

Supporting information

Manuscript title:

“The Joint Synthesis of 1,2-Propylene Glycol and Isopropyl Alcohol by the Copper-Catalyzed Hydrogenolysis of Solketal”

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8 Pages, 5 Figures, 1 Table

Catalyst preparation and characterization

The catalyst was prepared by the co-precipitation of copper and aluminium hydroxides from the corresponding nitrate solutions (1.2 M $\text{Cu}(\text{NO}_3)_2$ and $\text{Al}(\text{NO}_3)_3$ taken in the stoichiometric amounts) with the 20 wt. % NaOH aqueous solution. Reagents were mixed at 40-50°C with subsequent heating up to 90°C for 4 hours. The precipitate was washed with distilled water and centrifuged; the operation was repeated several times. The material obtained was calcined in air at 450°C for 6 hours and reduced in the 10 vol. % H_2/Ar flow at 300°C for 6 hours (temperature ramp 100°C/hour).

The bulk chemical composition of the catalyst was determined by the X-Ray fluorescence (XRF, Thermo ARL 4460). Copper content was found to be 54.8 wt. %.

The textural properties were evaluated using nitrogen low-temperature adsorption technique (ASAP 2020, Micromeritics). The following results have been obtained:

- BET specific surface area: 133.6 m^2/g
- mean pore volume: 0.24 cm^3/g
- mean pore diameter: 66.7 Å

The acidic properties were characterized by the ammonia TPD technique (USGA-101, Unisil). A sample was put to the quartz reactor and treated by the inert gas flow at 500°C for 1 hour. The saturation with ammonia (by its mixture with nitrogen) was performed at 60°C for 15 minutes, then the physically adsorbed ammonia was eliminated at 100°C in the helium flow (30 ml/min) for 1 hour and the sample was cooled down. To obtain the desorption curve, the sample was heated in the helium flow (30 ml/min) up to 900°C with the rate of 8°C/hour; the ammonia release was detected by a TCD.

The estimated total acidity of the catalyst amounted to 177 $\mu\text{mol}/\text{g}$.

The XRD spectra (Figure S1) were obtained with a Rigaku D/Max-RC diffractometer using Cu $K\alpha$ radiation.

