

## Electronic Supplementary Information (ESI)

### Supercritical fluid deposition of Ru nanoparticles into SiO<sub>2</sub> SBA-15 as a sustainable method to prepare selective hydrogenation catalysts

J. Morère<sup>a</sup>, M.J. Torralvo<sup>b</sup>, C. Pando<sup>a</sup>, J.A.R. Renuncio<sup>a</sup> and A. Cabañas<sup>\*a</sup>

<sup>a</sup>Department of Physical Chemistry I, Universidad Complutense de Madrid, 28040 Madrid. SPAIN

<sup>b</sup>Department of Inorganic Chemistry I, Universidad Complutense de Madrid, 28040 Madrid. SPAIN

\*Send correspondence to:

Prof. Albertina Cabañas

Department of Physical Chemistry I

Universidad Complutense de Madrid

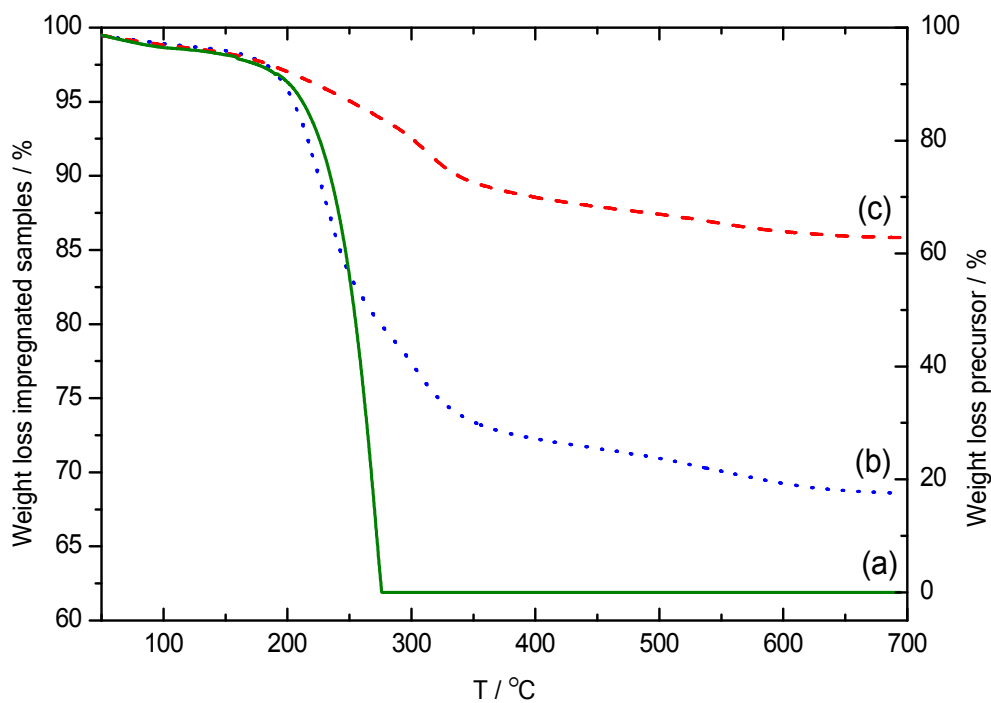
Ciudad Universitaria s/n, 28040 Madrid, SPAIN

Tlf: 34 + 91 3945225 Fax: 34 + 91 3944135

e-mail: [a.cabanass@quim.ucm.es](mailto:a.cabanass@quim.ucm.es)

## Section S1. Thermogravimetric analysis of the impregnated samples

TGA of the precursor  $\text{Ru}(\text{tmhd})_2(\text{COD})$ , and the  $\text{SiO}_2$  support impregnated with  $\text{Ru}(\text{tmhd})_2(\text{COD})$  at  $80^\circ\text{C}$  and  $13.5\text{ MPa}$  (sample 1) and  $80^\circ\text{C}$  and  $19.3\text{ MPa}$  (sample 2) in  $\text{N}_2$  flow are shown in Figure S1.



**Figure S1.** TGA analysis of the precursor  $\text{Ru}(\text{tmhd})_2(\text{COD})$  (a, —) and the  $\text{SiO}_2$  SBA-15 support impregnated with  $\text{Ru}(\text{tmhd})_2(\text{COD})$  at  $80^\circ\text{C}$  and  $13.5\text{ MPa}$  (b, ...) and  $19.3\text{ MPa}$  (c, ---).

TGA analysis of the precursor  $\text{Ru}(\text{tmhd})_2(\text{COD})$  showed that this compound sublimes between  $200\text{--}275^\circ\text{C}$  in  $\text{N}_2$ . However, TGA analysis of a  $\text{SiO}_2$  support impregnated with  $\text{Ru}(\text{tmhd})_2(\text{COD})$  revealed different weight loss events, the first one related to the

sublimation of the precursor adsorbed on SiO<sub>2</sub> at temperatures below 250 °C. At higher temperatures, the weight loss is associated to the decomposition of the precursor adsorbed onto the surface to its metal form. These results indicate that the hydrophilic SiO<sub>2</sub> support interacts weakly with the precursor and explain that the Ru mol percentage measured by EDX in the impregnated samples after reduction in H<sub>2</sub>/N<sub>2</sub> atmosphere is lower than the expected one considering the weight loss by TGA.

