

## Supplementary Information

### Significance of isomeric reaction intermediates in the hydrogenolysis of glycerol to 1,2-propanediol with Cu-based catalysts

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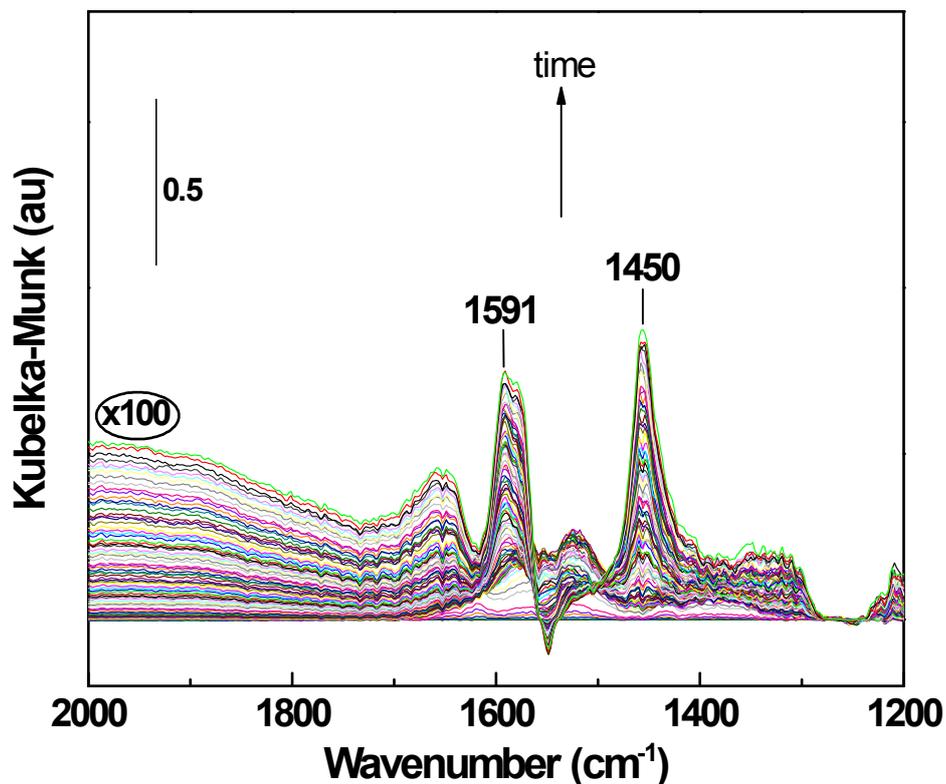
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#### 1. DRIFT spectra after adsorption of lactic acid on CuAl-c catalyst

To reliably assign the intense band at 1591 cm<sup>-1</sup> the following DRIFT experiment was carried out. Lactic acid (Sigma-Aldrich, purum>90 %) was fed to the infrared chamber in vapour phase by using a saturator at room temperature and using either Ar as carrier gas (5 mL·min<sup>-1</sup>). The DRIFT spectra were recorded at 493 K for 0.5 h. Each spectrum is the result of averaging of 32 scans for 12 seconds with a resolution of 4 cm<sup>-1</sup>. Figure 1 shows DRIFT spectra registered during the lactic acid adsorption on calcined copper catalyst (CuAl-c) at increasing time. Two infrared bands at 1591 and 1450 cm<sup>-1</sup> were clearly observed. They are assigned to  $\nu_{as}$  and  $\nu_s$  C-O vibrations of carboxylate group, respectively, in chemisorbed lactate on basic sites of alumina surface. Hence infrared bands observed at these same wavenumber generated after acetol adsorption (see Figure 2 in the manuscript) it can be concluded that these bands are also due to chemisorption lactate groups.

