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Phase-contact engineering in mono and bimetallic Cu-Ni cocatalysts for hydrogen photo-production materials

Mario J. Muñoz-Batista,^[a] Debora Motta Meira,^[b] Gerardo Colón,*^[c] Anna Kubacka,*^[a] Marcos Fernández-García*^[a]

Abstract: Understanding how a photocatalyst modulates its oxidation state, size and structure during a photocatalytic reaction under operando conditions is strongly limited by the mismatch between (catalyst) volume sampled by light and, to date, the physico-chemical techniques and probes employed to study them. Here we present a synchrotron micro-beam X-ray absorption spectroscopy study together with the computational simulation and analysis (at the X-ray cell) of the light-matter interaction occurring in powdered TiO₂-based monometallic Cu, Ni and bimetallic CuNi catalysts for hydrogen production from renewables. The combined information unveils an unexpected key catalytic role involving the phase contact between the reduced and oxidized non-noble metal phases in all catalysts and, additionally, reveals the source of the synergistic Cu-Ni interaction in the bimetallic material. The experimental methodology is applicable to operando studies of a wide variety of photocatalytic materials.

Hydrogen production from renewables such as bio-alcohols and water is a potentially clean means for fuel generation. Currently few methods achieve this objective. Catalytic reforming is one of them but a photocatalytic (reforming) process would be a better choice owing the significantly less demanding technological (temperature, pressure) requirements and the simplicity of the concept. Most active reforming photocatalysts contain titania as a semiconductor and noble or non-noble metals as co-catalyst.^[1,2] Moreover, as happens in many catalytic processes, significant activity improvement is usually obtained by formulations containing bimetallic components. Among them, the Cu-Ni system has shown strong activity enhancement in a significant number of photocatalytic reactions, including hydrogen production, with respect to their monometallic counterparts.^[3-5]

The photocatalytic process involves excitation of a semiconductor such as TiO_2 upon illumination and subsequent production of electron-hole pairs. These pairs either recombine or generate chemistry at the surface of the material. In the case of hydrogen production, the presence of the co-catalyst is needed to trap photo-excited electrons (mostly) generated at the semiconductor and transfer them to hydrogen ions originally coming from the alcohol molecule.^[1,2] The process is modulated

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by the physico-chemical properties of the co-catalyst but their insitu, e.g. under the simultaneous influence of the reactants and light, analysis is hidden by the mismatch between the portion of the sample illuminated and the sample volume commonly probed by physico-chemical characterization techniques.

While it is well established that physico-chemical properties such as oxidation state or phase composition, as well as particle size and atomic structure of the active phase(s) of a catalyst drive its functional catalytic output, their quantitative understanding is by no means easily achievable for a photocatalytic material. As indicated, axiomatic to in-situ or operando conditions for photocatalytic processes should be the requirement of carrying out measurements under the simultaneous influence of the light and the reactants. To reach this objective and maximize information we use a combination of two techniques, micro-XANES and micro-EXAFS, which will render significant and complete information about the above mentioned physico-chemical properties of a bimetallic CuNi co-catalyst supported on a high surface area anatase-TiO₂ oxide.^[6,7] We also focus on understanding the synergistic capability of the bimetallic CuNi photo-material with respect to monometallic Cu or Ni counterparts.

In this contribution, we analyzed the gas-phase photo-production of hydrogen from (1:9 v/v) methanol:water mixtures under continuous flow conditions using an experimental set-up (Figure 1, S1, and S2 of section 1.1 of the S.I.) based in a low dead volume reactor. In-situ micro-beam X-ray measurements were carried out in a fluorescence mode as detailed in section 1.2 of the supplementary information section. The computation of the light-matter interaction at the sample holder (carried out as described in section 1.3 of the S.I.) for our three systems renders the light intensity variation presented in Figure 2.



Figure. 1. Schematic view of the sample and experimental conditions. The sample is confined in a cell which allows simultaneous gas phase treatment and illumination from to top side. Arrows show the direction of the gas flow, illumination and incident X-ray micro-beam. The X-ray micro-beam probes non noble metal chemical states and structure as a function of the depth from the surface. Panels at the right hand depict the most relevant metal-containing phases (Cu(0) brown color; Cu(II) black color) for different depths described by the light intensity received. Cu and CuNi samples are considered.

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Figure. 2. Light intensity decay (Einstein cm⁻² nm⁻¹) as a function of the depth from the surface of the Cu (left), CuNi (center), and Ni (right) samples.