Total weight losses close to 30 and 13 mass % were obtained for samples 1 and 2 impregnated at 80 °C and 13.5 and 19.3 MPa, respectively, at the same Ru:SiO<sub>2</sub> molar ratio. The amount adsorbed decreased as the pressure and density of the supercritical phase increased. At the higher pressure, both the solubility of the precursor in the fluid phase and the concentration of CO<sub>2</sub> increased and consequently, the partition coefficient of the precursor changed, lowering its adsorption on the surface.

## Section S2. N<sub>2</sub> adsorption-desorption isotherms

Figures S2 and S3 show N<sub>2</sub> adsorption-desorption isotherms and pore size distributions obtained from the adsorption and desorption branches of the isotherms for the Ru/SiO<sub>2</sub> samples and the bare support not shown in the manuscript.

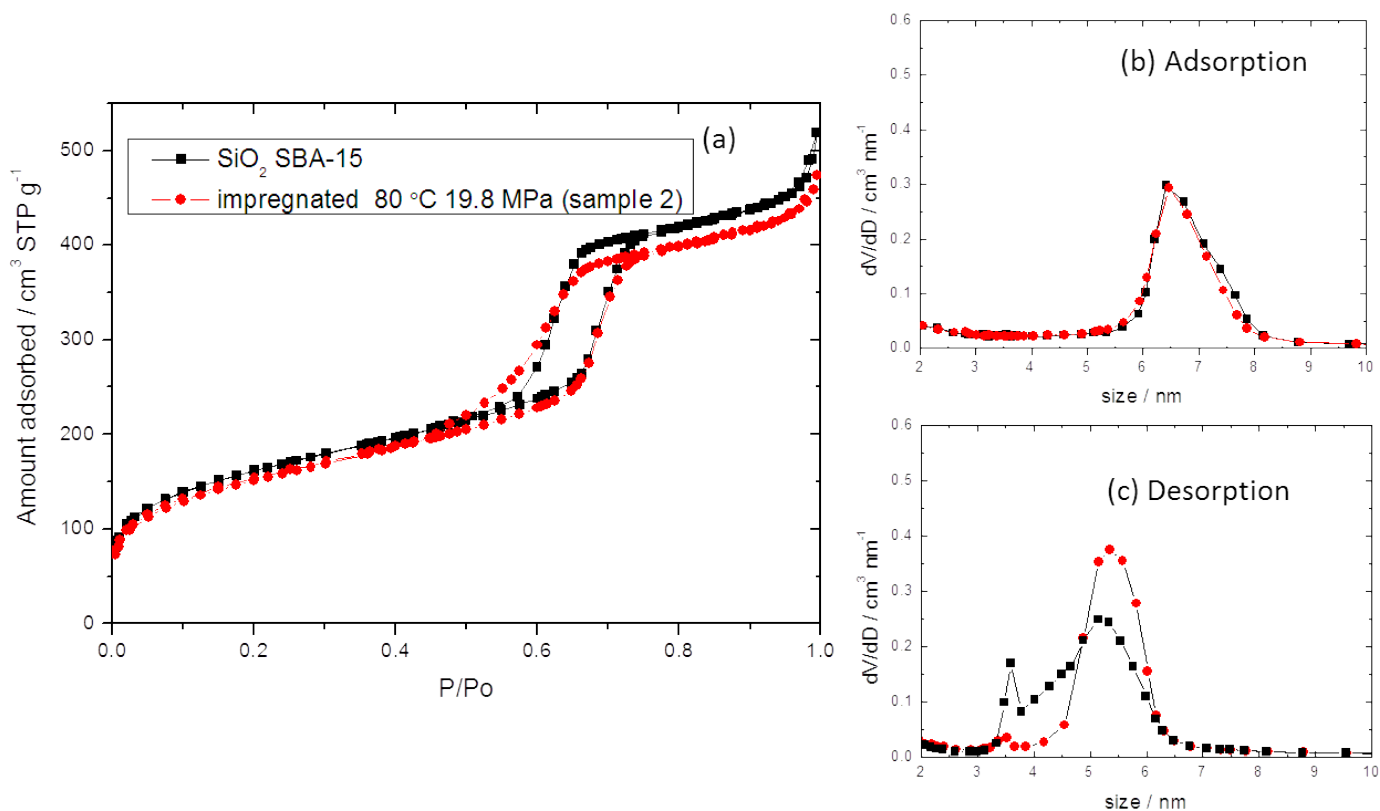
Isotherms exhibit a type IV, subtype H1, hysteresis loop which is found in mesoporous materials with well-defined cylindrical-like pore channels.

Adsorption isotherms of sample 2 produced by impregnation at 19.3 MPa were very close to those of the SiO<sub>2</sub> support (Figure S2). Due to the small amount of Ru deposited and the small particle size, deposition of Ru by impregnation into the support led to S<sub>BET</sub> and V<sub>p</sub> values very similar to those of the SiO<sub>2</sub> sample.