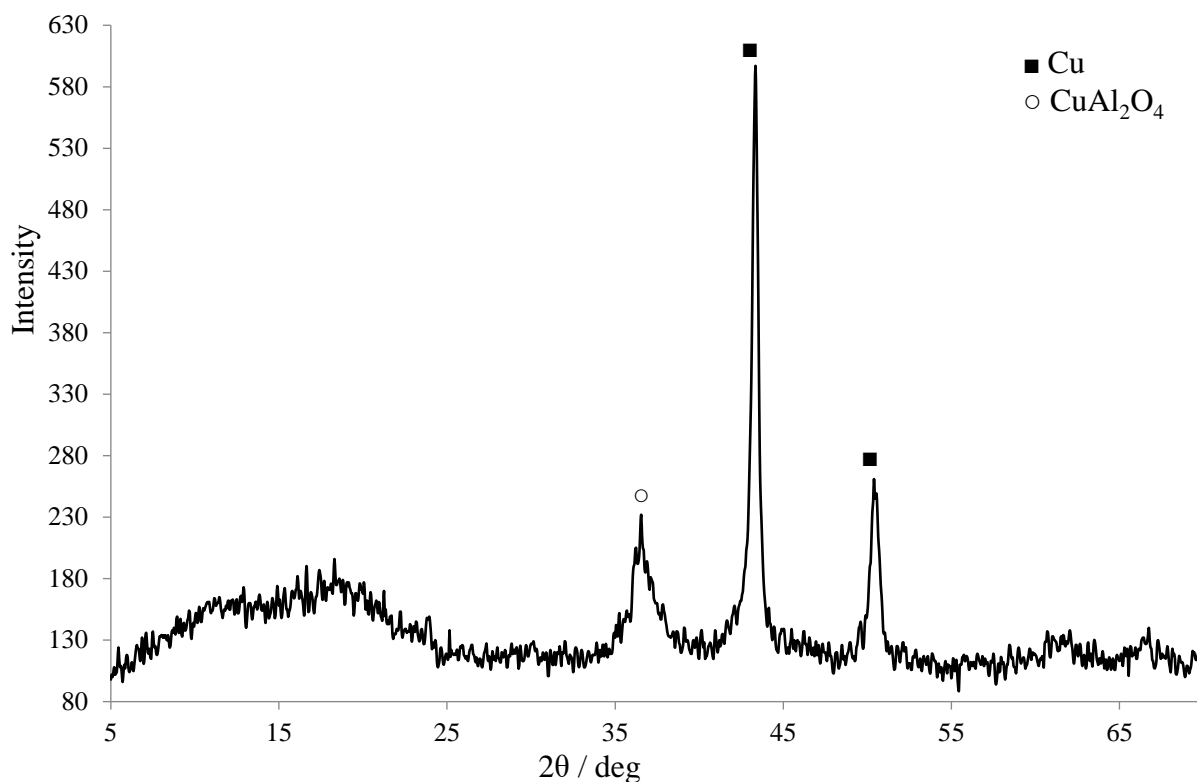


Figure S1. Powder XRD pattern for the 60%Cu/Al₂O₃ catalyst.

As it could be seen, the copper in the catalyst is consisted mainly of Cu⁰ with some extent of the mixed oxide phase (CuO·Al₂O₃).

The microphotographs of the catalyst surface were obtained by scanning electron microscopy (SEM) using JCM-6000 (JEOL, accelerating voltage 15 keV).

The typical microphotographs are given in Figure S2. From Fig. S2.(a-b) it could be seen that the material consists from uneven grains of irregular shape with the diameter from 1 to 1000 μm. At the photographs obtained with the magnification of 500-1000 (Figure S2(c-d)) a well-developed pore structure at the sample surface could be seen.

