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### **Electronic Supporting Information**

### Nanosized transition metals in controlled environments of phyllosilicate-mesoporous silica composites as highly thermostable and active catalysts

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#### 1. Experimental section

Chemicals: All chemicals required to prepare the mesoporous SBA-15 silica support transition metal containing materials were used and the as purchased: tetraethylorthosilicate (Si(OC<sub>2</sub>H<sub>5</sub>)<sub>4</sub>, TEOS, 98%, Sigma-Aldrich), non-ionic triblock co-Pluronic P123 (poly(ethyleneoxide)-block-poly(propyleneoxide)-blockpolymer poly(ethyleneoxide)-block), PEO<sub>20</sub>PPO<sub>70</sub>PEO<sub>20</sub>, molecular weight of 5800, BASF Corp.), hydrochloric acid (HCl, 37%, Sigma-Aldrich), cobalt nitrate (Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, 99%, Sigma-Aldrich), nickel nitrate (Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, 98%, Sigma-Aldrich) and copper nitrate (Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O, 98%, Sigma-Aldrich), urea CO(NH<sub>2</sub>)<sub>2</sub> 99.0 – 100%, (Sigma-Aldrich, ACS reagent). For catalytic runs, the chemicals were also used as purchased: trans-cinnamaldehyde (C<sub>6</sub>H<sub>5</sub>CH=CHCHO, 98%, Merck) as reagent and propylene carbonate (C<sub>4</sub>H<sub>6</sub>O<sub>3</sub>, 99%, Sigma-Aldrich) as solvent.

#### 1.1. Material synthesis

#### A. Support synthesis:

SBA-15 support was synthesized according to the procedure used by Zhao et al.<sup>S1</sup> In a typical procedure 4 g of Pluronic P123 and 1.6 M aqueous solution of HCl were stirred at 40 °C until the complete dissolution of surfactant. Then the silica source, 8.5 g of TEOS, was added dropwise, followed by magnetic stirring for 24 h. The resulting gel was submitted to a hydrothermal treatment at 100 °C for 48 h. The organic-free SBA-15 pore structure was obtained by calcination at 550 °C for 6 h in a muffle oven (heating ramp 1.5 °C min<sup>-1</sup>).

#### **B.** Transition metal containing materials:

**Incipient Wetness Impregnation (IWI):** Materials prepared by IWI (as a reference preparation route) are denoted in the text TM\_IWI, where TM is used for transition metal (TM = Co, Ni, Cu). For example, the freshly calcined support was impregnated with an aqueous solution of 0.8 mol L<sup>-1</sup> Co(NO<sub>3</sub>)<sub>2</sub> 6 H<sub>2</sub>O to obtain a TM loading of 5 wt.%. Under these conditions, the volume of impregnation solution ensures a complete wetting of support. The impregnated powder was dried at 120 °C for 12 h, and then calcined at 500 °C for 6 h in a muffle oven (heating ramp of 1.5 °C min<sup>-1</sup>).<sup>S2</sup>

Wet Impregnation (WI): Co\_WI was also prepared by the WI method, as second reference. Freshly calcined support was impregnated with an aqueous solution of 0.04 mol  $L^{-1}$  Co(NO<sub>3</sub>)<sub>2</sub> 6 H<sub>2</sub>O to obtain a metal loading of 5 wt.%. The volume of solution used in this case was much higher than that necessary for the wetting of support. The mixture was stirred at room temperature for 24 h. The solvent removal was carried out in an oven at 60 °C for 24 h. The dried sample was finally calcined at 500 °C for 6 h in a muffle oven (heating ramp of 1.5 °C min<sup>-1</sup>).

**Deposition Precipitation route to the phyllosilicate-mediated stabilization (DP):** Materials prepared by DP are denoted in the text TM\_DP, where TM is used for transition metal (TM = Co, Ni, Cu). The transition metal containing material was prepared from a suspension of calcined SBA-15 support in an aqueous solution of 0.14 mol L<sup>-1</sup> metal nitrate to obtain a final TM loading of 5 wt.%. The reaction was performed in a double wall thermostated reactor, at a temperature of 90 °C. Initially, the pH of suspension was adjusted to 2 by using nitric acid as pH-adjustor and then urea solution (3 mol L<sup>-1</sup>) was added dropwise. To ensure a complete and stable precipitation, the solution was stirred for 24 h. At the end of the reaction, and under the conditions selected, the pH obtained was 7.4 $\pm$ 0.1. pH evolution with time was monitored during all the reaction. The obtained solid was separated by filtration, followed by washing with distilled water and drying at 60 °C for 12 h before being calcined in a muffle oven at 500 °C for 6 h (heating ramp 1.5 °C min<sup>-1</sup>).<sup>S3</sup>

#### 1.2. Physico-chemical characterization

The samples were systematically characterized in oxidized state using XRD at high angles, nitrogen physisorption, TEM-EDXS, TPR, ICP-OES. Characterization was also performed after reduction in order to evalute the benefit of the phyllosilicate stabilization on the dispersion of the metallic phase in the final materials.

