and copper under UV light irradiation

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Abstract

The redox activity of copper in a nonoxidizing acid solution changes dramatically if the solution is irradiated by UV light. A new type of copper corrosion occurs in this case. Thus, for the first time we obtained H_2 in the stoichiometric rate $n(H_2):n(Cu)=1:1$ on irradiating copper in dilute hydrochloric acid. Intermediately at the interface between the bulk copper and the solution a black layer containing micro- and nanocrystalline CuCl is generated. So far our results are also of interest for the synthesis of surface immobilized CuCl, an appreciated photocatalyst or photocatalyst precursor. ©1999 Elsevier Science S.A. All rights reserved.

1. Introduction

As reported [1–3], H_2 is produced on irradiating the p-semiconductor CuCl (band gap 3.31 eV) suspended in dilute HCl with a medium-pressure mercury arc lamp. Photoexcited electrons in the semiconductor reduce H^+_{aq} and holes are consumed by oxidizing CuCl into $CuCl_2$.

$$CuCl_s + H^+_{aq} \xrightarrow{h\nu} Cu^{2+}_{aq} + Cl^-_{aq} + \tfrac{1}{2}H_{2,g} \qquad (1)$$

We carried out this reaction in the millimolar scale to verify the stoichiometry of Eq. (1). Thus, a stirred and irradiated suspension of 2 g (20 mmol) of CuCl in 450 ml of 1 M HCl provide 225 ml (10 mmol) of H_2 within 4 h. This corresponds to the stoichiometric rate $n(H_2):n(Cu)=1:2$. According to the well known comproportionation reaction of Cu^{II} and Cu^0 to Cu^I, we expected an increase of the obtained hydrogen volume on adding metallic copper into the irradiated suspension. This assumption was proved by starting from 20 mmol of CuCl and an excess of Cu powder suspended in 1 M HCl. The irradiation of this system provided 450 ml (20 mmol) of H_2 within 8 h. During the irradiation, a black layer was deposited on the Cu particles. Surprisingly, even copper powder without any addition of CuCl shows a similar behavior upon irradiation in hydrochloric acid, namely, hydrogen gas evolution and a black deposition. We report here our investigations on the composition and the microstructure of the black layer as well as the stoichiometry and the kinetics of the complete copper oxidation in hydrochloric acid under UV light irradiation.

2. Experimental

The irradiation experiments were carried out in a water cooled immersion lamp reactor with magnetic stirring equipped with a medium pressure mercury 150 W lamp. Copper powder ($d < 63$ μm; >230 mesh ASTM; purity > 99.7%; Merck, Catalogue No. 102703) and copper sheet (thickness: 0.1 mm; purity > 99.7%; Merck, Catalogue No. 2700.0250) were used. The copper powder (1.27 g, 20 mmol per run) was suspended in 450 ml of 1 M HCl.

The copper sheet ($10 \times 20\,cm^2$, 390 mmol per run) was formed to a tube and immersed in the acid solution, so that it wraps up the UV lamp at a distance of 10 mm.

For each run the hydrochloric acid solution was deoxygenated by purging with N_2 prior to irradiation. (Control experiments with air saturated solutions and with solutions containing H_2O_2 were proceeded — see Section 3). The reaction mixture was magnetically stirred (800 rpm). The hydrogen gas evolving during the irradiation was collected. The micro- and nanostructure of the black deposit was examined at a ZEISS 960 scanning electron microscope (SEM). X-ray diffractometry of the black deposit was performed at

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a XRD Siemens D 500 powder diffractometer respectively at a Siemens P4RA four cycle single crystal diffractometer.

3. Results and discussion

The irradiation of Cu powder (20 mmol) suspended in a continuously stirred 1 M hydrochloric acid solution provides hydrogen in the stoichiometric rate $n(H_2):n(Cu) = 1:1$. This corresponds to the Eq. (2).

$$Cu_s + 2H^+_{aq} \xrightarrow{h\nu} Cu^{2+}_{aq} + H_{2,g} \qquad (2)$$

Hydrogen evolution begins after a short induction period and occurs as shown in Fig. 1a. During the irradiation, a black layer is generated on the Cu particles, but gradually decomposes as well as the particles itself. If the suspension is continuously irradiated, but alternatively stirred only for 1 min followed by 1 h irradiation without stirring, the hydrogen gas evolution occurs stepwise as shown in Fig. 1b. Only small amounts of hydrogen gas are generated during the long periods without stirring, whereas a very efficient hydrogen evolution is observed during the short stirring periods.

