Synthesis of 2,5 furandicarboxylic acid by selective oxidation of 5-hydroxymethyl-2-furfural over Au-Cu/TiO$_2$ catalysts.

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Introduction

One of the most important sources of biomass is represented by sugars, which are widely available and easily transformable. Homogeneous dehydration of glucose and/or fructose leads to the formation of 5-hydroxymethyl-2-furfural (HMF) which is a key precursor for the synthesis of derivates with applications within pharmaceutical and polymer industry [1].

Recently, Au supported catalysts have been found to be very active for the 5-hydroxymethyl-2-furfural (HMF) oxidation to 2,5-furandicarboxylic acid (FDCA), a possible removable substitute of terephthalate acid. Many researchers have focused their attention in searching for the best supports and reaction conditions to improve the FDCA yield [2,3] nevertheless, catalyst stability and process productivity remain very low.

The aim of this work was to study the reaction of HMF oxidation using monometallic and bimetallic gold-copper nanoparticles supported on titania using mild reaction conditions (60-115°C, 10 bar).

A simple, microwave-assisted, strategy for producing Au and Au/Cu sols by glucose reduction in water was developed [4] and titania supported catalysts were prepared by immobilization of these preformed monometallic and bimetallic colloids.

Catalyst properties and reaction parameters have been studied thoroughly together with catalyst reusability. A deep characterization was performed on prepared catalysts using STEM-HAADF imagining, XEDS spectra, XRD, BET and TG analysis. The effect of oxygen pressure, metal loading, reaction time, amount of base and temperature were studied in detail and a 99% yield of FDCA was achieved under optimized reaction conditions.

Experimental

Au/TiO$_2$, Cu/TiO$_2$ and Au-Cu/TiO$_2$ catalysts were prepared by immobilization on the TiO$_2$ surface of the preformed monometallic and bimetallic colloids. Bimetallic Au-Cu colloids using PVP as stabilizer and having Au:Cu molar ratios of 1:1, as well as monometallic Au and Cu colloids, were synthesized by the microwave assisted reduction of HAuCl$_4$ and CuSO$_4$ ·5H$_2$O with β-D-glucose in alkaline water [5,6]. The PVP-coated colloids were prepared by using a microwave oven (Microsynth Plus, Milestone).

Before use, the as-prepared sols were concentrated and washed with distilled water using ultrafiltration (Millipore) with a 100.000 Da filter to eliminate the excess PVP and other reagents dissolved in the aqueous media. The Au an Au-Cu colloids were then immobilized onto TiO$_2$ using four different metal weight ratios (0.5, 1, 1.5, 2 %wt.)

The oxidation of 5-hydroxymethyl-2-furfural (HMF) was carried out using an autoclave (Parr Instruments) reactor of 100 mL capacity and equipped with a magnetic stirrer (0–1200 rpm) and provision for measurement of temperature and pressure.

Results and Discussion

Our studies indicated that the use of high amounts of base in absence of catalyst leads to the complete degradation of HMF after 2.5 h of reaction with formation of by-products such as formic acids.

Figure 1 shows the time on line that was performed to understand the pathway of the oxidation. The aldehydic group of HMF is quickly oxidized to the carboxylic acid and a yield of 90% in 5-hydroxymethyl-2-furancarboxylic acid (HMFCA) is achieved within 50 min. The subsequent functionalization of the HMF hydroxyl group was found to be the rate limiting step. After 4 h at 95°C a yield of 90-99% of 2,5-furandicarboxylic (FDCA) was achieved without the formation of any by-products. This demonstrates the importance of having a very active catalyst that acts to inhibit the decomposition reaction pathways by selectively oxidizing the 5-hydroxymethyl-2-furfural to 2,5-furandicarboxylic acid.
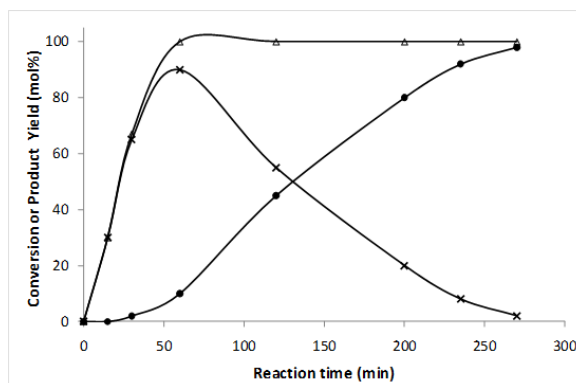
Figure 1: HMF conversion and product yields as a function of reaction time. Catalyst 1.5(AuCu)-Ti. Reaction conditions: 95°C, 10 bar of oxygen pressure 1 mmol of HMF and HMF:Metal Loading:NaOH molar ratio 1:0.01:4. Legend: $\triangle$ HMF Conversion; ● FDCA yield; × 5-hydroxymethyl-2-furancarboxylic acid (HMFCA) yield.

Interestingly, all the bimetallic Au-Cu supported catalysts displayed an improved activity, by at least factor of 2 with respect to their corresponding monometallic Au catalysts, due to the ability of the copper in dispersing gold nanoparticles.

Furthermore, after reaction, the bimetallic Au-Cu catalysts can be recovered by filtration and reused without any loss of activity and selectivity (Figure 3a). In contrast, monometallic gold catalysts are not stable upon re-use under reaction conditions (Figure 3b).
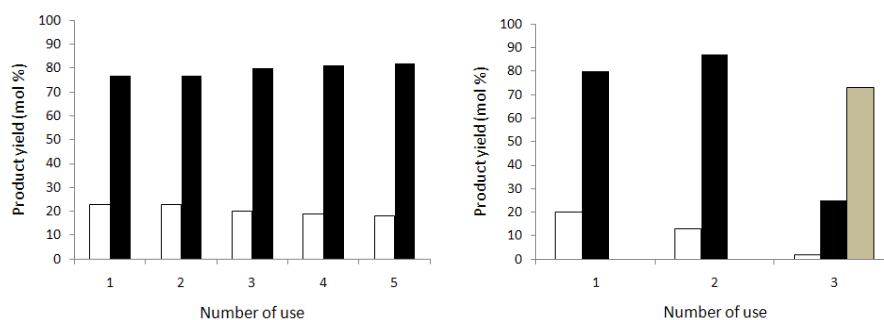
Figure 3: Reusability study for the oxidation of HMF using AuCu/TiO$_2$ (a) and Au/TiO$_2$ (b) as catalysts. Molar yields are given at total conversion of HMF. Reaction conditions: 60°, 240 min, 10 bar of oxygen pressure. Legend: □ FDCA and ■ (HMFCA) ■ polymers.

Conclusions

Obtained results [7] emphasize the importance of the synthesis procedure and of the essential synergistic interaction between copper and gold, in order to evidence Cu promotional effect.

Au-Cu/TiO$_2$ catalysts were found to exhibit remarkable degree of stability with respect to Au based materials and, to the best of our knowledge, this is the first report of a catalytic system stable for HMF oxidation in the presence of base.

References

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