**ICP-OES**: Analyses were performed on a Perkin Elmer Optima 2000 DV sequential scanning inductively coupled plasma optical emission spectrometer to determine the chemical composition (Si, Co, Ni and Cu) of the solids. Before analysis, a known amount of sample was dissolved in a diluted HF-HCl solution, and then heated under microwave until complete dissolution.

**Nitrogen physisorption**: N<sub>2</sub>-physisorption isotherms were recorded at -196 °C on an Autosorb 1-MP automated gas sorption system (Quantachrome Instruments). Before analysis, the samples were outgassed under dynamic vacuum at 350 °C for 3 h. The textural properties were determined from the adsorption/desorption isotherms by using the Autosorb 1 software, version 1.55. BET surface area was determined using the multipoint BET algorithm in the P/P<sub>0</sub> range from 0.1 to 0.25. The *t*-plot method was applied to quantitatively determine the micropore volumes and to assess the micropore surface areas (de Boer statistical thickness of 3.8–6.5 Å). The mesopore size distribution was determined by NLDFT equilibrium algorithm for cylindrical pores.

**Transmission electron microscopy (TEM):** Micrographs were recorded on a JEOL 2100 UHR instrument (operated at 200 kV with a LaB6 source and equipped with a Gatan Ultra scan camera), with a resolution of 0.19 nm, and equipped with an Energy Dispersive X-ray Spectroscopy EDXS detector. All the samples were embedded in a polymeric resin (spurr) and cut into section as small as 50 nm using an ultramicrotome equipped with a diamond knife. The cuts were then deposited on a carbon grid. TEM/EDXS analyses were used for characterize the pore structure and the distribution of TM in the materials, respectively.

**Powder XRD:** Patterns were recorded on a PanAnytical Empyrean X-ray diffractometer, Bragg Benttano comfiguration, with CuK $\alpha$  radiation ( $\lambda = 1.54184$  Å) as X-ray source. The data were collected in the  $2\theta$  range from 10 to 80° with a step of 0.05° (step time of 120 s). Phase identification was made by comparison with the ICDD database. Crystal sizes were calculated using the Scherrer equation:  $D_{hkl} = K.\lambda/\beta.cos\theta$ , where K is a structure constant (0.9 for spherical crystals);  $\lambda$  is the incident ray wavelength;  $\beta$  is the peak width at half height after correction for instrumental broadening; and  $\theta$  is the Bragg angle.

**In-situ powder XRD:** Patterns were recorded on a Bruker D8 ADVANCE X-ray diffractometer equipped with a VANTEC-1 detector, using a CuK $\alpha$  radiation ( $\lambda = 1.54184$  Å) as X-ray source. The calcined samples were placed on a kanthal filament (FeCrAl) cavity, and then subjected to thermo-programmed reduction under a flow of 3.0 vol.% H<sub>2</sub> in He (30 mL min<sup>-1</sup>) from 30 °C to 500 °C (heating ramp of 5 °C min<sup>-1</sup>). The *in situ* diffractograms were recorded at definite temperatures in the  $2\theta$  range from 15 to 70° with a step of 0.05° (step time of 2 s). Crystal phase identification was made by comparison with ICDD database.

**Temperature programmed reduction under H**<sub>2</sub> (**TPR**): Experiments were conducted on an Autochem chemisorption analyzer from Micromeritics, equipped with a TCD and coupled with a mass spectrometer (Omnistar, Pfeiffer) to follow possible desorption (H<sub>2</sub>O, O<sub>2</sub>, CO<sub>2</sub>) from the catalyst surface or possible leak (N<sub>2</sub>) during the experiments. Quantification of H<sub>2</sub> consumed during the reduction test was derived from the TCD signal after appropriate calibration. About 100 mg of calcined catalyst was inserted in a U-shape microreactor. Before the TPR run, the catalyst was activated up to its calcination temperature (500 °C for 1 h, heating ramp of 5 °C min<sup>-1</sup>) under simulated air at a total flow rate of 30 mL min<sup>-1</sup>. After cooling to 50 °C, the H<sub>2</sub> containing flow was stabilized (30 mL min<sup>-1</sup>, 3.0 vol.% H<sub>2</sub> in Ar) and the temperature programmed reduction was performed (from 50 °C to 800 °C, heating ramp of 5 °C min<sup>-1</sup>).