The intensity decay from the sample surface is obviously wavelength dependent but the three samples show rather similar results as a consequence of the dominant contribution of the anatase support. The wavelength averaged result for the CuNi sample as a function of the distance from the surface (depth) is presented using the same color code (as in Figure 2) in Figure 1. From this result it becomes obvious that a beam spot well below 5 microns is required to obtain meaningful results.

Photo-catalytic activity measurements (experimental set-up presented in Figure S3, section 1.5 of the S.I.) indicate that the bimetallic CuNi powder presents a strong synergistic interaction with respect to the monometallic counterparts (enhancement ratios x2.5 and x5 measured per surface metal atom, with respect to Cu and Ni samples, respectively, see Figures S4 and S5 at section 2 of the S.I.). The co-catalyst(s) physico-chemical properties as a function of the sample depth from the surface were analyzed with the help of several conventional techniques (summary of result at Tables S1 and S2 and Figure S6 at section 3 of the S.I.) and, more importantly, XAS techniques. Operando XANES spectra at the Cu and Ni K-edges are presented in Figures S7 and S8, respectively. Samples under illumination and dark conditions were evaluated in independent experiments. A first shocking result appears when examining Cu K-edge results at the "surface" position (as described in section 1.3 of the S.I. using XAS we measured the "surface" within 4 microns in depth). Among the positions scanned in this study, the outermost layer is the only one that suffers differences when illuminated, irrespective of the (copper-containing) sample measured. Previous to the light switching on, copper is in a fully reduced state by interaction with the reductant alcohol during saturation time. Then, under illumination both the monometallic Cu and bimetallic CuNi suffer an oxidation process from such fully reduced state. Experiments presented in Figures S9 and S10 and concerning effects of time and light swithching indicate that the oxidation process is fully reversible and requires the joint effect of light and the reaction mixture. Just below the surface, copper remains reduced up to a depth where the effect of the gas phase on the solids disappears. Contrarily to the copper case, XANES demonstrates that Ni maintains always a dominant Ni(II) oxidized state at the surface and bulk positions

of the catalysts, with negligible changes under dark or illuminated conditions (Figure S8).

Factor Analysis (details at Table S3, section 4.1.2 of the S.I.) was utilized to shed more light into the oxidation process taking place under illumination for the copper component of the catalysts previously contacted with the gas mixture (e.g. in a previous fully reduced state according to dark experiments). Figure 3 summarizes the results of the study which confirms the presence of a Cu(II) oxidation state only in the illuminated zone of the materials. More concretely, ca. 38 and 11 mol. % of copper appears in a oxidic Cu(II) environment for Cu and CuNi samples, respectively, while the rest of copper remains as Cu(0). So, a first difference between our copper-containing samples concerns the degree of oxidation. The XANES spectra corresponding to the pure chemical species (Cu(0) and Cu(II)) expand the differences between the samples. As can be seen in Figure 3 subtle differences are presented in the Cu(II) state but more acute ones are visible in the Cu(0) state. The typical shape of the Cu foil is reasonable followed by the Cu sample. The CuNi displays a typical 1s \rightarrow 4p pre-edge transition but the characteristic valley between the 5sp resonances is less marked as a consequence of the (energy) smearing of the corresponding continuum states, a typical effect of alloying (the XANES spectrum is further discussed in section 4.1.3 of the S.I; Figure S11).^[8,9] Note however that this would occur with a rather limited quantity of Ni (Cu-rich alloy) as the Ni K-edge does not show a significant reduction of Ni. This limits the Ni content of the alloy well below 10 at. %.

The analysis of the supported phases was completed with the structural view rendered by *operando* EXAFS.¹⁰ Absence of significant differences at the Ni K-edge is observed between Ni and CuNi samples under dark or illumination conditions (see section 4.2 of the S.I.; Figure S12). Ni is not responding to the gas phase or illumination to a significant degree. At the Cu K-edge, comparative analysis of the EXAFS fitting results (shown in Figures 4 and S13) for the Cu and CuNi samples can be carried at the surface and below it. At the surface (see Table S4 of S.I.) the Cu sample displays a metallic-type Cu-M (M: Cu, Nil) contribution (distance characteristic of the metal) absent in the CuNi sample. This is qualitatively observed in the imaginary part

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Figure. 3. Contour plot of Cu K-edge XANES spectra obtained under illumination for the Cu (left) and CuNi(right) samples. For the surface position, the two previous states (fresh sample and after gas saturation) are included. Concentration profiles (central part) and XANES spectra (lower panels) corresponding to pure chemical species obtained from PCA are included. Colors in the central panel are assigned to pure species: black, Cu(II); orange, Cu(0).

