

Silica supported copper nanoparticles prepared via Surface Organometallic Chemistry, active catalysts for the selective hydrogenation of 2,3-Dimethylbutadiene

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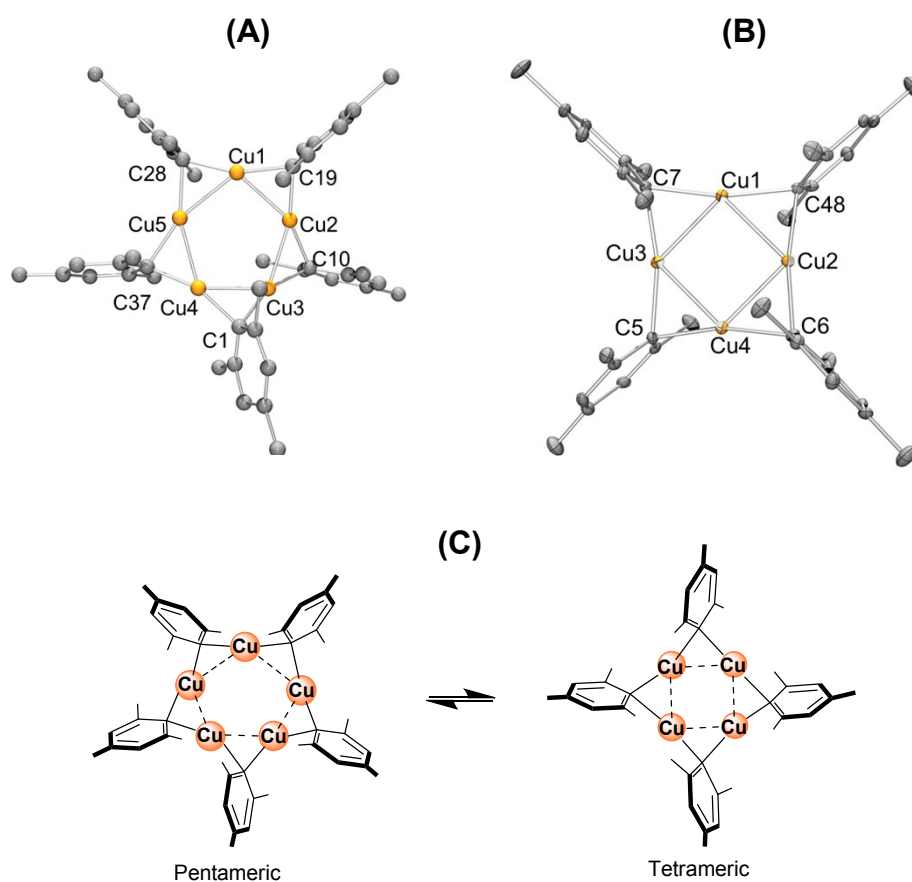
I. General experimental procedures

All experiments (mesitylcopper synthesis and grafting reactions) were performed under moisture and oxygen free argon using either standard Schlenk and glove-box techniques. Pentane, toluene were distilled over NaK, THF were distilled from Na/Benzophenone, degassed and stored over activated 4 Å molecular sieves. Silica was hydrated using water and compacted, calcined and dehydroxylated for 16 h at two different temperatures 200°C and 700°C that led to two different supports, denoted as SiO₂₋₂₀₀ and SiO₂₋₇₀₀ respectively. Elemental analyses were performed by the Mikroanalytisches Labor Pascher; Remagen, Germany. ¹H and ¹³C liquid state NMR were performed on an AC-300 spectrometer (¹H 300 MHz, ¹³C 75 MHz), spectra were recorded using the residual peak of the deuterated solvent as internal standard, ¹³C chemical shifts are given in ppm (δ) relative to TMS (tetramethylsilane). ¹³C CP MAS solid state NMR spectra were collected on a Bruker avance 500 NMR spectrometer. The 4 mm zirconia (ZrO₂) impeller was filled with the desired product and sealed with a kel-f stopper. It was then transferred into the probe of the Bruker spectrometer allowing rotation of the rotor at a speed of 10 kHz. The time between two acquisitions was always optimized to allow complete protons relaxation. Diffuse reflectance Fourier-transformed infrared (DRIFT) spectra were recorded on a Nicolet 6700-FT spectrometer using a cell equipped with CaF₂ window. Typically, 64 scans were accumulated for each spectrum (resolution 4 cm⁻¹). Powder X-ray diffraction (XRD) patterns were carried on a Siemens Bruker AXS D-500 instrument using Cu Kα₁ radiation in Bragg-Brentano reflecting geometry. Prior to analysis, the sample preparation was done by grinding the material to fine powder, followed by addition of ethanol and in the end deposition of a suspension on a glass plate. Transmission electron microscopy (TEM) observations were carried out on Philips CM120 instrument with an acceleration voltage up to 120kV.

