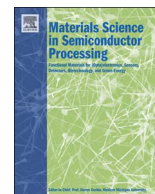




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## On the role of Cu, Ag and Pt in active titania for gas-phase ethanol photo-reforming

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## ABSTRACT

The influence of the synthesis method for the preparation of metal-loaded TiO<sub>2</sub> with Cu, Ag, Pt and bimetallic Cu-Ag and Cu-Pt for the gas-phase ethanol photo-reforming and the evaluation of the effect of water during the reaction have been studied. The analysis of H<sub>2</sub> and of the by-products obtained through the oxidation path have demonstrated that copper is a promising material for this process, either as single co-catalyst or by modulating the properties of the other metallic species.

## 1. Introduction

The sustainable generation of hydrogen is an essential process in order to fulfill the directives for the deployment of renewable energies and a circular CO<sub>2</sub> economy [1]. For this reason, it is fundamental to develop alternatives to the gas natural steam reforming process, such as photoelectrochemical or photocatalytic water splitting [2] or photovoltaics coupled to electrolysis [3]. Though, because of the inherent thermodynamic limitations for the water oxidation, the H<sub>2</sub> generation through photo-reforming of oxygenated compounds is a promising approximation [4–6]. This process presents feasible thermodynamic constrictions, entailing easier implementation into a circular economy by using biomass-derived fuels such as ethanol. In fact, the attention attracted by this process is reflected on the growing number of papers published into this direction. TiO<sub>2</sub> has shown to be an effective photocatalyst for this reaction, given its favorable photoactivity for the oxidation half-reaction. Furthermore, the H<sub>2</sub> generation is efficiently boosted by coupling with noble metal co-catalysts like Pt, Pd or Au [7–10]. However, because of the cost restrains supposed by the use of expensive materials, the interest into the use of other metals like Cu or Ni for this reaction has grown. In fact, copper-loaded TiO<sub>2</sub> has demonstrated to be efficient in the photo-reforming of alcohols (methanol, ethanol, ethylene glycol and glycerol) and carboxylic acids (formic acid, oxalic acid), in processes both in liquid and gas phase [5,11–16]. Interestingly, although several deposition methods have been studied, leading to different oxidation states of the Cu species, it has been observed that the co-catalytic effect could be ascribed to several forms, given the dynamic charge transfer process during which Cu can be both reduced and oxidized [5,6,17]. Besides copper, silver

might be a less expensive alternative for this reaction, despite its lower catalytic activity for the hydrogen evolution reaction [4,18]. Modification of the H<sub>2</sub> generation mechanism with Ag by means of additives and/or deposition of a bimetallic Ag-Cu have been also evaluated and improvements in the performance have been achieved [19,20]. Given these considerations, in the present work we evaluate the deposition of metallic and bimetallic co-catalysts on TiO<sub>2</sub> and the influence of the reaction conditions on the performance of each metal, considering the reduction and oxidation products, during the gas-phase ethanol photo-reforming process.

## 2. Experimental

## 2.1. Preparation of the photocatalysts

For the synthesis of the TiO<sub>2</sub> samples, a sol-gel method followed by a hydrothermal treatment was used [21]. In short, a Ti<sup>4+</sup> colloidal solution was prepared and used in two ways: i) obtaining the xerogel by drying and directly grinding and performing a thermal treatment (TiO<sub>2</sub>-sg), or ii) submitting to hydrothermal treatment and a further calcination (TiO<sub>2</sub>) (Supporting Information). Cu-modified TiO<sub>2</sub> samples (1 wt % Cu) were prepared by following two methods: the first one, following a wet impregnation of the TiO<sub>2</sub> sample (TiO<sub>2</sub>-Cu) and the second one, by incorporating a low amount of Cu on the Ti-sol prior to the hydrothermal treatment (TiO<sub>2</sub>-Cu-HT). Both samples were further thermally treated. Bimetallic TiO<sub>2</sub> samples were obtained from the TiO<sub>2</sub>-Cu samples by impregnation with low content (0.5 wt%) of Ag (TiO<sub>2</sub>-Cu-Ag) or Pt (TiO<sub>2</sub>-Cu-Pt), using a similar procedure than with the Cu. A two-step thermal treatment was carried out: first under air atmosphere

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and second under  $H_2/Ar$  (5%) gas. For comparison, metal photo-deposition of Ag and Pt on  $TiO_2$  was also carried out [22].

