Supplementary Information to

Catalytic Hydrogenation of Dihydrolevoglucosenone to Levoglucosanol with a Hydrotalcite/Mixed Oxide Copper Catalyst

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Materials, methods and instrumentation

Chemicals

Double distilled dihydrolevoglucosenone (Cyrene) was provided by the Circa company and used as is.

Batch reactions

To 2 mmol dihyrolevoglucosenone was added to 5 mL of distilled water. The mixture was added to a high-pressure reactor and pressurized 3 times with Argon and another 3 times with H_2 (typically by loading ~ 20 bar of the gases and releasing the pressure). Finally 60 bar of H_2 pressure was added. The stirring rate (magnetic stirrer bar) was ~ 500 rpm. Reaction times were 18 h.

Flow reactions

Flow reactions were conducted at 353 K using 1 (or 5) wt% Cyrene in H_2O under 60 bar H_2. The flow conditions were: Cyrene/H_2O solution flow: 0.03 mL min^{-1} and H_2 gas flow: 20 mL min^{-1}. Calcination and reduction of the catalyst always followed a heating rate of 1 °C min^{-1} to 623 K (350 °C) followed by an isothermal period of 3 h at 623K. Air or H_2 gas flows were 6 s/5 cc. Prior to reaction the Cyrene/H_2O solution was degassed using ultrasound. Catalyst was (calcined)/reduced in the flow reactor.

Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES)

Potential Cu, Al and Mg leaching was evaluated using a PerkinElmer Plasma 400 ICP Emission Spectrometer and a PerkinElmer Optima 2000 ICP-AES. To the reaction samples was added 2 drops of 70wt% HNO_3 to guarantee a pH < 1. Calibration curves of Cu, Mg and Al were made using a multistandard solution obtained from "High Purity Standards" (www.highpuritystandards.com] [Cat. #ICP-200.7-6; EPA Method 200.7 Standard 6 Solution A μg mL^{-1} in 2% HNO_3 + Tr HF].

N_2O Titration

The number of Cu surface sites was determined by N_2O titration. Prior to the measurement, catalysts were reduced at 623 K (with a heating rate of 1 K min^{-1}) under an H_2 flow for 4 h. After reduction, the samples were cooled to 363 K and the cell was evacuated to 10^{-5} Torr. Subsequently, N_2O was dosed into the cell at 363 K and oxidized the surface according to the following stoichiometry $N_2O + 2Cu_s \rightarrow (Cu_s)_2 + N_2$. After equilibration for 2 h, the remaining N_2O was condensed and the amount of N_2 produced was quantified by monitoring the pressure using a gas handling system and a volumetric system employing Baratron capacitance manometers for precision pressure measurement. Detailed information regarding the gas handling system is described in:

> *Wiedmann, M. K.; Jackson, D. H. K.; Pagan-Torres, Y. J.; Cho, E.; Dumesic, J. A.; Kuech, T. F. Atomic Layer Deposition of Titanium Phosphate on Silica Nanoparticles. J. Vac. Sci. Technol., A 2012, 30, 01A134.*

X-ray Photoelectron Spectroscopy (XPS).

The oxidation states of copper in the supported nanoparticles (before and after reaction) were characterized by XPS using a K-alpha XPS (Thermo Scientific) instrument with a microfocused monochromatic Al Kα X-ray source. Initial catalyst samples (i.e. before reaction) were reduced in H_2 at 623 K for 2 h, transferred to a glovebox under inert gas, and mounted on a transfer vessel (Transfer Vessel KAlpha). The latter vessel was transferred from the glovebox to the chamber of the XPS without air and moisture exposure. The Cu $2p_{1/2}$ region was collected over multiple scans at a pass energy of 57.8 eV, dwell time of 50 ms, and 30 scans. The experimental spectra were fitted to Gaussian/Lorentzian lines after removal of an S-shaped background

Scanning Transmission Electron Microscopy (STEM)

Scanning transmission electron microscopy (STEM) studies were performed using an FEI Titan STEM with a Cs probe aberration corrector operated at 200 kV with spatial resolution < 0.1 nm. High-angle annular dark-field (HAADF) mode was applied to record images, with HAADF detector angle ranging from 54 to 270 mrad, probe convergence angle of 24.5 mrad, and probe current of approximately 25pA. The samples were suspended in ethanol and then dropped on a carbon-coated copper grid. STEM grids were plasma cleaned before being loaded into the microscope.