In order to obtain more information about the black layer we proceeded the irradiation of a copper sheet and obtained 1200 ml of hydrogen gas within 24 h (see also Fig. 1c). After this time the copper surface was covered by a black deposit. The microphotograph in Fig. 2 shows, that the deposit contains colorless crystals, mainly at the edges of the metal piece. In the lower section of the SEM image in Fig. 3 one may recognize a stack of alternating bright and dark layers of about 1 μm thickness.

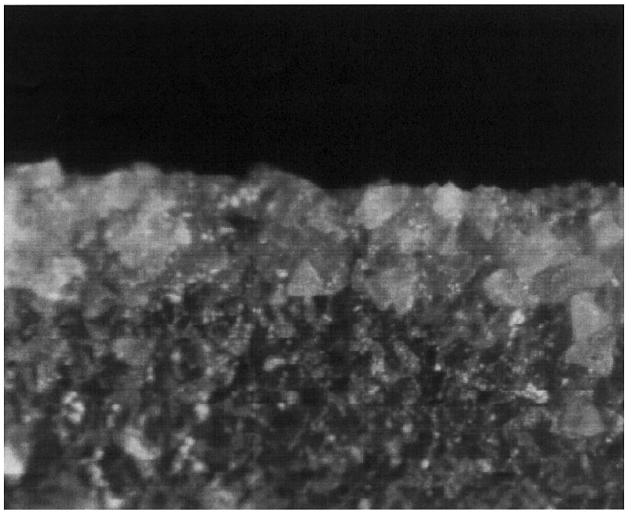

Fig. 2. Microphotograph of the black deposit obtained by UV light irradiation of a copper sheet in 1 M HCl; the larger crystals occur at the edge of the sheet (magnification: 64×).

The perfect alignment of the layers within one stack is noteworthy. Time shifted SEM images of the irradiated copper sheet show that the initially smooth surface becomes rough after 3 h of irradiation, looking like a crater landscape (see Fig. 4a and b). At this stage no black deposition is observed. By further irradiation one observes macroscopically the black coloration of the sheet and the SEM image shows particles entangled in the porous copper surface (Fig. 4c).

The black deposit has been identified as CuCl by the following experimental facts:

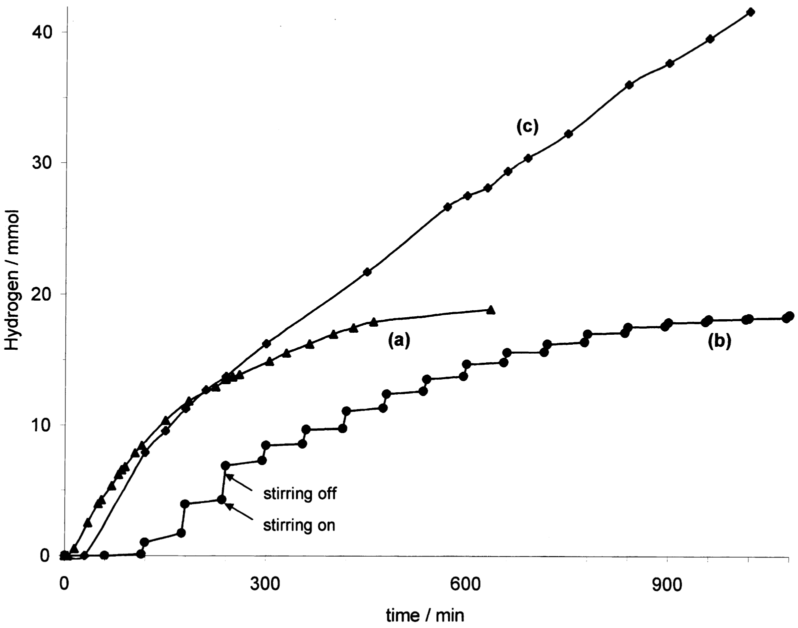

Fig. 1. Time schedules of H_2 evolution by the UV light irradiation of copper in 1 M HCl (for experimental details see text): (a) continuously stirred suspension of Cu powder; (b) alternatively unstirred and stirred suspension of Cu powder; (c) Cu sheet in continuously stirred HCl.