In order to perform the photocatalytic tests, the samples (100 mg) were deposited on glass substrates by drop-casting.

## 2.2. Physicochemical and functional characterization

The crystalline structure of the samples was measured by XRD and the crystallite sizes were determined with Scherrer equation. The morphology was observed with a FE-SEM equipped with an EDX system and TEM. The optical characterization was performed in a UV-vis-NIR spectrometer by Diffuse Reflectance measurements. The chemical analysis was carried out by XPS. BET surface area and porosity were analyzed by  $N_2$ -adsorption (see SI for further details). The gas-phase photo-reforming tests were carried out by continuously sparging an inert gas through a saturator with a Water/Ethanol and passing this mixture through a photocatalytic reactor equipped with a quartz window. UV-vis irradiation source was used and the outlet gas was analyzed in Micro-GC system (see SI for more details on the Experimental part. An scheme has been included describing the synthesis procedure).

## 3. Results and discussion

The XRD results are shown in Fig. 1A. All the obtained materials present a single phase structure corresponding to anatase  $TiO_2$  (JCPDS: 21-1272). As expected for the low nominal contents, no additional signals are detected after the metal impregnation. Despite all the samples exhibit similar crystallite sizes (around 18 nm), the second thermal treatment performed over the bimetallic systems entails slight particle size increments. The comparison with the  $TiO_2$ -sg and the  $TiO_2$ -Cu-HT (see Fig. S2) shows a similar crystallite size for the samples submitted to

hydrothermal treatment in the absence of dopant and in the presence of Cu during the treatment (14–18 nm).

As seen in the UV-vis absorbance spectra in Fig. 1B, the  $TiO_2$ -Cu sample exhibits two wide absorption bands associated to Cu species: one between 400–570 nm, which might be related to  $Cu^+$  dispersed on the CuO [13], and a second at longer wavelengths associated to  $Cu^{2+}$  environments. Concerning the bimetallic samples, a wide absorption band above 400 nm is observed. For the  $TiO_2$ -Cu-Ag, a small band with absorption at  $\lambda \sim 496$  nm agrees with the one observed in literature for Ag-Cu alloys [19]. In the same manner, the  $TiO_2$ -Cu-Pt presents a wide absorption band which can be attributed to the resonance plasmon characteristic of metallic Pt particles [10,23]. According to the micrographs of the bimetallic  $TiO_2$  samples, Figs. 1c and 1d, the samples are constituted by small  $TiO_2$  grains with metallic particles. Regarding the  $TiO_2$ -Cu-Ag, the Cu-Ag metallic alloys have relatively large sizes ( $\phi = 50$ –100 nm) with lower relative amount of Ag (see Fig. S3). Oppositely, TEM micrographs show that the  $TiO_2$ -Cu-Pt sample is composed by very small nanoparticles. However, no signal associated to Pt was detected by EDX, probably because of the higher dispersion and low Pt content.

The physicochemical properties collected in Table S1 show minor differences among the samples. In particular, both the BET areas and pore volume are very similar, indicating no surface or pore losses after metal impregnation. Similarly, the intrinsic band gap calculated from the UV-vis spectra indicate that a minor red shift occurs as consequence of Cu addition, although the values are in the expected range for anatase  $TiO_2$ .