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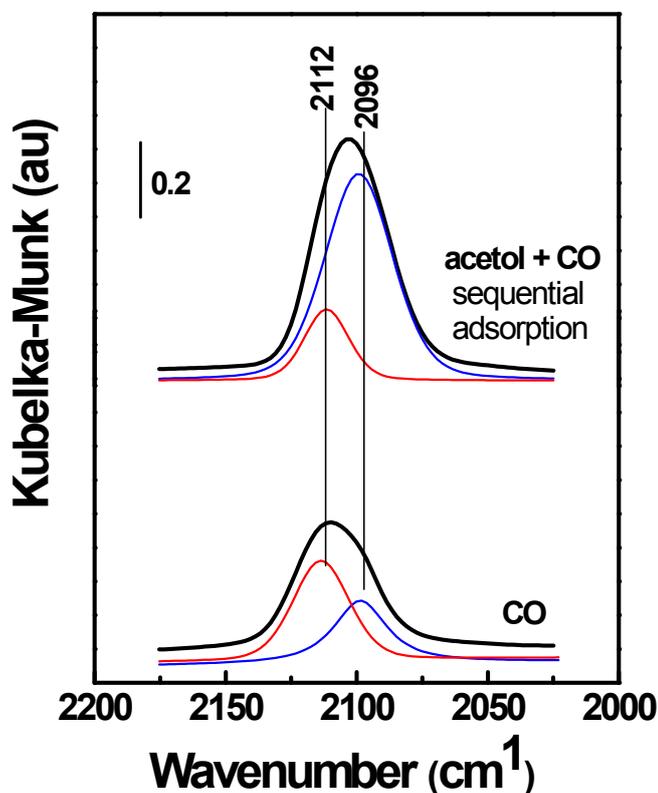


**Figure S1** DRIFT spectra during lactic acid adsorption on CuAl-c catalyst.

## 2. Redox process during the adsorption of acetol on CuAl-c

To confirm the existence of a redox process due to the interaction of acetol with oxidized surface copper species, where these species are reduced whereas acetol molecules are oxidized, and the following experiment was performed. The relative population of oxidized and reduced Cu species before and after acetol sorption was determined by DRIFT spectroscopy of adsorbed CO as probe molecule. Spectra were collected after flowing 50 mL·min<sup>-1</sup> of a 1 vol.% CO/Ar mixture of at 273 K for 1h. The physically adsorbed CO was removed by flowing Ar for 1 h at the same temperature. In this case, the spectra were collected with a resolution of 4 cm<sup>-1</sup> by averaging 256 scans.

The spectrum of solid sample at the corresponding temperature was properly subtracted to all spectra.