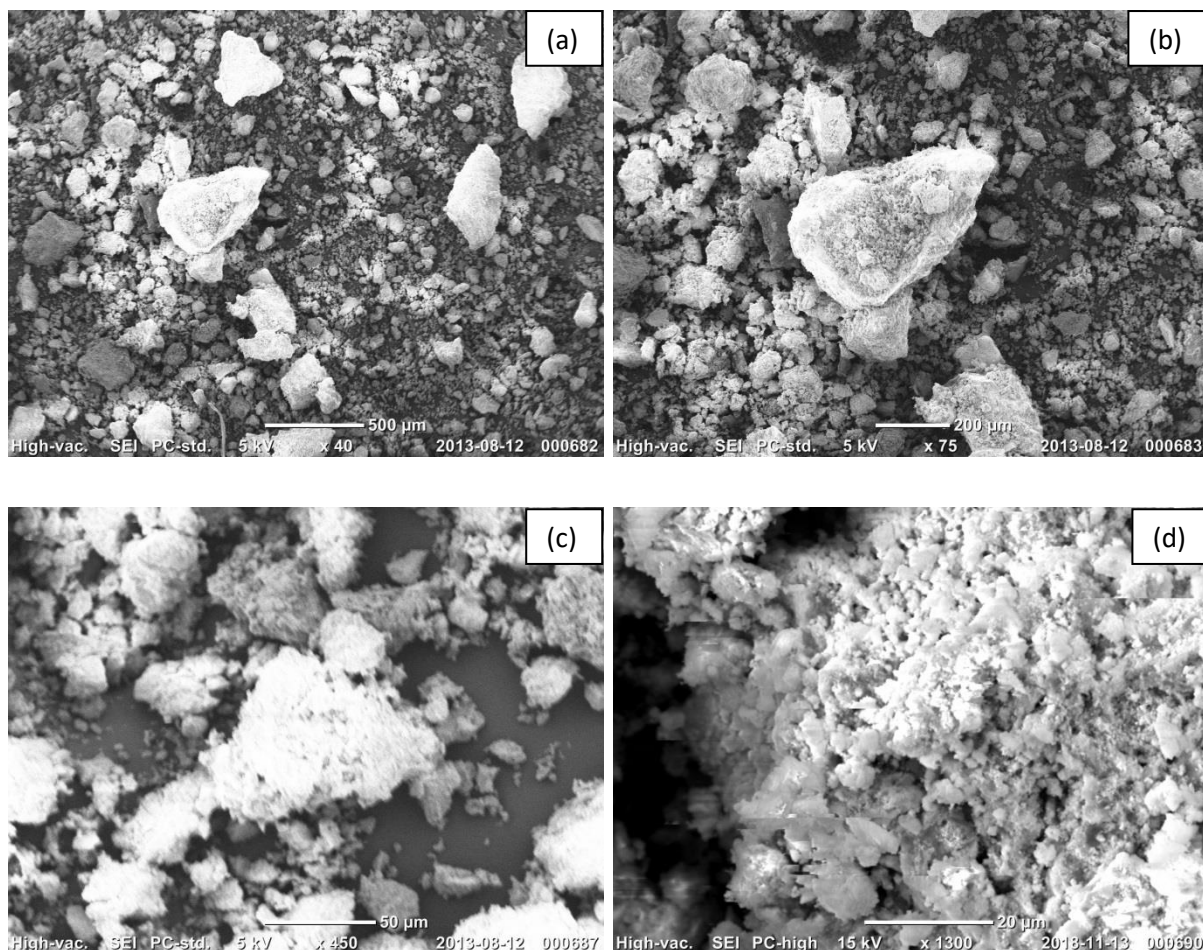


Figure S2. SEM microphotographs of the 60% Cu/Al₂O₃ catalyst at (a) magnification 40; (b) magnification 75; (c) magnification 450; (d) magnification 1300.

Using the SEM-EDX technique, the copper particles were detected and their mean size was estimated. From the Fig.S3 it could be seen that the copper particles were mainly from 1 to 10 μm. By statistical processing of a series of the microphotographs, the histogram of the copper particles size distribution (Figure S4) was obtained. For the estimation of the total Cu⁰ specific surface area the surface areas for the particles were calculated; the sum was compared with the total specific surface area of the catalyst.

The copper specific surface area amounted to 32 m²/g (of the catalyst).