## **1.3.** Evaluation of the metal accessibility by catalytic tests in the liquid phase hydrogenation of cinnamaldehyde

The reaction was operated in a triphase system at atmospheric pressure, in a thermostated three-neck glass reactor equipped with reflux condenser, hydrogen bubbler and magnetic stirrer. The following reaction conditions were applied: temperature of 150 °C, 1.05 g of trans-cinnamaldehyde, 25 mL of propylene carbonate, 0.265 g of catalyst, hydrogen flow of 1 L h<sup>-1</sup> and stirring rate of 900 rpm. Prior to the catalytic runs, the calcined samples were gently crushed and sieved to obtain a granulometric fraction lower than 0.126 mm. The material was then reduced to the metallic form at 500 °C for 10 h (heating ramp of 6 °C min<sup>-1</sup>) under H<sub>2</sub> flow (1 L h<sup>-1</sup>). Preliminary tests made with different granulometric fractions and loadings of catalyst, and different stirring rates disclosed no diffusional limitations under the selected conditions. Aliquots of reaction mixture were withdrawn periodically and analyzed by gas chromatography (HP 5890 equipped with a DB-5 capillary column and a FID detector). The identification of the reaction products was achieved from the retention times of pure compounds and occasionally by GC-MS (Agilent 6890N system equipped with an Agilent 5973 MSD detector and a DB-5-ms column). The conversion of cinnamaldehyde and selectivity in the different hydrogenation products were calculated by taking into account the FID response factors for each compound.

#### 2. Supplementary characterization results



#### 2.1. XRD diffraction patterns for Ni- and Cu- containing materials

Figure S1. XRD patterns recorded for:

- Ni-containing materials, references: ICDD 43-0664 (Ni<sub>3</sub>Si<sub>4</sub>O<sub>10</sub>(OH)<sub>2</sub>·5H<sub>2</sub>O, Nickel-kerolite bottom) and ICDD 47-1049 (NiO top) (left);
- Cu-containing materials, references ICDD 43-1462 (Cu<sub>5</sub>(SiO<sub>3</sub>)<sub>4</sub>(OH)<sub>2</sub>, Shattuckite bottom) and ICDD 48-1548 (CuO top) (right).



#### 2.2. N<sub>2</sub> physisorption results for TM-containing materials

**Figure S2.** N<sub>2</sub> adsorption/desorption isotherms for parent SBA-15 and Co-containing materials (A); DP derived TM-containing materials (B).

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2.3. TPR profiles for Ni- and Cu- containing materials



Figure S3. TPR profiles recorded for: a) Ni\_DP; b) Cu\_DP.

#### 2.4. TEM observation of Cu\_DP materials



Figure S4. Representative TEM images for Cu\_DP sample: a) oxidized state; b) reduced state.



#### 2.5. Thermoprogrammed reduction followed by in situ XRD

**Figure S5.** *In situ* XRD patterns after thermoprogrammed reduction for Co-containing materials: Co\_WI (bottom reference: ICDD 42-1467, Co<sub>3</sub>O<sub>4</sub>); Co\_IWI (bottom reference: ICDD 42-1467, Co<sub>3</sub>O<sub>4</sub>); Co\_DP (bottom reference: ICDD 21-0871, Co<sub>3</sub>(Si<sub>2</sub>O<sub>5</sub>)<sub>2</sub>(OH)<sub>2</sub>)); ^, metallic cobalt (ICDD 15-0806).



**Figure S6.** *In situ* XRD patterns after thermoprogrammed reduction for Ni- and Cu-derived DP materials: Ni\_DP (bottom reference: ICDD 43-0664, Ni<sub>3</sub>Si<sub>4</sub>O<sub>10</sub>(OH)<sub>2</sub>·5H<sub>2</sub>O, Nickel-kerolite); Cu\_DP (bottom reference: ICDD 43-1462, Cu<sub>5</sub>(SiO<sub>3</sub>)<sub>4</sub>(OH)<sub>2</sub>, Shattuckite); ^, metallic copper (ICDD 04-0836).

# **2.6.** Catalytic activity of the metallic phase evaluated for the hydrogenation of cinnamaldehyde



**Scheme S1**. Reaction pathways for the hydrogenation of cinnamaldehyde (CNA); CNOL: cinnamyl alcohol, HCNA: hydrocinnamaldehyde, HCNOL: hydrocinnamyl alcohol.

Sample	X <sub>CNA</sub> <sup>a</sup> (mole %)	Selectivity <sup>b</sup>		
		S <sub>CNOL</sub> (mole %)	S <sub>HCNA</sub> (mole %)	S <sub>HCNOL</sub> (mole %)
Co_WI	4.5	66.2	24.1	9.7
Co_IWI	4.9	67.8	19.6	12.6
Co_DP	12.4	54.1	36.4	9.5
Ni IWI	52.0	1.7	94.1	4.2
Ni_DP	100.0	3.2	93.1	3.7
Cu_IWI	1.9 <sup>c</sup>	-	-	-
Cu_DP	25.7	49.4	39.8	10.8

**Table S1**. Results of catalytic activities as well as the selectivities measured for the materials presented in this work.

<sup>a</sup>,  $X_{CNA}$  is the conversion measured after 150 min of reaction; <sup>b</sup>, Selectivity to CNOL, HCNA and HCNOL at iso-conversion ( $X_{CNA}$  of ~ 15 mole %); <sup>c</sup>, The very low activity displayed by Cu\_IWI does not allow the evaluation of the selectivity.

#### 3. References

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