II.1. Mesitylcopper preparation:

Mesitylcopper was synthesized according to previously described methods.¹⁻³. Briefly, a suspension of anhydrous CuCl was placed under argon in a Schlenk vessel (15 mmol, 30 ml THF) and continually stirred, then cooled to -30 °C 15 mmol of MesMgBr in THF solution was added drop-wisely. The solution was stirred over night at room temperature. Then 9.5 ml dioxane was added and the mixture was stirred for 1 hour. Thereafter the liquid phase was filtrated and extracted under vacuum and 40 ml of toluene was added. The solution was further concentrated to 10 ml by extraction under vacuum and next moved to the glove-box. The crystallization was carried out at -20°C during five days and the yellow crystals formed (pentameric clusters) were separated and washed with cold toluene before their storage in a freezer. As previously shown, the NMR spectra of dissolved mesitylcopper demonstrated two different structure configurations: pentameric and tetrameric¹ (Scheme S1). The ¹H NMR spectrum (toluene-d₈) agrees with the presence of two types of Cu clusters, one described as a pentamer, with chemical shifts at 1.91, 2.91 and 6.58 ppm for *p*-CH₃, *o*-CH₃ and *m*-C-H respectively and the other, described as a tetramer with chemical shifts at 2.03, 2.96 and 6.68 ppm (Fig. S1). The ¹³C NMR spectrum (benzene-d₆) also indicates a mixture of the two

clusters with chemical shifts at 20.96, 29.12, 128.92, 140.38 and 152.47 ppm for p-CH₃, o-CH₃, o-C, p-C and m-C signals of the pentamer and at 21.05, 28.75, 126.38, 140.91 and 154.53 ppm for the tetramer (Fig. S2). The ipso carbon atoms, directly bound to the copper centers, have never been observed.



Scheme S.1 X-ray mono crystal structure of mesitylcopper pentamer (crystallization at -20°C) (A), tetramer (crystallization at -30°C) (B), Mesitylcopper configurations in liquid phase (C).¹

II.2. Preparation of CuMes@SiO₂₋₇₀₀, CuMes@SiO₂₋₂₀₀ and CuO@SiO_{2-wi}

II.2.1. Grafting of mesitylcopper on silica 700:

A solution of 219 mg of mesitylcopper (1.2 mmol, 6 equiv) in 15 ml of toluene was added to 800 mg of SiO₂₋₇₀₀ (0.250 mmol/g - 0.75 OH/nm²). After stirring the suspension overnight at room temperature, the solid was filtrated and washed 5 times with 2 ml toluene and then 4 times with 2 ml pentane to remove the excess. The filtrate solutions were combined and analyzed by GC in order to quantify the amount of mesitylene released. The yellow material was dried under high vacuum (10⁻⁵ mbar) and stored in glovebox.

II.2.2. Grafting of mesitylcopper onto silica 200:

In order to obtain a similar Cu loading on SiO₂₋₂₀₀ (0.830 mmol/g - 2.5 OH/nm²) (while the concentration of the surface OH anchoring sites is much higher than SiO₂₋₇₀₀), a solution of 105 mg of mesitylcopper (ca. 4.6 wt% Cu /SiO₂₋₂₀₀, limited amount of Cu, unsaturated solid, colorless resulting solution) dissolved in 15 ml of toluene was added to 800 mg of SiO₂₋₂₀₀. The pale yellow solid was recovered by filtration and dried under high vacuum (10⁻⁵ mbar). The amount of the mesitylene released was quantified by GC.

