

DEPOSITION OF Ru AND Ni NANOPARTICLES INTO POROUS SUPPORTS THROUGH IMPREGNATION AND REACTION OF METAL ORGANICS AND INORGANIC SALTS IN SUPERCRITICAL CO₂

J. Morère*, A. Cabañas, C. Pando, J.A.R. Renuncio
Department of Physical Chemistry I
Universidad Complutense de Madrid - UCM
Ciudad Universitaria s/n 28040 Madrid, Spain
E-mail: jmorere@quim.ucm.es

ABSTRACT

Ru and Ni nanoparticles were deposited into mesoporous silica SBA-15 using supercritical CO₂ (scCO₂). Several synthetic routes using metal organics and inorganic salts were used: *impregnation*, *reactive deposition with H₂* and *reactive deposition with EtOH*. Ru(tmhd)₂(cod), RuCl₃/EtOH and Ni(cp)₂ were used as the metal precursors. Composite materials were characterized by XRD, TEM, EDX and N₂-adsorption experiments. TEM images of the composite materials show Ru and Ni incorporation into the cylindrical SiO₂ SBA-15 channels. In both cases the nanoparticles are well distributed within the SiO₂ matrix, being the cluster size limited by the pore size of the support.

Keywords: ruthenium, nickel, nanoparticles, mesoporous materials

INTRODUCTION

Supercritical CO₂ (scCO₂) is emerging as an excellent medium to deposit metal nanoparticles into porous supports. Metal nanoparticles exhibit very interesting properties in comparison to their bulk counterpart. Apart from their significantly higher surface to volume ratio, their reduced cohesive energy turns the surface atoms very reactive offering many opportunities in catalysis, electronics, information storage, fuel cell technology...[1]. When metal nanoparticles are deposited into porous supports, particles are stabilized against aggregation.

The use of scCO₂ in metallization processes presents several advantages over the conventional techniques. Besides the environmental benefits, its high diffusivity and low viscosity and surface tension favour the penetration of scCO₂ and its mixtures into nanostructures such as nanopores and nanotrenches/holes. Furthermore, the support structure is preserved upon the CO₂ treatment.

The deposition of different metals into porous supports involves the dissolution of the metal precursor into scCO₂ and its adsorption (impregnation) onto the support. Then the precursor is decomposed in the supercritical fluid following thermal or chemical reduction or, after depressurization, by thermal treatment in a controlled atmosphere [2]. Depending on the decomposition method, different structures are obtained: nanoparticles, nanowires or films [3].

At our laboratory we are using scCO₂ to deposit metal nanoparticles into porous supports [4,5]. In this communication we present examples of deposition of Ru and Ni nanoparticles into mesoporous SiO₂ SBA-15 using metal organic precursors and inorganic salts.

MATERIALS AND METHODS

Materials

Tetraethylorthosilicate (TEOS, 99+% pure), poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol) (Mw=5800) (PEO-PPO-PEO) and ruthenium chloride [RuCl₃·xH₂O] were obtained from Aldrich. Bis(2,2,6,6-tetramethyl-3,5-heptanedionato)(1,5-cyclooctadiene)ruthenium(II) [Ru(tmhd)₂(cod)] and bis(cyclopentadienyl)nickel, [Ni(cp)₂] were obtained from Strem Chemicals. Chemicals were used as received. CO₂ purity >99.99%, H₂ purity >99.999% and Forming Gas (H₂<6%) were supplied by Air Liquide. Mesoporous silica SBA-15 was prepared following the procedure described by Zhao et al. [6]. SiO₂ SBA-15 presents a mesoporous structure formed by cylindrical pores of ca. 6-7 nm arranged in a hexagonal fashion. BET surface for this support varies from 600 to 700 m²/g.

Experimental procedure

The experiments were conducted in a 100 mL stirred stainless-steel bolted closure high-pressure reactor in the batch mode (Autoclave Engineers Inc.). SiO₂ SBA-15 (ca. 50-150 mg) and the metal precursor (ca. 25-75 mg) were loaded into the reactor. For the experiments involving inorganic salts a small amount of EtOH (ca. 10-20% mol in CO₂) was also placed inside the reactor. The reactor was then heated to the working temperature and was filled with CO₂ using a high-pressure syringe pump (Isco Inc., Model 260D).

Three different methodologies were used to deposit Ru and Ni nanoparticles into the mesoporous SiO₂ support:

1) *Impregnation*: The metal precursor was dissolved in scCO₂ and contacted with the support where became adsorbed. Equilibration time was fixed to 24 hours. After the impregnation step, the reactor was depressurized and the reduction of the precursor was carried out in a tubular furnace with a forming gas (H₂/N₂) flow at 400°C for 5 hours. This methodology was used for Ru(tmhd)₂(cod) and Ni(cp)₂ dissolved in scCO₂ at 80°C and 13.5 MPa or 60°C and 11.0 MPa, respectively.

2) *Reactive deposition with H₂*: As in the previous methodology, both Ru(tmhd)₂(cod) and Ni(cp)₂ were dissolved in scCO₂ and the support was impregnated but, in this case, the reduction step was carried out *in situ* by loading a small amount of H₂ in large stoichiometric excess. H₂ was introduced into the reactor using a 30 mL stainless-steel auxiliary cell constructed with ¾" Swagelok pipe. The reduction was initiated by raising the temperature to 150°C in the case of Ru nanoparticles and to 250°C in the case of Ni nanoparticles.