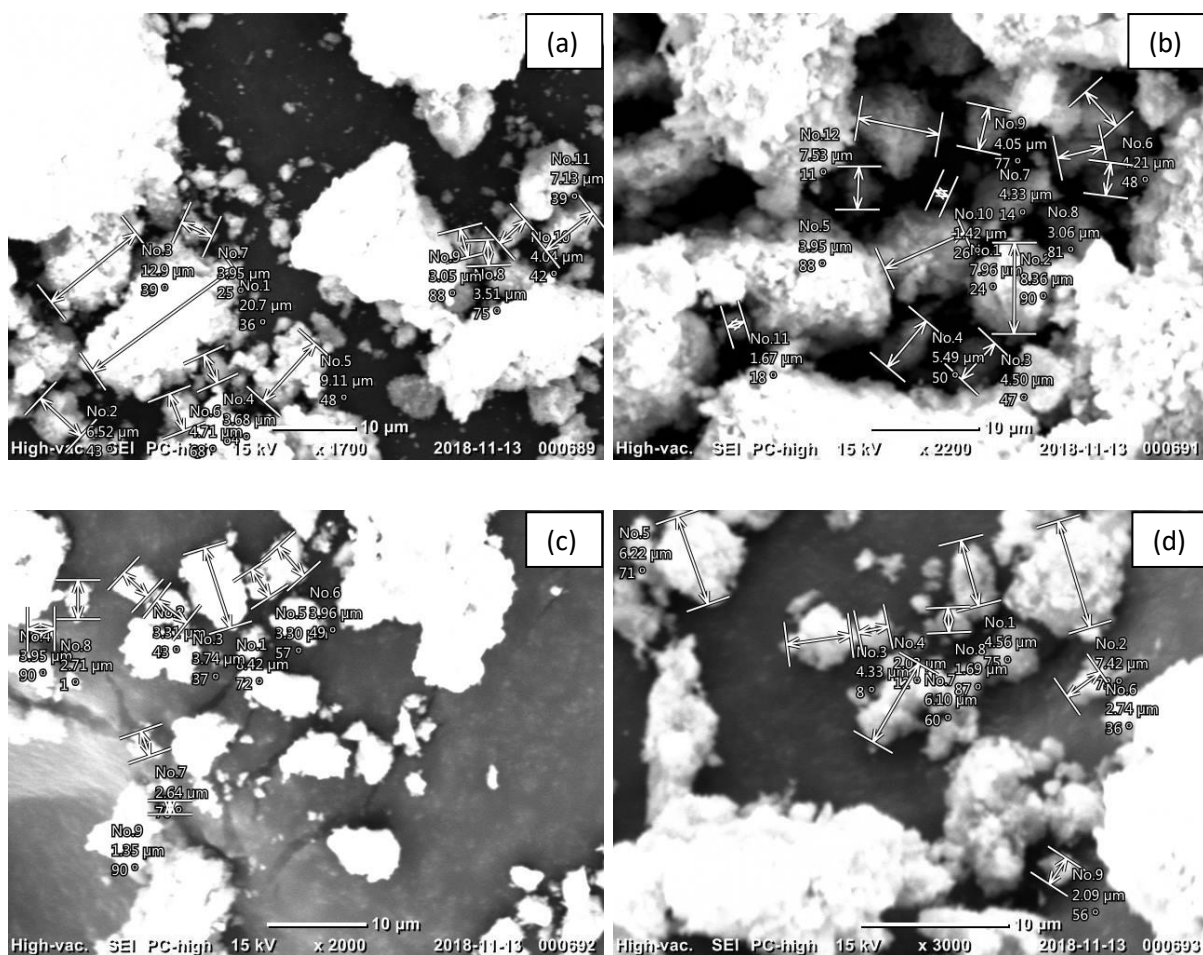


Figure S3. SEM microphotographs of 60% Cu/Al₂O₃ with copper particle sizes measured.

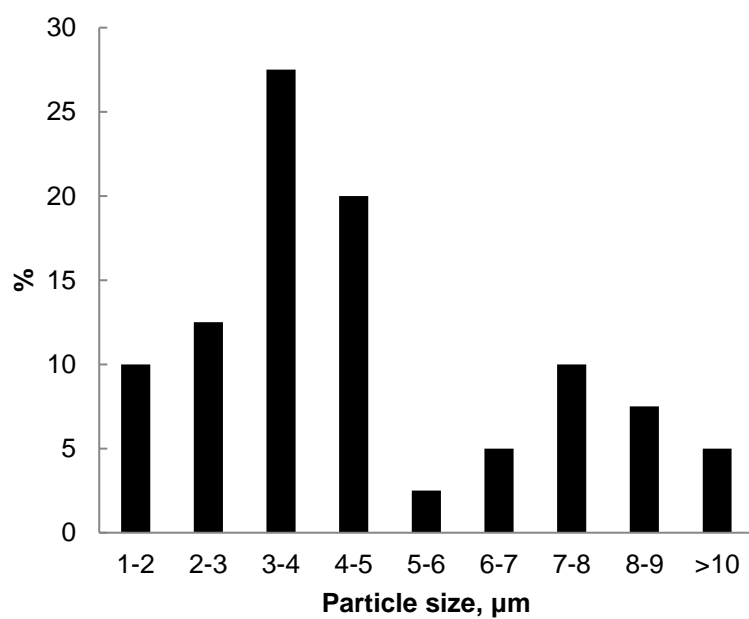


Figure S4. Histogram of the particle size distribution of the copper in the 60% Cu/Al₂O₃ catalyst.

Conversion, selectivities and yields calculation representative example

The reaction under the standard conditions was performed as follows: to the stainless steel batch reactor (inner volume 50 ml) solketal (2.5 ml), distilled water (0.5 ml) and the catalyst (100 mg) were loaded together with the stirrer bar. The reactor was closed, evacuated (20 Torr), loaded with hydrogen (initial pressure 40 bar), weighed and installed in the electric heater. The heating and the stirring were started; this moment was considered to be the reaction start.

After 5 hours the stirring and the heating were stopped, the reactor was put out of the heater and readily chilled out with cold water. The pressure was then gently released, the reactor was weighed again, the reaction mixture was collected and the catalyst was separated by centrifugation. The liquid product has been analyzed by means of GC.

The liquid composition obtained from the GC analysis is given in the Table S1.

Table S1. The composition of the solketal liquid-phase hydrogenolysis reaction mixture.

Compound	Concentration, mol %
acetone	4.2
isopropyl alcohol	48.0
1,2-propylene glycol	46.6
solketal	1.2
2,2,4-trimethyldioxolane-1,3	traces (<0.1)
propanol-1	traces (<0.1)

The following calculation was done by normalizing the total quantity to 100 mmol for the sake of convenience.

