Chemicals from bioethanol: tailoring copper electronic properties to enhance its performance on the one-pot ethyl acetate synthesis

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The USA and Brazil are responsible for approximately 90 % of the biomass-derived ethanol produced worldwide. Therefore, these countries share the interest in the transformation of bioethanol into chemicals, such as ethyl acetate. This ester is widely used as a replacement for aromatic solvents in paints, inks and dyes; moreover, it can be used in the pharmaceutical, cosmetic, and food industry. Ethyl acetate is commercially obtained from non-renewable sources though multiple reaction processes. Recent studies have shown that ethyl acetate can be obtained from bioethanol though a one-pot reaction catalyzed by copper-based catalysts (for example, $CuCr_2O_4$ and Cu/ZrO_2 catalysts). The reaction mechanism involves the dehydrogenation of ethanol on the metal surface, followed by coupling of the newly formed aldehyde with an ethanol molecule (Step 1: $CH_3CH_2OH \rightleftharpoons CH_3CHO + H_2$; Step 2: $CH_3CHO + CH_3CH_2OH \rightleftharpoons CH_3CO_2CH_2CH_3 + H_2$). Our group has shown that Cu/ZrO_2 is a remarkable catalyst for this reaction and proposed that the reaction takes place in the interface between metal and support. It was also shown that the equilibrium Cu^0/Cu^+ plays a major role in the catalytic performance. However, the low specific surface area of zirconia does not favor the formation of a large extent of interface metal-support.

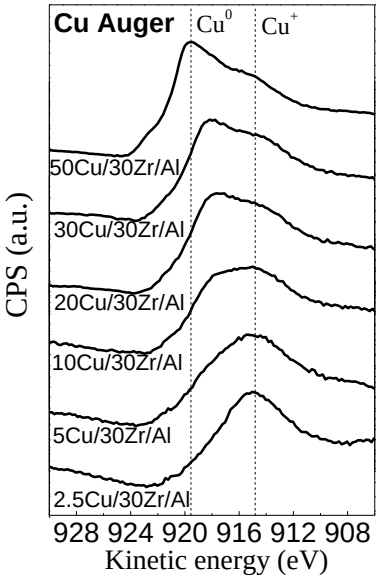


Fig 1. XPS of Cu Auger core level for reduced Cu supported on 30 wt. % Zirconia on Alumina.

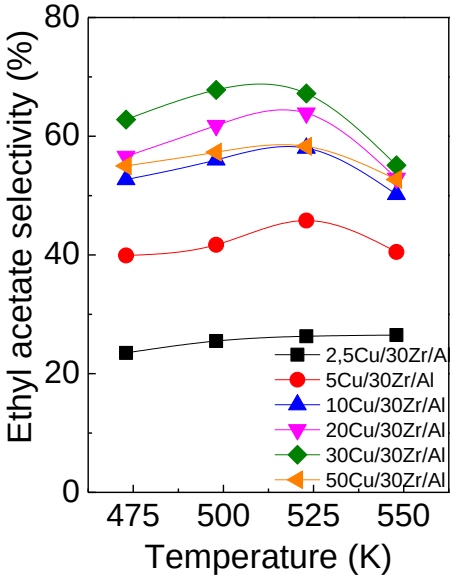


Fig 2. Evolution of the selectivity to ethyl acetate over xCu/30Zr/Al (where x is the wt. % of copper)

For catalysts syntheses, zirconia and copper were dispersed in a high surface area alumina support (370 $m^2\ g^{-1}$) in order to increase the interface copper/zirconia. Different ratios alumina/zirconia/copper were studied aiming to find the optimal catalyst composition. The

catalysts were studied by several characterization techniques, such as X-ray diffraction, nitrogen physisorption, and temperature programmed reduction. Analyses of infrared of the samples adsorbing carbon monoxide showed that copper is placed primarily on the zirconia surface, however, at high copper loadings a significant amount of copper is also observed in the alumina surface. Another important characterization technique used was X-ray photoelectron spectroscopy (XPS), which showed that increasing copper loading led to an higher Cu^0/Cu^+ ratio on the metal nanoparticle surface (as shown in Fig. 1). Comparing Fig. 1 and 2, it can be observed that the samples containing 20 and 30 % of copper (20Cu/30Zr/Al and 30Cu/30Zr/Al) were the ones with the optimum ratio of Cu^0 over Cu^+, since they displayed the highest selectivity for ethyl acetate (60-70 %). For the samples with lower copper loading (2.5Cu/30Zr/Al, 5Cu/30Zr/Al, and 10Cu/30Zr/Al), the higher Cu^+ concentration on the surface led to an increasing concentration of acetaldehyde on the metal surface and, therefore, facilitated the condensation reactions to heavy byproducts. Increasing the copper loading to 50 % (50Cu/30Zr/Al) led to the formation of bulk copper particles, which are selective to acetaldehyde formation, but lacks in the interface with zirconia, diminishing the formation of ethyl acetate.

It is important to mention, that Cu supported in alumina presents a low selectivity for ethyl acetate, and therefore zirconia is essential on providing active sites for the coupling reaction. If compared with the classical Cu/ZrO_2 catalyst, Cu/30Zr/Al (both at the same copper loading) has similar activity to ethanol conversion, however it shows significant improvement in the selectivity and reaction rate for ethyl acetate. This behavior can be attributed to the higher copper/zirconia interface on the Cu/30Zr/Al catalysts, once both zirconia and copper are highly dispersed in the alumina support.

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