Nuclear Magnetic Resonance (NMR)

The NMR spectra at the University of Wisconsin-Madison (Department of Chemistry) were taken using an Avance-500 with DCH cryoprobe and SampleXpress. The used DCH cryoprobe allows for state-of-the-art ^{13}C sensitivity. Conversion/selectivity calculations were made from quantitatively recorded ^{13}C NMR spectra. Typically 256 scans were taken with a relaxation time of 5s. The length of the relaxation time needed to yield quantitative ^{13}C NMR spectra was determined empirically. Sample preparation: to ~0.5 mL aliquots of the reaction mixture was added ~0.25 mL DMSO-d6 (with added TMS).

N$_2$ physisorption and Hg intrusion porosimetry

The pore size distribution of catalysts was determined by mercury intrusion porosimetry, using an AutoPore III instrument (Micromeritics). Degassing of the samples prior to analysis was performed under vacuum below 0.05 mPa. The pore diameter was calculated by means of the Washburn equation [1], using surface tension of 0.489 N/m and contact angle of 135°.

[1] E.W. Washburn, *Proc. Natl. Acad. Sci.*, 1921, **7**, 115-116.

Nitrogen adsorption-desorption isotherms were recorded at -195 °C and relative pressure (P/P_0) ranging between 0.001 and 0.998, using an ASAP 2010 instrument (Micromeritics). Prior to the measurements, the samples were degassed at 200 °C for 12 h under a vacuum of 0.01 mPa. The specific area was calculated according to the BET equation and the pore size distribution was determined using the BJH method [2]

[2] K. Sing, *Colloids Surf. A*, 2001, **187-188**, 3-9.
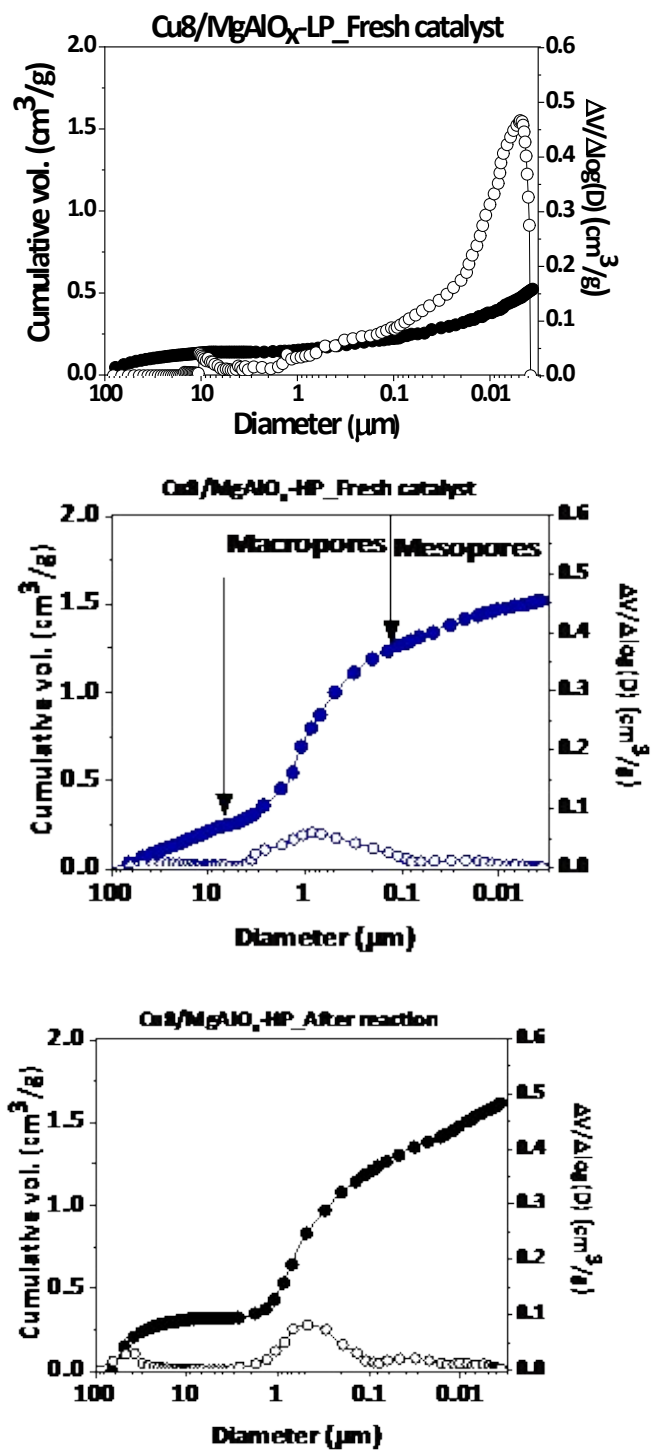
Supplementary figures