The XPS spectra of the  $TiO_2$ -Cu and  $TiO_2$ -Cu-Ag samples before and after a photo-reforming test with their corresponding deconvoluted peaks are depicted in Fig. 2. Generally, all the materials present similar metallic species. In the Cu  $2p_{3/2}$  region, two main signals located at  $\sim 934$  and  $\sim 932.4$  eV are discerned, being those related to  $Cu^{2+}$  and less oxidized species such as  $Cu^+$  or  $Cu^0$ , respectively. A more detailed

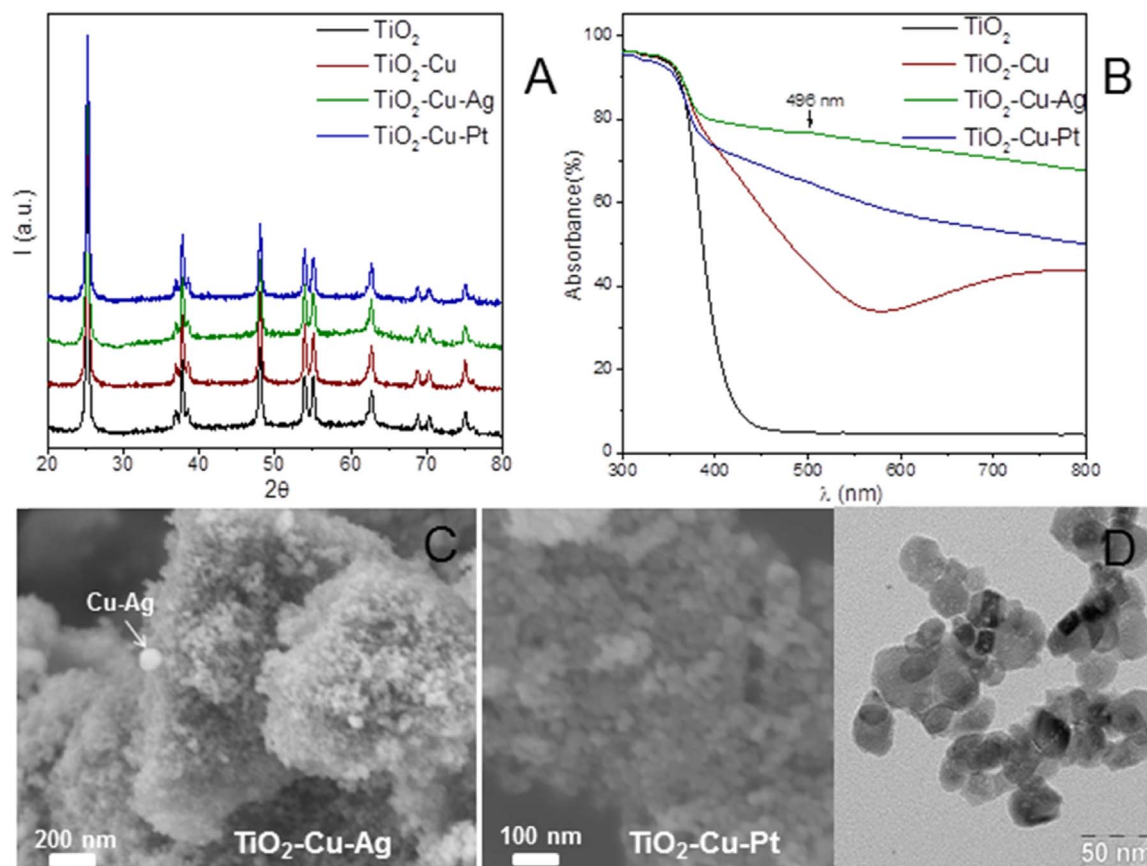


Fig. 1. XRD results (A) and UV-vis absorbance (B) of the different samples. In (C), an SEM image of the  $TiO_2$ -HT-Cu-Ag, and in (D) an SEM and a TEM of the  $TiO_2$ -HT-Cu-Pt.

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