of the Fourier Transform in Figure 4 (bottom panels) and is quantitatively assessed in section 4.2.2 of the S.I. (Figure S14; Table 5). Combined with the XANES results indicating the presence of Cu(0) in both catalysts, the joint analysis proofs a different contact between the Cu(0) and the Cu(II) phases detected within the surface region of the catalysts. As Cu is fully reduced before light switching on, illumination renders a coreshell type structure (depicted in Figure 1) for the Cu sample. Others interpretations of the EXAFS results would not be possible as the metallic core has a size significantly lower than the particles at dark conditions (ca. 15 vs. 50 atoms, according to calculations summarized in Tables S4 and S6 and considering metal-metal first shell coordination numbers of 5.3 and 7.4, respectively). Due to the more facile oxidation of copper nano-particles as the particle size decreases, [11] such result indeed indicates the formation of a metallic core and dismisses an interpretation based in a fraction of (the smallest) particles not oxidized. For the CuNi sample, zerovalent Cu atoms do not show significant Cu-M (M=Cu, Ni) interactions (section 4.2.2 of S.I.), indicating that they corresponds to rather small clusters dispersed in a Cu(II) matrix. This is likely an effect of Ni (limited) presence in the initial zerovalent phase as no (differential) size effect is expected between the Cu and CuNi samples (analysis of metallic particles size at dark conditions presented in Table

S6, section 4.2.3 of S.I.). The chemical and structural differences between the two (Cu and CuNi) samples at the surface are graphically summarized in Figure 1. Below the surface, some differences between the fully reduced state of Cu and CuNi samples can be encountered (these are discussed in section 4.2.3 of the S.I). In particular, EXAFS shows some size differences between these two samples (see Figure S15 and Table S6, section 4.2.3 of S.I.), but they do not significantly change the dispersion of the corresponding non-noble metal phase (0.82±0.04 for all cases) as a consequence of the small metal particle size in both samples, always below 1.5 nm.

The study thus shows that copper vividly responds under *operando* conditions while nickel has a significantly lower response and thus chemical role in bimetallic systems. The higher activity of copper is a known fact in the literature and is here corroborated by the catalytic experiments.^[3-5,12-14] Focusing on the comparison of copper containing catalysts, the results are however radically different from previous studies based on a conventional use of XPS, TPD^[12-14] or EXAFS.^[13-14] All these previous reports indicate the significance of copper reduced states in photo-activity. This agrees with our results as an average of the sample subjected to the gas phase contact (see Figure 1), but it is not certainly the view coming from the sample part upon the simultaneous influence of light and gas phase, a

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Figure 4. Upper panels: Fourier Transform magnitude and imaginary part of the Cu K-edge EXAFS signals (red curves) obtained for the Cu and CuNi samples. Fitting results (black curves) are also included. Lower panels; low-R detail of the Fourier Transform obtained at the surface of the materials (red curve). The lower panel figures include the normalized Cu foil (blue curve) and CuO (black curve) references.

fact achievable by the first use of X- ray micro-beam and the understanding of the light-matter interaction at the measurement cell. For the Cu sample we observed a core-shell structure where the metallic copper facilitates the electron handling properties while the surface chemical role is played by the oxidized copper phase. Larger photo-activity is nevertheless obtained for the CuNi sample, with a secondary chemical role played by nickel. In this case, the copper-rich component is composed by metallic entities with limited atomicity (according to EXAFS) finely dispersed into a copper oxide matrix (according to XANES). As a result, the key effect of nickel is to shape the phase contact among copper-rich phases and to control the electronic and structural properties of both (but particularly the metallic type state), leading to a synergistic interaction with significant influence in photo-activity. Thus, the combination of truly operando micro-XANES and -EXAFS at relevant light/Xray beam probe "lengths" unveils a new perspective in both monometallic and bimetallic catalysts, which can be useful in a significant number of photocatalytic studies.

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Conflict of interest

The authors declare no conflict of interest.

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interaction • Photocatalysis • Bio-alcohol reforming • Hydrogen production

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Synchrotron micro-beam X-ray absorption spectroscopy study together with the computational simulation and analysis (at the X-ray cell) of the light-matter interaction occurring in powdered TiO₂-based monometallic Cu, Ni and bimetallic CuNi catalysts for hydrogen photoproduction from renewables



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