II.2.3. Preparation of CuO on silica by wet impregnation:

This catalyst was prepared as reported in the literature.⁴ Typically to 1 g of silica was added a solution of copper (II) nitrate trihydrate ($\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$) (178 mg, 0.73 mmol) in 5 ml of distilled water. The suspension was stirred in the Erlenmeyer flask until the water has evaporated to the atmosphere. The powder was then recovered and calcined under air in a muffle oven at 500 °C overnight

II.3. Preparation of the catalyst reduction:

Prior to the catalytic tests, the supported copper materials were reduced under hydrogen in a continuous-flow reactor with a flow of mixed gases of H_2 , 4.6 mL/min and Ar, 15.0 mL/min for 18 h at 350°C. Thereafter the two dark-brown powder were cooled to room temperature and stored in glovebox.

II.4. Catalytic test (hydrogenation of 2,3-dimethylbutadiene):

In a continuous-flow reactor, a flow of 15 ml/min H_2 enclosing 10% of 1,2-dimethylbutadiene (v.p. 100 mbar at 10°C), was sent through the catalyst (amount of material containing 2.3 mg of Cu). The temperature was maintained at 75°C. Every 17 min, an automatically withdrawn amount was injected in the GC (Column: $\text{KCl}/\text{Al}_2\text{O}_3$, 50 m x 0.32 mm x 0.25 μm).

The XRD analyses of the $\text{Cu}@\text{SiO}_{2-200}$ (Fig. S7) showed no peaks that can be attributed to metallic copper for 2θ higher than 30°. Therefore we concluded that no large copper particles are formed. The peak at $2\theta = 22$ attributed to SiO_2 , as well the peak at $2\theta = 26^\circ$ produced by the measurement instrument window.