3) *Reactive deposition with EtOH*: A solution of RuCl₃ in EtOH as the metal source and the reducing agent was placed inside the reactor. Then the reactor was loaded with CO₂ at 35°C and 8.5-9.0 MPa. After the impregnation step, the temperature was raised to 120-150°C to promote the metal reduction in the supercritical mixture.

Materials characterization

Materials were characterized using transmission electron microscopy (TEM), N₂-adsorption and X-ray diffraction (XRD). TEM were carried out on a JEOL-JEM 2100 electron microscope operating at 200 kV equipped with a double tilting ($\pm 25^\circ$). Samples were dispersed in 1-butanol over copper grids and dried in air. Energy-dispersive Detection X-ray analysis (EDX) was conducted on selected samples using TEM microscopes. N₂ adsorption-desorption isotherms at 77 K were obtained using an ASAP-2020 equipment from Micrometrics.

RESULTS

XRD of the Ru samples produced by reactive deposition using H₂ or ethanol revealed the presence of metallic Ru. In contrast, samples obtained by impregnation and further reduction in forming gas, showed a mixture of Ru and RuO₂, possibly due to the partial oxidation of the small nanoparticles produced.

TEM images of the Ru composites materials obtained with the three methodologies studied are shown in Figure 1. EDX analysis was performed on the TEM images and confirmed the presence of Ru in the samples. Ru content varies from 1.5 to 7.4 mol %.

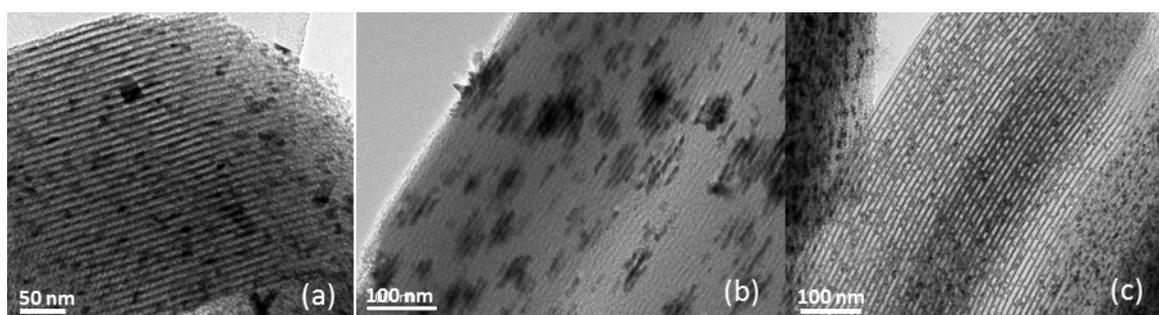


Figure 1. TEM images of Ru nanoparticles on mesoporous silica SBA-15 obtained by. (a) impregnation of Ru(tmhd)₂(cod) at 80°C and 13.5 MPa and reduction with H₂/N₂ flow at 400°C at low pressure, 5 hours. (b) reactive deposition of Ru(tmhd)₂(cod) with H₂/CO₂ at 150°C. (c) reactive deposition of RuCl₃ with EtOH/CO₂ at 150°C.

The amount of Ru incorporated into the mesoporous support and the morphology of the nanoparticles depend on the methodology used. For example, the reactive deposition of Ru(tmhd)₂(cod) into mesoporous silica SBA-15 following impregnation at 80°C and 13.5 MPa and further reduction with an excess amount of H₂ in scCO₂ at 150°C (Fig. 1b) yields nanoparticles with a nanorod-like structure along the channels. For this sample, the Ru content measured by EDX is ca. 6 mol %. Ru can catalyse reduction reactions, making the process self-catalytic and therefore larger particles are grown. On the other hand, spherical Ru nanoparticles were very well dispersed following either impregnation (Fig. 1a) or ethanol reduction (Fig. 1c). Whilst impregnation is controlled by the adsorption equilibrium, ethanol reduction of RuCl₃ proceeds to completion and a larger Ru contents can be deposited (7.4 mol% by EDX in Fig. 1c).

The porosity of the Ru/SiO₂ SBA-15 composite materials was studied by N₂-adsorption. Adsorption isotherms exhibit a type IV, subtype H1, hysteresis loop which is found in mesoporous materials. In every case, deposition of Ru into the support decreases the BET surface and the pore volume from ca. 700 to 450 m²/g. Analysis of the pore size distribution revealed a slight reduction of the pore sizes in the Ru-SiO₂ samples suggesting partial coating of the mesopores with the metal.

The catalytic activity of the Ru/SiO₂ composite materials is currently being tested for simple hydrogenation reactions.

As to the deposition of Ni into SiO₂ SBA-15 from Ni(cp)₂ dissolved in scCO₂, neither impregnation, nor reactive deposition with EtOH gave satisfactory results. This is partly due to the higher reduction temperature required to deposit Ni (200-250 °C), as well as to the high reactivity of this precursor (sensitive to air and light) and the low affinity for the SiO₂ substrate. In this case, however, well distributed Ni nanoparticles were obtained performing the synthesis via reactive deposition of Ni(cp)₂ with H₂ at 250°C.

CONCLUSION

We have shown that scCO₂ can be used as reaction and impregnation medium to deposit Ru or Ni nanoparticles into mesoporous silica SBA-15. For Ru, both metal organics and inorganic salts have been used, yielding well dispersed Ru nanoparticles within the support. Metal load and its distribution can be tuned by the initial precursor concentration, temperature, pressure and the decomposition method. The impregnation and reactive deposition using ethanol methods generally yield very good metal dispersions. These materials can be used as catalysts in hydrogenation reactions.

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