Figure 1S: pore size distributions (open symbols) and cumulative pore volumes (closed symbols) as determined by mercury intrusion porosimetry, for (a) Cu8/MgAlOx-LP_Fresh catalyst, (b) Cu8/MgAlOx_Fresh catalyst and (c) Cu8/MgAlOx-HP_After reaction.
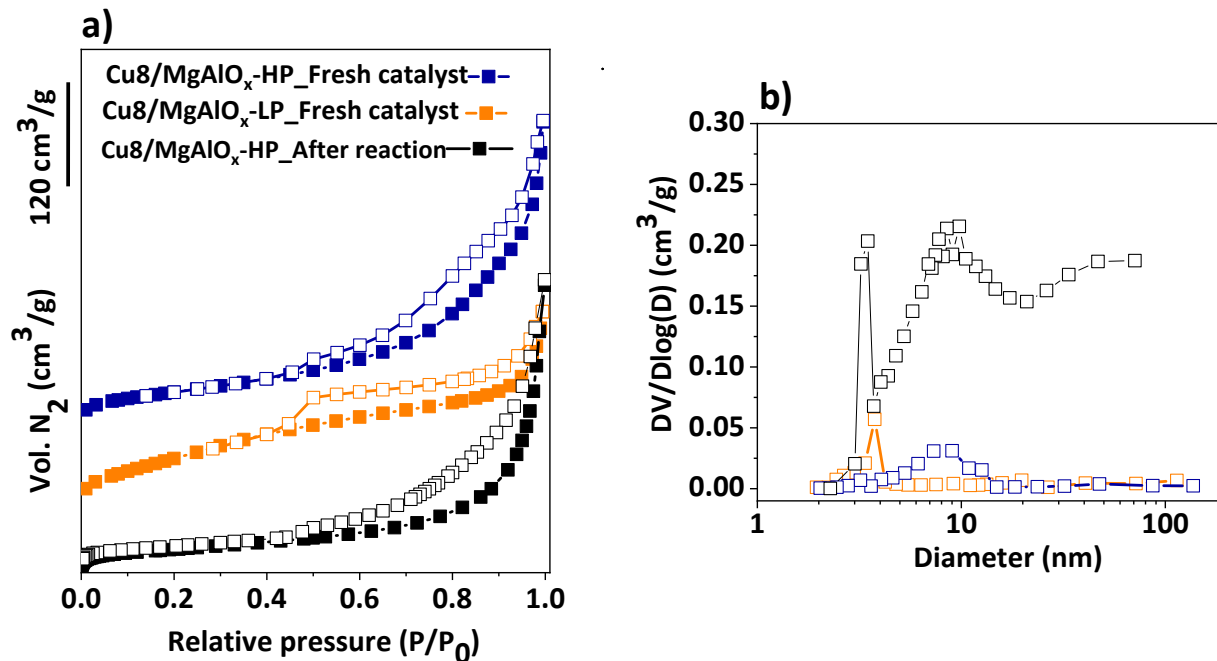
Figure 2S: (a) N_2 adsorption-desorption isotherms and (b) BJH pore size distributions for Cu8/MgAlOx-LP_Fresh catalyst, Cu8/MgAlOx_HP_Fresh catalyst and Cu8/MgAlOx-HP_after reaction.
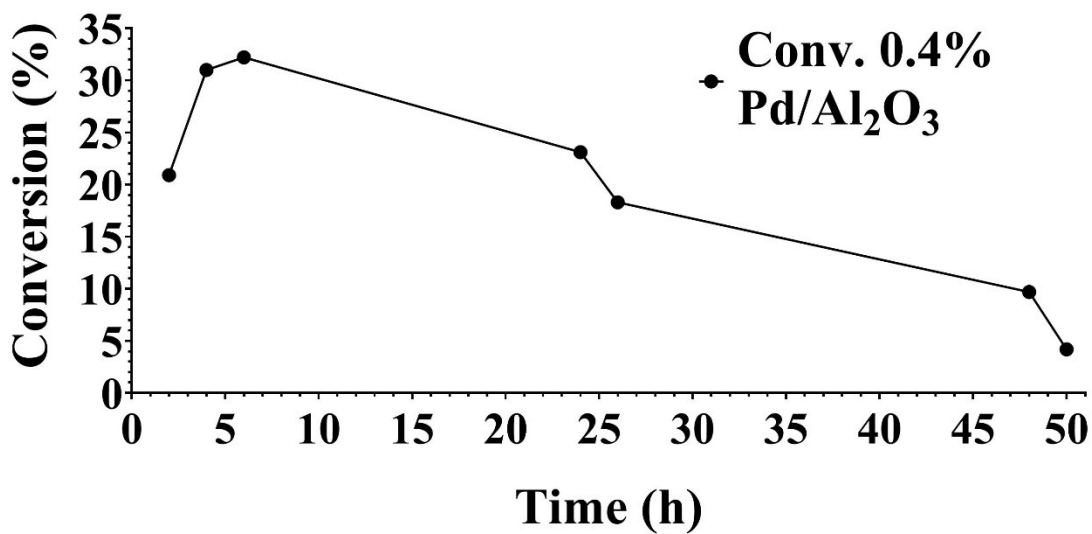