III.1. NMR spectra of Mesitylcopper in solution

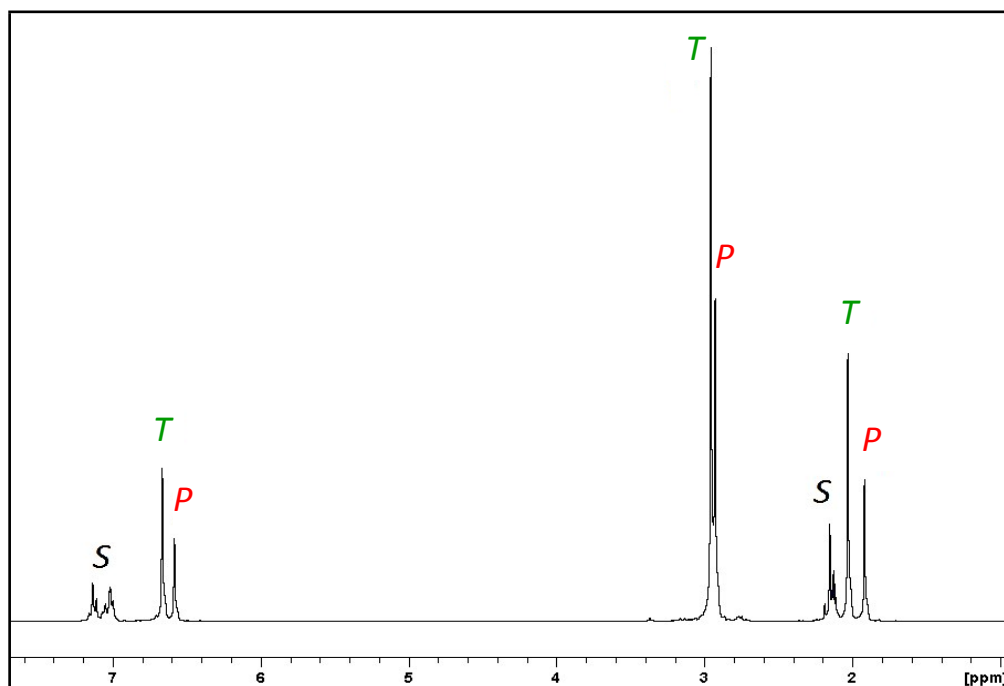
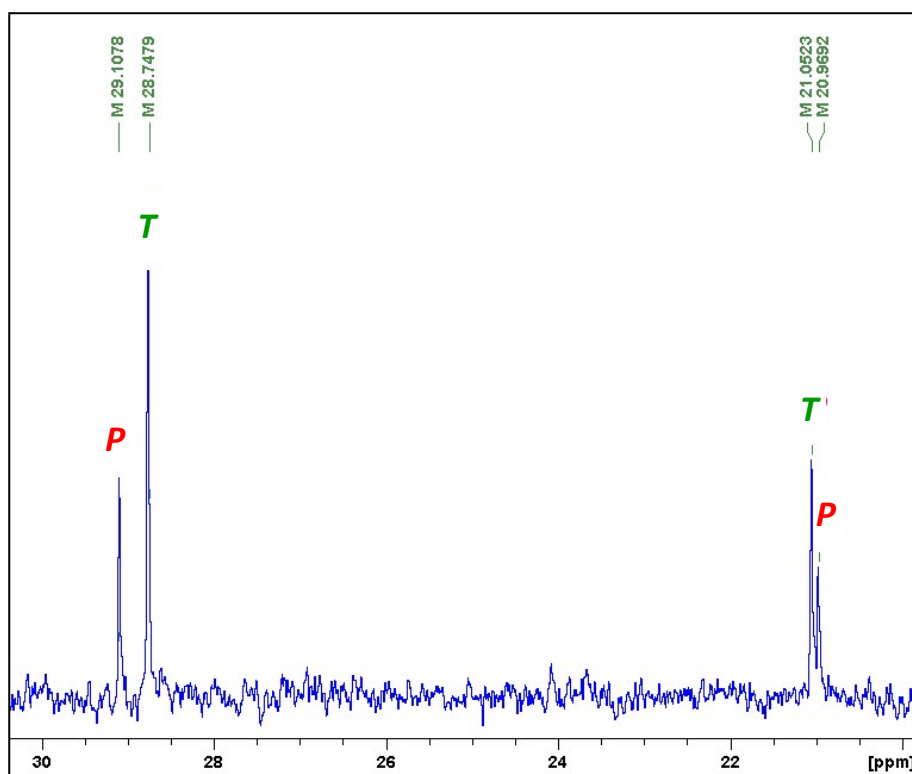


Fig. S1 ^1H NMR (300 MHz, toluene- d_8) spectrum of Mesitylcopper (T: Tetranuclear cluster; P: Pentanuclear cluster; S: Solvent).

a)



b)