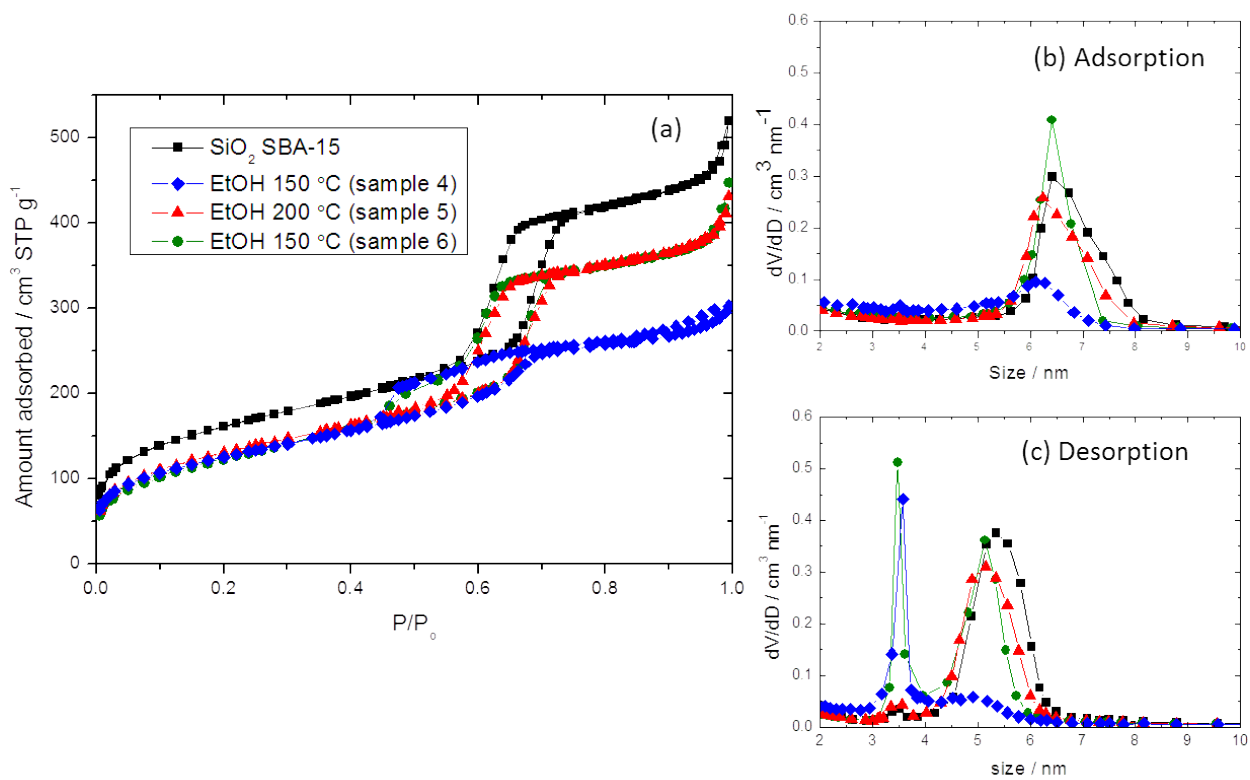
However, adsorption isotherms of samples 4 to 6 reduced using EtOH showed larger differences in comparison to those of the bare SiO<sub>2</sub> support (Figure S3). This is due in part to the larger amount of Ru deposited for samples 5 and 6, but it is also related to the presence of unreacted RuCl<sub>3</sub>·xH<sub>2</sub>O or reaction by-products in the samples deposited using EtOH as determined by EDX. No attempt to correlate the surface area and the pore volume with the concentration and nature of the impurities was made.

Analysis of the pore size distribution of the SiO<sub>2</sub> SBA-15 support obtained from the adsorption branch of the isotherm gave a narrow pore size distribution with a maximum at 6.8 nm. In comparison, there was only a slight reduction of the pore size in all the Ru/SiO<sub>2</sub> samples. The pore size distributions estimated from the desorption branch of the isotherm showed a new maximum at ca. 3.6 nm. This phenomenon is due to ink-bottle like sections

created by the nanoparticles in the mesopores [V. Meynen, et al., Synthesis of siliceous materials with micro- and mesoporosity, Microporous and Mesoporous Materials 104 (2007) 26-38].



**Figure S2.**  $N_2$  adsorption-desorption isotherms (a) and pore size distributions obtained from the adsorption (b) and desorption (c) branches of the isotherm for  $\text{SiO}_2$  SBA-15 and the  $\text{Ru/SiO}_2$  SBA-15 sample obtained by impregnation of  $\text{Ru}(\text{tmhd})_2(\text{COD})$  in  $\text{scCO}_2$  at  $80^\circ\text{C}$  and 19.3 MPa (sample 2).



**Figure S3.**  $N_2$  adsorption-desorption isotherms (a) and pore size distributions obtained from the adsorption (b) and desorption (c) branches of the isotherm for  $SiO_2$  SBA-15 and the Ru/ $SiO_2$  SBA-15 samples obtained by EtOH reduction of  $RuCl_3 \cdot xH_2O$  in  $scCO_2$  (samples 4-6).