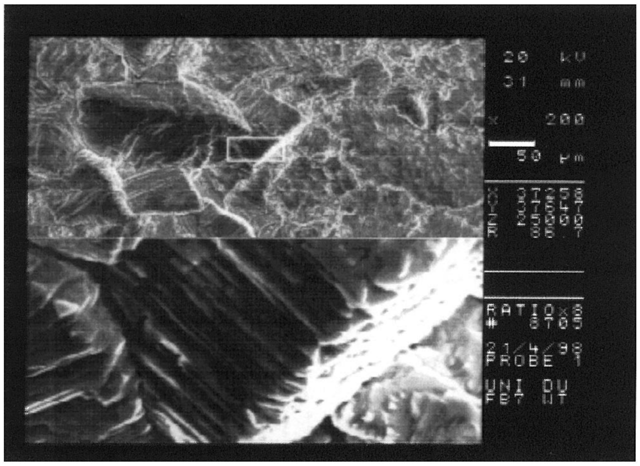

Fig. 3. SEM images of the black deposit obtained by UV light irradiation of a copper sheet in 1 M HCl; the lower insert shows a stack of aligned layers in a pseudo crystal.

1. The energy-dispersive and wavelength-dispersive analysis of the K_α X-ray emission of the black deposit shows, that only the elements Cu and Cl (but not O) are contained in the deposit.
2. The composition of the layer was confirmed to be CuCl by X-ray diffraction structure investigation (powder as well as a single crystal).
3. If the black deposit is heated in a H_2 flow metallic Cu and gaseous HCl is obtained.
4. The black deposit is not soluble in 1 M HCl, but is dissolved in 5 M HCl generating Cu^I complex ions.
5. In the presence of oxygen the black deposit is oxidized leading to green $CuCl_2$.

Control experiments with air saturated solutions have been done as well as experiments with solutions containing H_2O_2 in the ratio $n(H_2O_2):n(Cu) = 3:1$. Under these conditions the oxidation of copper occurs even in the dark and in a completely different way. In contrast to our basic experiments which were performed in oxygen free acid media, the presence of oxidizing agents results in very fast oxidation of Cu^I to Cu^{II} as reported by other autors [4,5]. In these cases no hydrogen is formed and no black deposition on the copper surface can be observed.

We assume that during the initial induction period small amounts of solved and/or colloidal CuCl are generated. Probably the first reaction step occurs on the copper surface and consists of a photoelectron transfer from excited Cl^{-*} to H^+_{aq} Eq. (3) leading to adsorbed hydrogen H_{ad} and Cl radicals which oxidize Cu^0 to Cu^I very fast Eq. (4). In a well stirred system the formation and desorption of molecular hydrogen occurs rapidly Eq. (5).

$$Cl^-_{aq} + H^+_{aq} \xrightarrow{h\nu,\,(Cu)} Cl_{ad}^{\bullet} + H_{ad} \qquad (3)$$