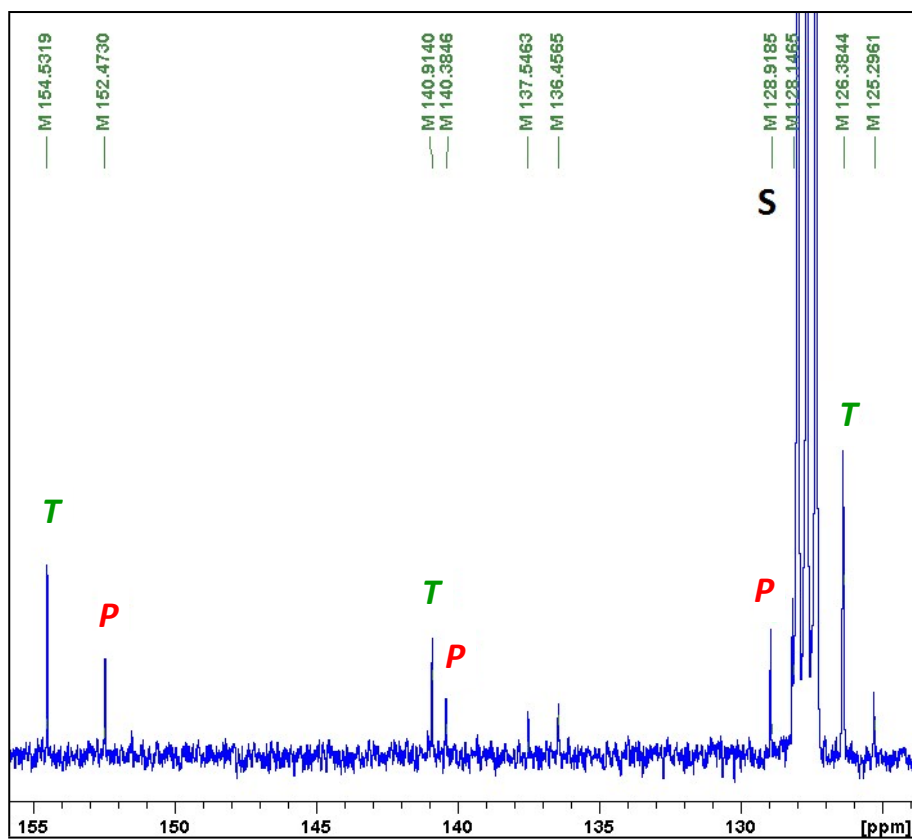


Fig. S2 ¹³C NMR (75MHz, benzen-d₆) spectrum of Mesitylcopper, a) aliphatic ¹³C range; b) aromatic ¹³C range (T: Tetranuclear cluster; P: Pentanuclear cluster; S: Solvent, C₆D₆).

III.2. DRIFT spectra of CuMes@SiO₂₋₂₀₀

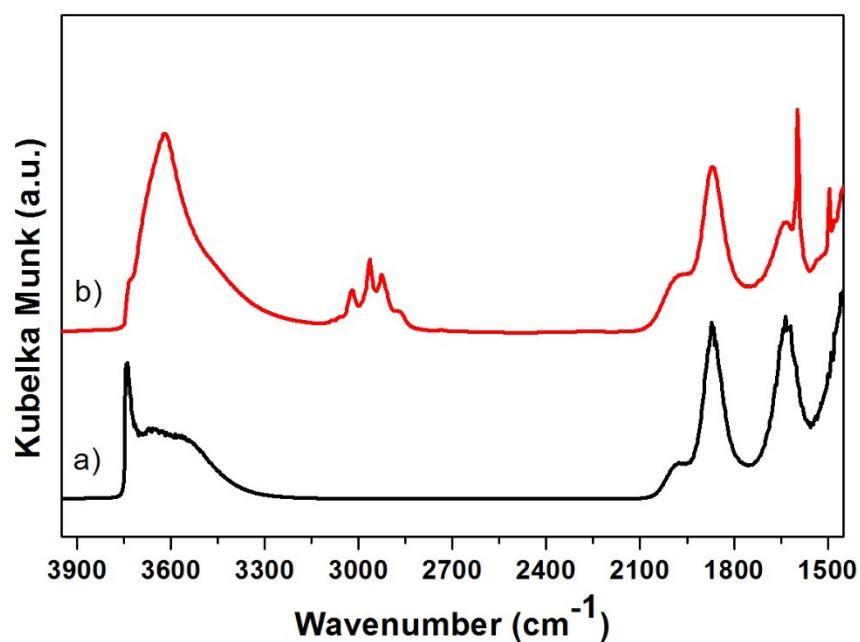


Fig. S3 DRIFT spectra corresponding to Cu- SiO₂₋₂₀₀ (a) before grafting, silica dehydrated at 200°C for 16h; (b) after grafting of mesitylcopper onto silica₂₀₀ (2b)