Figure 3S: Cyrene/LGOL flow hydrogenation reaction using 0.4% Pd/Al_2O_3. Reaction conditions: 353 K, 60 bar H_2, 1wt% Cyrene in H_2O. Flow conditions: Cyrene/H_2O solution: 0.03 mL min^{-1}, H_2 gas: 20 mL min^{-1}.
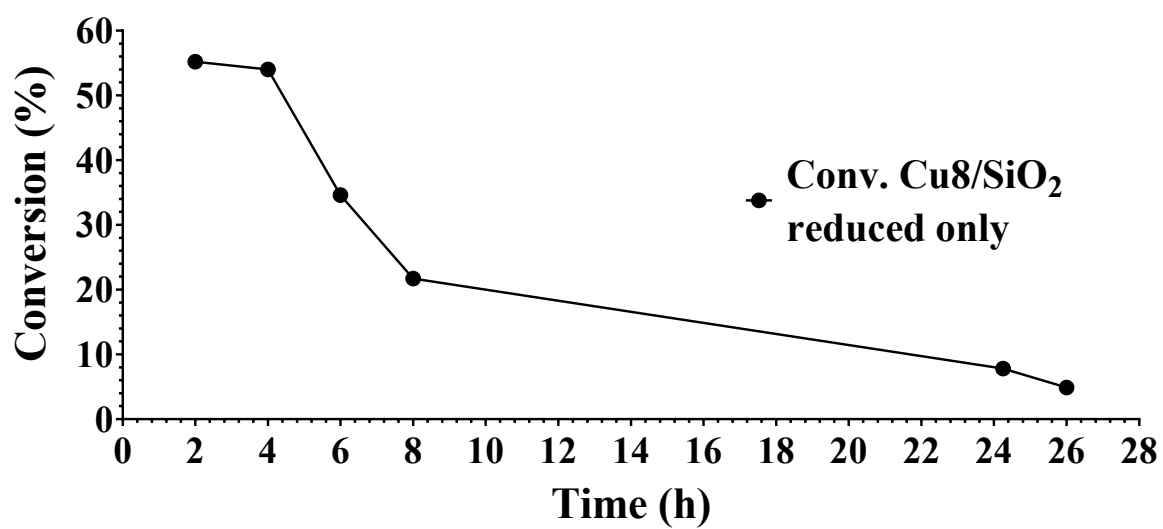
Figure 4S: Cyrene/LGOL flow hydrogenation reaction using solely reduced Cu8/SiO$_2$. Reaction conditions: 353 K, 60 bar H$_2$, 1wt% Cyrene in H$_2$O. Flow conditions: Cyrene/H$_2$O solution: 0.03 mL min^{-1}, H$_2$ gas: 20 mL min^{-1}.

Table 1S: a survey of the reaction rates as a function of reactor set up, Cyrene concentration in water, temperature and used catalyst. All 60 bar hydrogen. Flow conditions: Cyrene/H_2O solution: 0.03 mL min^{-1}, H_2 gas: 20 mL min^{-1}.

Entry	Type of reactor set up	wt% Cyrene in water	Temperature (K)	Catalyst	Rate (s^{-1})
A)	batch	5	333	Cu8/AlMgO$_x$-**HP**	0.0117
B)	batch	5	353	Cu8/AlMgO$_x$-**HP**	0.0405
C)	batch	5	373	Cu8/AlMgO$_x$-**HP**	0.1160
D)	batch	5	333	Cu8/AlMgO$_x$-**LP**	0.0093
E)	flow	1	353	Cu8/AlMgO$_x$-**HP**	0.013
F)	flow	1	353	Cu8/AlMgO$_x$-**LP**	0.0105
G)	flow	5	353	Cu8/AlMgO$_x$-**HP**	0.011 (max)/ 0.005 (end)