$$Cl_{ad}^{\bullet} + Cu_s \rightarrow CuCl_{aq,col} \qquad (4)$$

$$nH_{ad} \rightarrow \frac{n}{2} H_{2,g} \qquad (5)$$

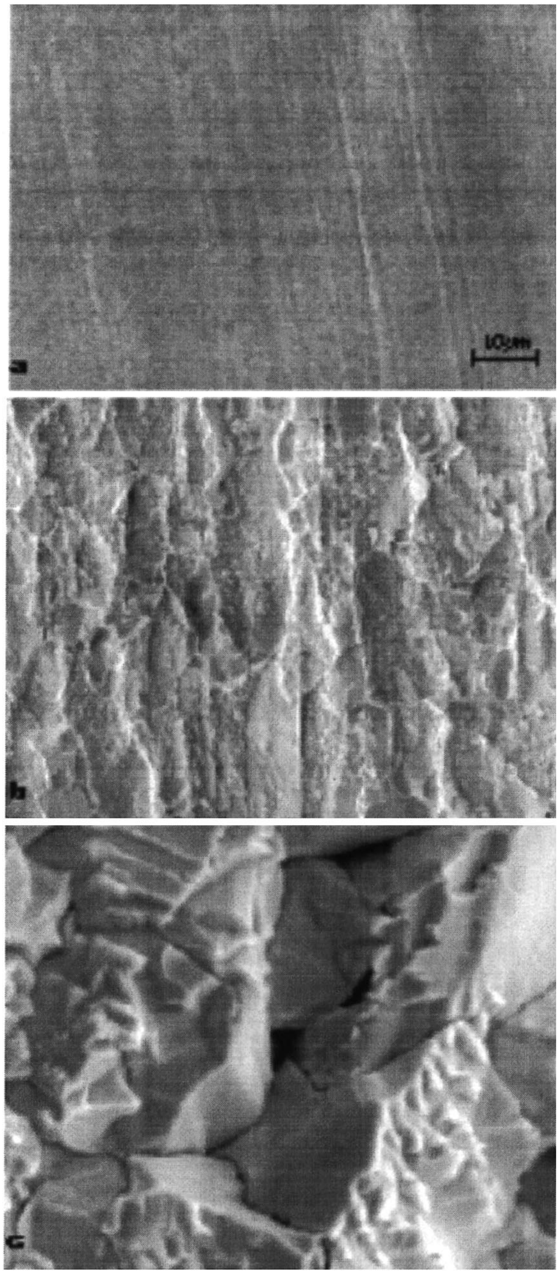

Fig. 4. SEM images of the starting copper sheet (a), after 3 h (b), and after 12 h (c) of irradiation in 1 M HCl.

Colloidal solutions containing very small particles ($d <$ 100 nm) remain clear. In our case colloidal semiconductor particles of CuCl resulting by (4) are photoactive. According to the Eq. (1), where $CuCl_s$ will by replaced by $CuCl_{col}$, additional amounts of hydrogen are generated and simultaneously Cu^I is oxidized to Cu^{II}. By further irradiation of the system $CuCl_s$, is deposited on the copper surface due to the comproportionation indicated by Eq. (6) as well to the limited solubility of CuCl Eq. (7)

$$Cu^{2+}_{eq} + Cu^0_s \rightarrow CuCl_s \qquad (6)$$

$$CuCl_{aq} \rightarrow CuCl_s \qquad (7)$$

The macroscopic appearance of the deposition as a black layer is caused by the very fine distribution of the CuCl nano- and microparticles on the copper bulk (see Figs. 2 and 3). The surface immobilized $CuCl_s$, particles also are photoactive and contribute to the hydrogen production according to Eq. (1). As a consequence of the described processes in a well stirred system (800 rpm) the H_2 evolution rate increases after the induction period almost linearly for some time depending on the copper amount used in the run (see Fig. 1a and c).

We explain the storage effect of the irradiated but unstirred suspension as a diffusion-controlled process at the interface between the solid particles and the liquid medium. On the surface of a CuCl particle a space charge layer can be generated as the result of the photoexcitation in the semiconductor [6,7]. Additionally, H atoms generated by the interfacial electron transfer from the CuCl conduction band to H^+_{aq} Eq. (1) can migrate from the CuCl particles to the metal leading H_{ad} [8]. The accumulation of H_{ad} is favored if the CuCl particles are integrated in the pores of the bulk metal (see Figs. 3 and 4) and if the system is not stirred. So it seems evident that the formation and desorption of $H_{2,g}$ must be accelerated by stirring the system.

4. Conclusions and outlook

The photocorrosion of copper reported above may be interesting in the point of view of material sciences. The only one paper known to us treating this subject describes the corrosion of copper and copper-based materials used for the manufacture of nuclear waste containers by the exposition to a gamma radiation field [9]. Regarding the synthetic point of view the described photochemical generation of CuCl is of significant importance, because thin layers of surface immobilized CuCl are available. In further investigations CuCl nano- and microparticles of well defined structures, fixed on a Cu surface should be synthesized and tested on their photocatalytic activity. Also surface fixed CuCl should be converted into immobilized Cu_2O, recently found to be an effective catalyst for overall water splitting [10,11].

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