III.3. Solid state NMR spectra of CuMes@SiO₂₋₂₀₀

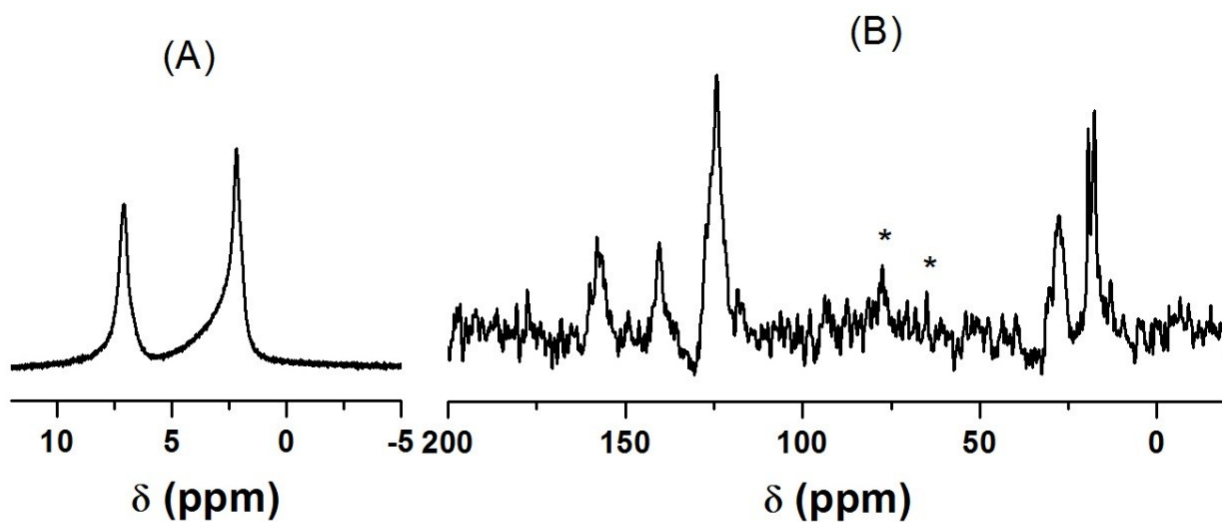


Fig. S4 NMR (500MHz) characterization of **2b**, supported onto SiO₂₋₂₀₀: ¹H MAS NMR (10 kHz) (A) and ¹³C CPMAS NMR (B); *: Spinning side bands.

III.4. DRIFT spectra of Cu@SiO₂₋₇₀₀ and Cu@SiO₂₋₂₀₀

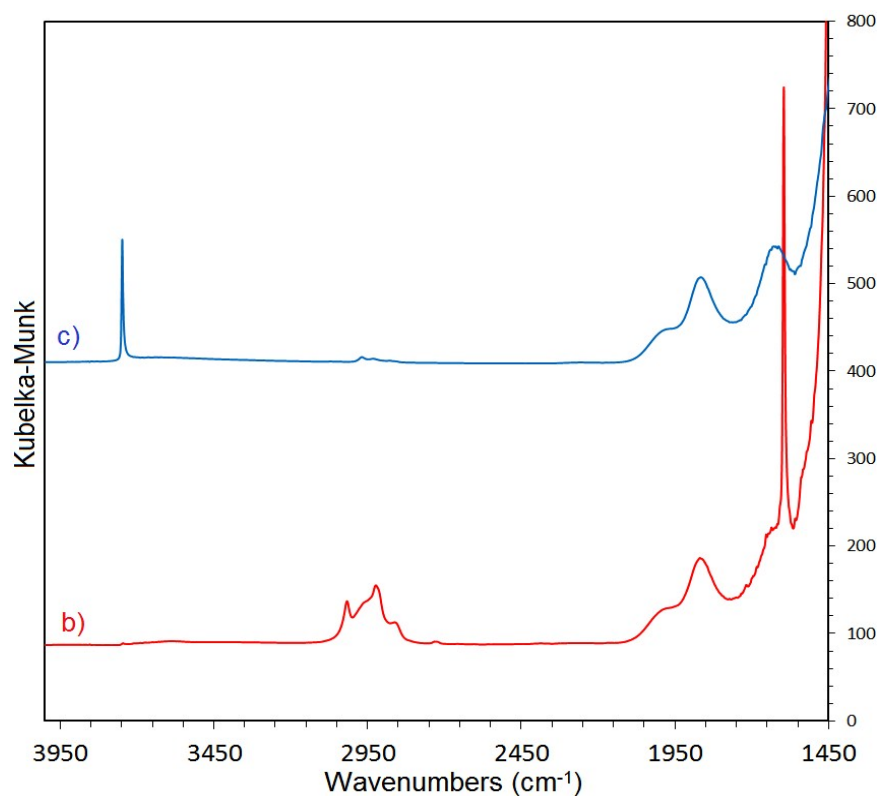


Fig. S5 DRIFT spectra of Cu-SiO₂₋₇₀₀ catalyst: b) Mesitylcopper grafted onto SiO₂₋₇₀₀ (2b); c) After reduction at 350°C (3b).