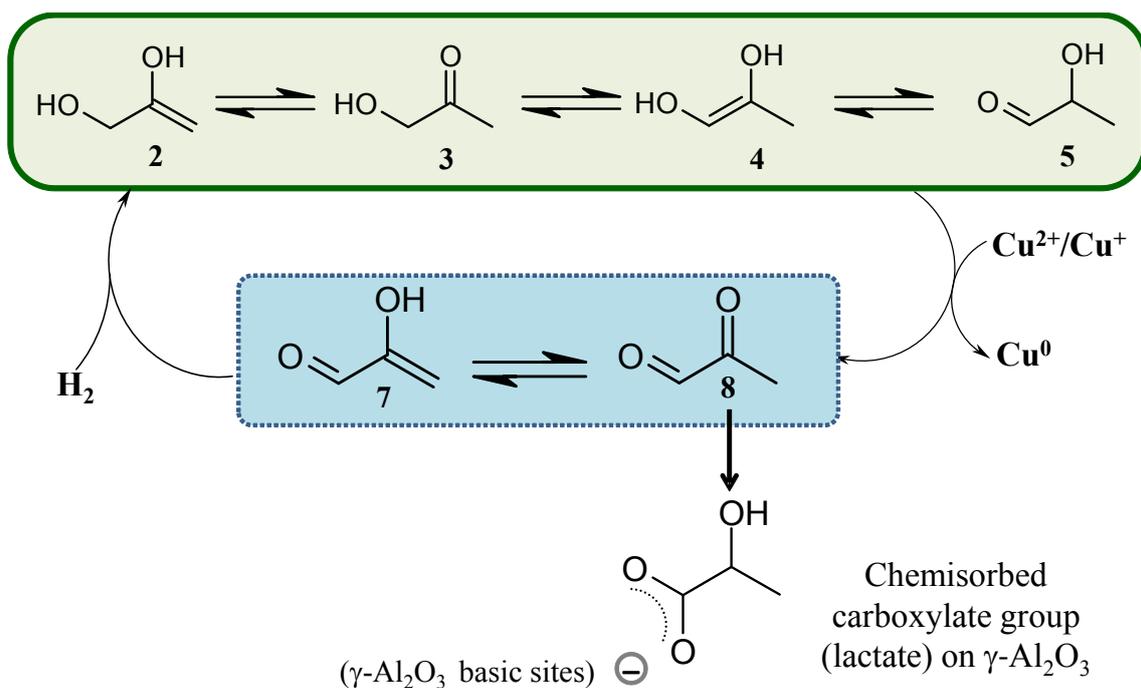


**Figure S2** DRIFT spectra of CO adsorption before and after to acetol adsorption on CuAl-c catalyst.

Figure S2 shows the DRIFT spectra using CO like probe molecule before and after adsorption of acetol on CuAl-c sample. Spectra were deconvoluted in two components at 2112 and 2096  $\text{cm}^{-1}$  ascribed to C-O stretching vibration of chemisorbed CO in  $\text{Cu}^+$ -CO and  $\text{Cu}^0$ -CO species, respectively. The deconvolution spectrum after CO chemisorption on CuAl-c before acetol contact gives rise, besides to  $\text{Cu}^+$ -CO species, to  $\text{Cu}^0$ -CO species despite the fact that a previous reductive process was not done. It is well known that CO can reduce small amounts of  $\text{Cu}^{2+}$  in copper oxide even at 273 K.

Fig. S2 results clearly shows that the amount of metallic copper species increases after acetol adsorption, suggesting that a reduction process of oxidized copper surface species has taken place during acetol treatment. Simultaneously acetol species were oxidized to lactate species (see Figure 2 of the article). This demonstrates the existence of an oxidative pathway in which acetol is oxidised by oxidized species and therefore lactate and  $\text{Cu}^0$  species are formed. The same redox process has been observed for CuAl-r catalyst.

It is well known that  $\alpha$ -hydroxyketones like acetol show a reductive capacity similar to reducing sugars and these are able to react with the Fehling solution (based on  $\text{Cu}^{2+}$  salts). Moreover  $\gamma\text{-Al}_2\text{O}_3$  supported copper catalysts have been used in acid lactic synthesis reaction from glycerol in basic medium. The reaction goes through the formation of pyruvaldehyde by dehydration of glycerol and subsequent intramolecular Cannizzaro reaction to product lactate. Accordingly it can be suggested that the formation of chemisorbed lactate takes place through the route described in the following scheme of Figure S3. In this case the basic sites required for the intramolecular Cannizzaro reaction is suggested to be supplied by basic sites of  $\gamma\text{-Al}_2\text{O}_3$ , a well-known amphoteric oxide.

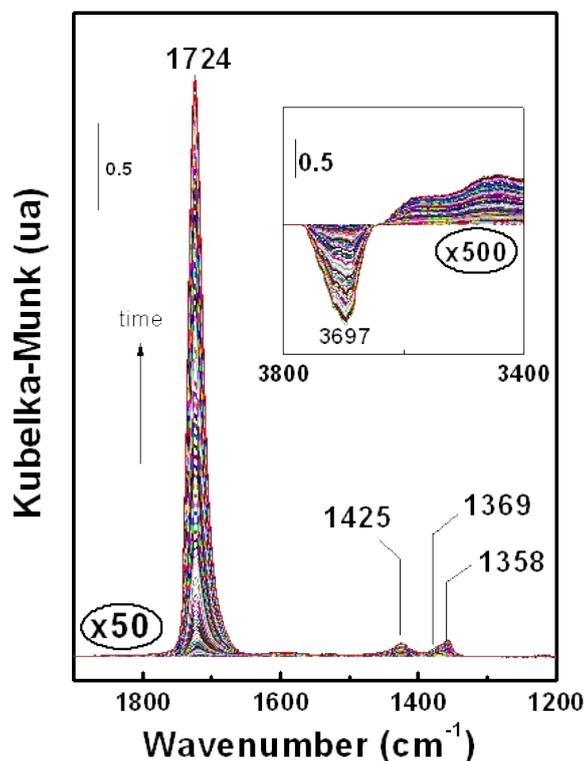


**Figure S3** Proposed pathway to generate chemisorbed carboxylate species (lactate) on the glycerol hydrogenolysis on CuAl catalysts.