The quantity of solketal conversion products, releasing equivalent quantity of acetone/IPA upon formation:

$$n_1 = n_{PG(1)} + n_{Gly(1)} + n_{PrOH(1)} = n_{Ac+IPA(2)} = 46.6 \text{ mmol} \quad (1)$$

The actual total quantity of acetone and IPA in the product:

$$n_{Ac+IPA(1)} = n_{Ac(1)} + n_{IPA(1)} = 4.2 + 48.0 = 52.2 \text{ mmol} \quad (2)$$

The quantity of the overhydrogenation-derived products (acetone and/or IPA) formed from the glycerol moiety of solketal:

$$n_{over} = \frac{n_{Ac+IPA(1)} - n_{Ac+IPA(2)}}{2} = \frac{52.2 - 46.6}{2} = 2.8 \text{ mmol} \quad (3)$$

Thus, of the total 52.2 moles of acetone and IPA 2.8 moles were formed as the result of the overhydrogenation of the bounded glycerol.

Initial quantity of solketal:

$$n_{Sol(0)} = n_{PG(1)} + n_{Gly(1)} + n_{TMD(1)} + n_{PrOH(1)} + n_{over} + n_{Sol(1)} = 46.6 + 2.8 + 1.2 = 50.6 \text{ mmol} \quad (4)$$

Solketal conversion:

$$X_{Sol} = \frac{n_{Sol(0)} - n_{Sol(1)}}{n_{Sol(0)}} \times 100\% = \frac{50.6 - 1.2}{50.6} = 97.6\%. \quad (5)$$

Selectivity to 1,2-PG:

$$S_{PG} = \frac{n_{PG(1)}}{n_{Sol(0)} - n_{Sol(1)}} \times 100\% = \frac{46.6}{50.6 - 1.2} = 94.3\% \quad (6)$$

1,2-propylene glycol yield:

$$Y_{PG} = X_{Sol} \times S_{PG} \times 0.01 = 97.6 \times 94.3 \times 0.01 = 92.1\%. \quad (7)$$

Conditional conversion of acetone into IPA (ratio between total acetone and IPA quantities in the product):

$$\alpha_{Ac} = \frac{n_{IPA(1)}}{n_{IPA(1)} + n_{Ac(1)}} \times 100\% = \frac{48.0}{48.0 + 4.2} \times 100\% = 92.0\%. \quad (8)$$

An example of a representative chromatogram of the solketal liquid-phase hydrogenolysis product

The chromatogram (Fig. S5) is obtained using Kristallyuks-4000M GC with helium carrier gas and FID detection using a 25 m*0.25 mm*0.1µm CP-Wax column and the temperature ramp from 40 to 210°C).

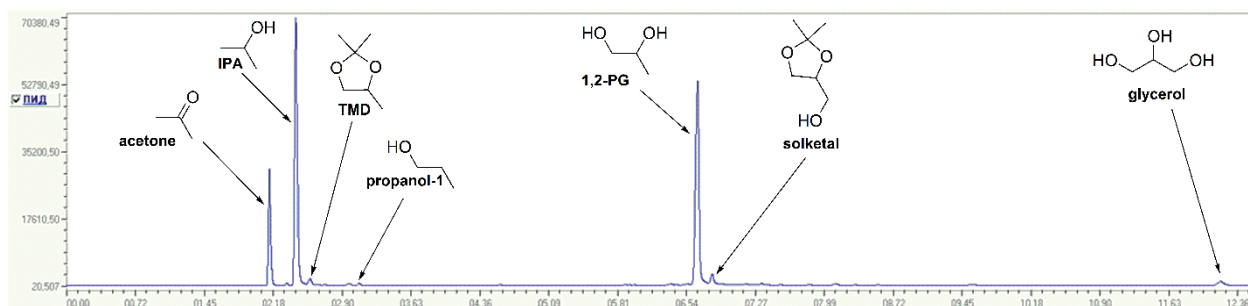


Figure S5. The chromatogram of the product of solketal liquid-phase hydrogenolysis over 60 wt.% Cu/Al₂O₃ ($T = 240^{\circ}\text{C}$, $p(\text{H}_2) = 40$ bar).