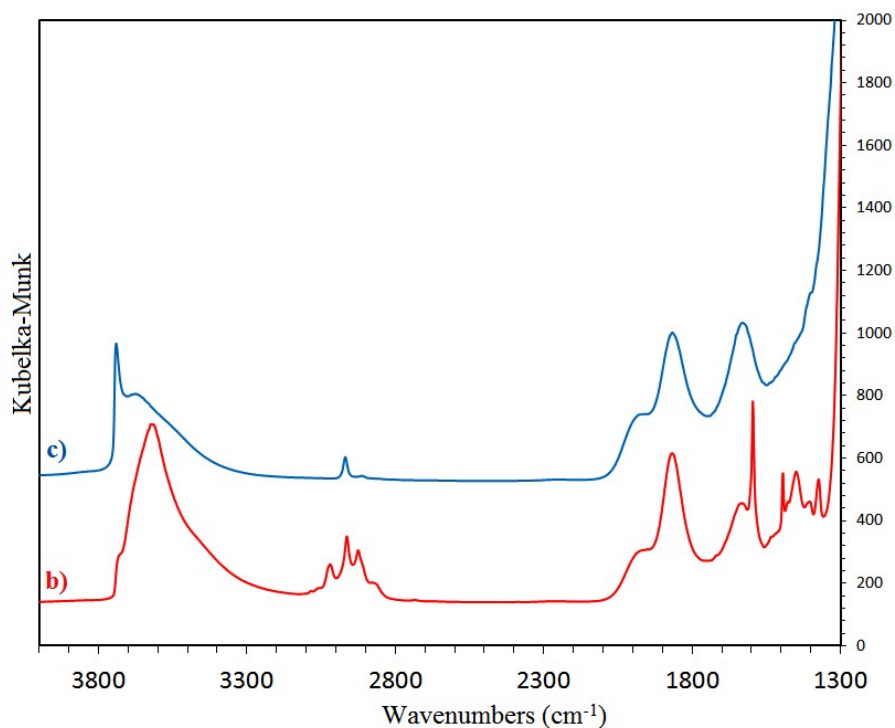


Fig. S6 DRIFT spectra of Cu-SiO₂₋₂₀₀ catalyst: b) Mesitylcopper grafted onto SiO₂₋₂₀₀ (2b); c) After reduction at 350°C (3b).

III.5. XRD

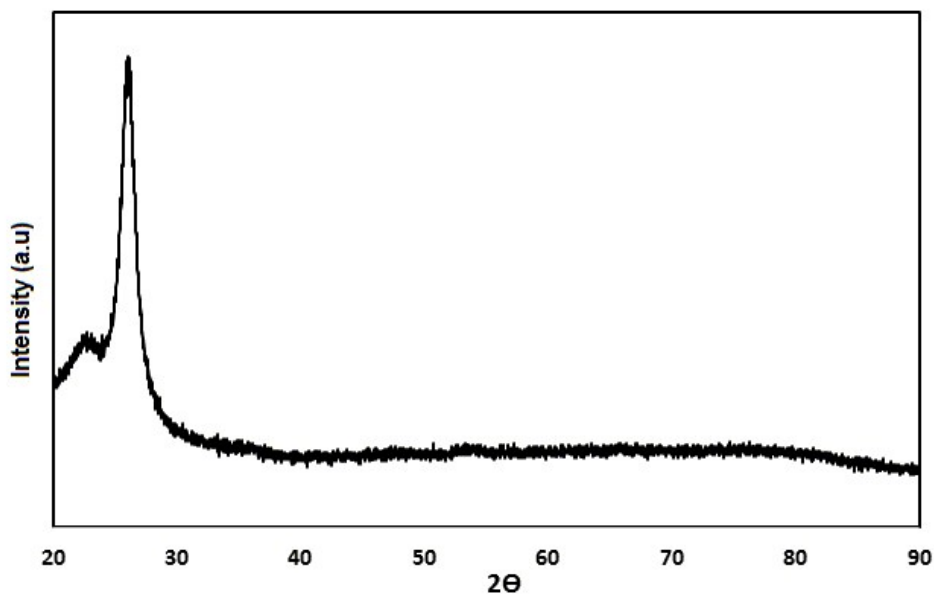


Fig. S7 Powder X-Ray diffraction pattern of Cu@SiO₂₋₂₀₀ material.