### 3. DRIFT spectra during the acetol adsorption on $\alpha$ -Al<sub>2</sub>O<sub>3</sub>

DRIFT spectra of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> in presence of acetol have been displayed in the Figure S4. For this sample a main infrared band was observed at 1724 cm<sup>-1</sup> which can be attributed to C=O stretching vibration. Moreover some small bands at 1425, 1369 and 1358 cm<sup>-1</sup>, associated to C-H bending modes of CH<sub>2</sub> y CH<sub>3</sub> from acetol are present as well. These bands are used as reference and they arise from weakly chemisorbed acetol: no interaction practically was expected between acetol in the gas phase and the very low surface area of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> solid (lower than 5 m<sup>2</sup>·g<sup>-1</sup>). The intensity of these infrared bands is very low in comparison with those presented in the article and increases with acetol adsorption time. The frequencies remain unchanged, suggesting that acetol was weakly chemisorbed over  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>. In the higher wavenumber region (see *inset*) a very

low intensity negative band is observed at  $3697\text{ cm}^{-1}$ , evidencing an interaction of the carbonyl acetol group with weak acidic sites from  $\alpha\text{-Al}_2\text{O}_3$  surface.

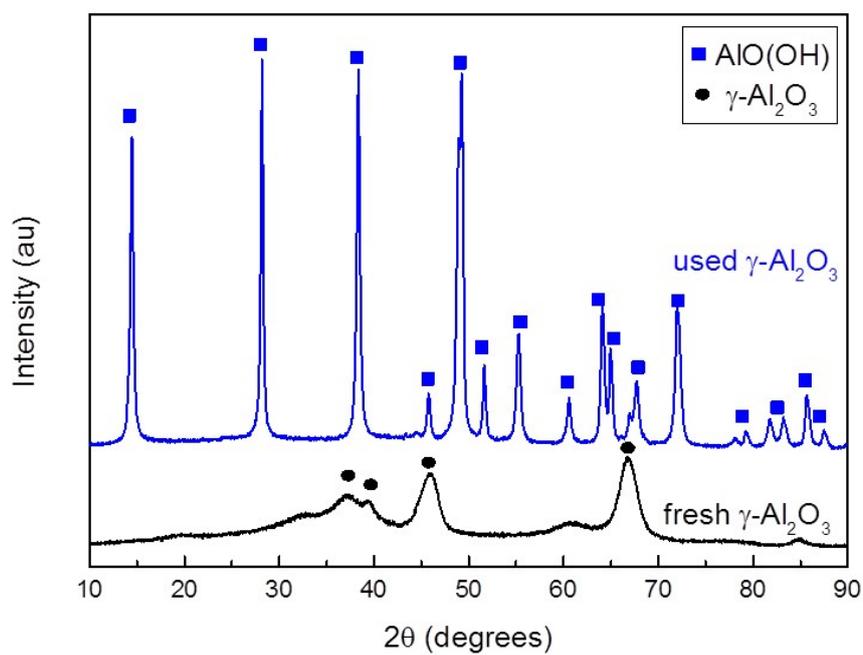


**Figure S4** DRIFT spectra during acetol adsorption at 298 K on  $\alpha\text{-Al}_2\text{O}_3$  sample.

#### 4. Transformation of the $\gamma\text{-Al}_2\text{O}_3$ phase into boehmite ( $\text{AlOOH}$ ) after its use in the reaction of hydrogenolysis of glycerol

In order to confirm that the surface of  $\gamma\text{-Al}_2\text{O}_3$  support is fully hydroxylated under the reaction conditions the following experiment was conducted. The aqueous glycerol solution and an amount of fresh  $\gamma\text{-Al}_2\text{O}_3$  support were loading into the Parr reactor, where a test under the same reaction conditions of the glycerol hydrogenolysis was carried out. Once the reaction ends, it is centrifuged and the solid is separated and

dried. Then both the fresh support as used under the reaction conditions are analyzed by X-ray diffraction. The diffractograms are shown in Figure 5S where it is clearly observed that after reaction, highly crystalline boehmite (JCPDS card 01-083-2384) has been formed.



**Figure S5.** XRD patterns of fresh and used  $\gamma\text{-Al}_2\text{O}_3$  under reaction conditions of the hydrogenolysis of glycerol