

Supporting material

Unravelling the properties of supported copper oxide: can the particle size induce acidic behaviour?

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Experimental details

Materials

The dispersed copper catalyst, obtained by Chemisorption-Hydrolysis technique (CH) with 12% by weight of copper loading was prepared by adding silica (SiO_2 , SSA = $480 \text{ m}^2/\text{g}$; PV = 0.75 mL/g) to a $1.3 \text{ M } [\text{Cu}(\text{NH}_3)_4]^{2+}$ solution. Typically 2.5 mL of solution per gram of silica were used.

After 20 min under stirring the mixture was transferred in a flask and slowly diluted with water by keeping the reactor at 0°C . After the hydrolysis step the suspension was filtered off and the solid obtained was dehydrated overnight in oven at 120°C and then calcined at 350°C for 4 hours in air.

The Incipient Wetness (IW) sample was prepared by impregnating the support with a copper nitrate solution of proper concentration and volume in order to obtain a 12% loaded catalyst over the same silica as the support.

TPR analysis

TPR analysis was performed with a modified version of the Micromeritics Pulse Chemisorb 2700 apparatus. Catalysts (25 mg) were diluted with a proper amount of quartz in order to have the same copper concentration), calcined at 500°C under O_2 (40 mL/min), and then reduced at $8^\circ\text{C}/\text{min}$ under a flow (15 mL/min) of a 8% H_2/Ar mixture.

The experimental conditions (heating rate, gas concentration) were the same for all the sample

FT-IR of adsorbed Pyridine

FTIR of adsorbed pyridine (Py) were registered on catalysts pellets (15-20 mg) using a home made glass chamber with CaF_2 windows and a Biorad FTS-40 FTIR spectrophotometer. Prior to Py adsorption, the samples were pretreated by dehydration at 270°C (20 min in air + 20 min under vacuum) and then cooled down to RT.

After this pretreatment, they were exposed to Py vapors for 15 min and infrared spectra were recorded at RT after out-gassing for 30 min at RT, 50, 100, 150, 200 and 250°C , respectively.

A comparison experiment was carried out on a not-pretreated sample of 12CuO/Si CH, showing results comparable to those reported for the pretreated one (See Figure S1 vs Figure 6)

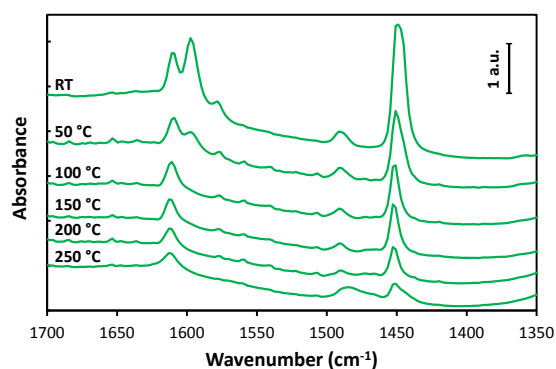


Figure S1

Py adsorption patterns at different desorption temperature for **not pretreated** 12CuO/Si CH: a) RT; b) 50 °C; c) 100 °C; d) 150 °C; e) 200 °C; f) 250 °C

HRTEM analysis

The morphology and distribution of the supported metal particles were evaluated by HRTEM. The powder samples were further ground and dispersed in isopropyl alcohol in an ultrasonic bath. A drop of the suspension was deposited on a perforated carbon film supported on a copper TEM grid. The specimen, after solvent evaporation overnight, was inserted in the column of a ZEISS LIBRA200FE HRTEM. Micrographs were taken spanning wide regions of several support grains in order to provide a truly representative map of the catalyst system. Specimens were stable during the measurements under the TEM operating conditions. Distribution histograms of metal particle fraction versus diameter were evaluated up to 350 counts per sample.

DRUV analysis

Diffuse reflectance UV–Vis (DRUV-Vis) analysis: spectra of carefully ground powders were measured on a Thermo Scientific spectrophotometer (Evolution 600), which was equipped with a diffuse reflectance accessory Praying–Mantis sampling kit (Harrick Scientific Products, USA). A Spectralon® disk was used as reference material for background measurement. All the samples were measured under ambient conditions.

XRD analysis

X-ray powder diffraction patterns were recorded within the range of 10° to 70° 2θ , with a step of 0.02° 2θ and counting time 1 or 4 sec/step on Philips PW-3020 powder diffractometer Ni-filtered Cu $K\alpha$ radiation. The peak of CuO (111) at $2\theta=35.5^\circ$ was used for line-broadening determinations. Copper oxide crystallite sizes were estimated using the Scherrer equation.