III.6. Catalysts selectivities

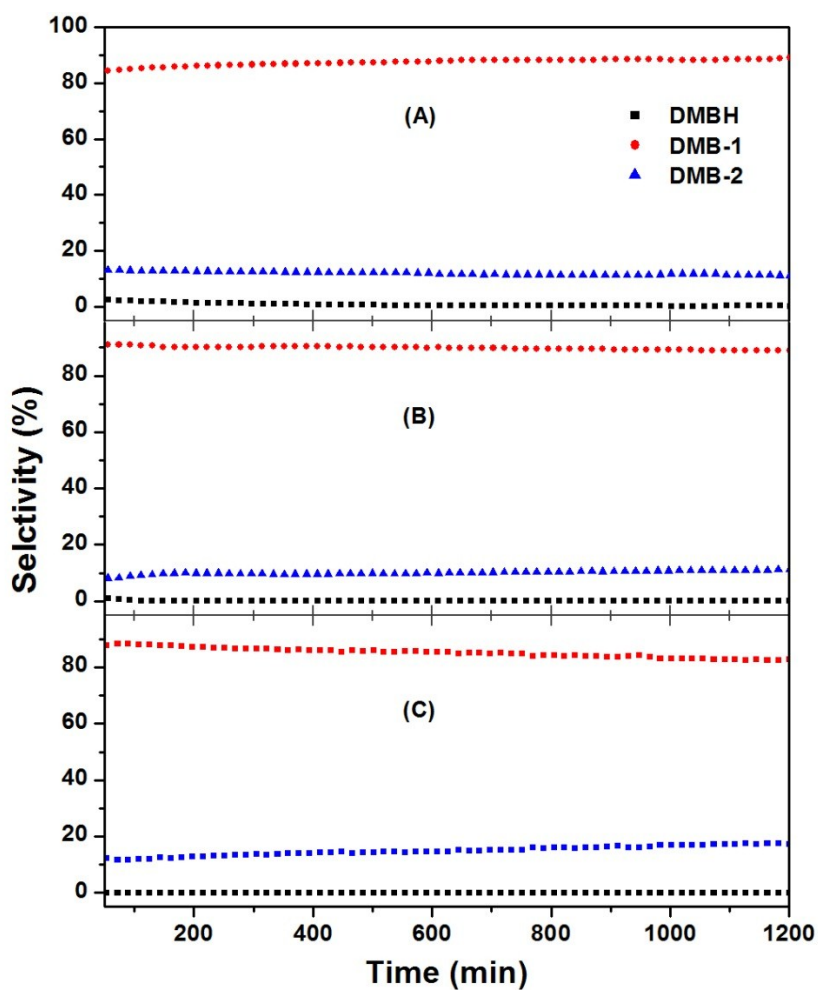


Fig. S8 Selectivities towards DMB-1, DMB-2 and DMBH during the selective hydrogenation of DMBD in a continuous flow reactor at 75°C: in the presence of Cu@SiO₂₋₇₀₀ (A), Cu@SiO₂₋₂₀₀ (B), Cu@SiO_{2-rwt}.

IV. Bibliography

1. H. Eriksson and M. Hakansson, *Organometallics*, 1997, 16, 4243-4244.
2. S. Gambarotta, C. Floriani, A. Chiesi-Villa and C. Guastini, *J. Chem. Soc., Chem. Comm.*, 1983, 1156-1158.
3. E. M. Meyer, S. Gambarotta, C. Floriani, A. Chiesi-Villa and C. Guastini, *Organometallics*, 1989, 8, 1067-1079.
4. P. Cruz, Y. Perez, I. del Hierro and M. Fajardo, *Microporous Mesoporous Mater.*, 2015, 220, 136-147.