Deposition of Metal Nanoparticles into Porous Supports Using Supercritical CO_2

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Abstract

Supercritical CO_2 ($scCO_2$) is emerging as an excellent medium to deposit metal nanoparticles into porous supports. These metal-composite materials have numerous applications in catalysis, microelectronics, gas separation, hydrogen storage, sensors, and fuel cells [1]. The use of $scCO_2$ in metallization processes presents several advantages over the conventional techniques. Beside the environmental benefits, its high diffusivity and low viscosity and surface tension favor the penetration of $scCO_2$ and its mixtures into nanostructures such as nanopores and nanotrenches/holes. Furthermore, the support structure is preserved upon the CO_2 treatment.

The deposition of different metals into porous supports involves the metal precursor dissolution into $scCO_2$ 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]. In this presentation, we give examples of the deposition of Pd, Ru and Ni nanoparticles into mesoporous silica and graphene sheets.

The deposition of Pd into mesoporous silica SBA-15 was chosen as a model system to study the different steps of the process in a comprehensive way [3,4]. Palladium hexafluoroacetylacetonate [$Pd(hfac)_2$], which is very soluble in $scCO_2$, was used as precursor. Best results were obtained when $scCO_2$ was used just to impregnate the support and the precursor reduction was not performed under supercritical conditions. Figure 1a shows a TEM image of the Pd-SiO_2 SBA-15 material obtained by impregnation at 40 ºC and 85 bar with $Pd(hfac)_2$ in $scCO_2$ and further reduction in pure H_2 at 40 ºC and 60 bar. The image shows ca. 6-7 nm Pd nanoparticles, very uniformly dispersed, deposited within the cylindrical channels of the mesoporous support. The size of the particles is limited by the pore size of the support. By changing temperature, pressure and precursor concentration, the loading of the metal on the support was controlled.

Similar results were found for the deposition of Ru using bis(2,2,6,6-tetramethyl-3,5-heptanedionato)(1,5-octadiene) ruthenium (II) [$Ru(tmhd)_2$(COD)]. In this case, the impregnation was performed at 80 ºC and 185 bar in $scCO_2$, whilst the reduction was performed at low pressure in N_2/H_2 at 400 ºC 5 h (Figure 1b). Although the precursor decomposition was carried out in a reducing atmosphere, XRD showed the presence of a Ru and RuO_2 mixture. The small size of the particles deposited and the large concentration of oxygen on the silica surface may favor particle oxidation. The same precursor was also used to deposit Ru nanoparticles onto graphene sheets. The support was impregnated with $Ru(tmhd)_2$(COD) and reduced in a supercritical H_2/CO_2 mixture at 150 ºC. Ru nanoparticles ca. 10 nm were dispersed homogeneously on this support.

Deposition of Ni was also performed using different precursors and decomposition routes. This compound is more difficult to deposit because of the low affinity of most suitable Ni precursor towards silica supports and the higher decomposition temperatures required. Successful results were obtained following H_2 reduction of nickelocene [$Ni(Cp)_2$] in $scCO_2$ at 200-250 ºC.

Materials were characterized by TGA, XRD, TEM, SEM, EDX, ICP-OES and N_2-adsorption experiments. The catalytic activity of these materials was also assessed for hydrogenation reactions in liquid, gas and supercritical medium. The properties of the composite materials produced in $scCO_2$ compare favorably with those of similar materials produced using other more conventional techniques.

References

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Figures

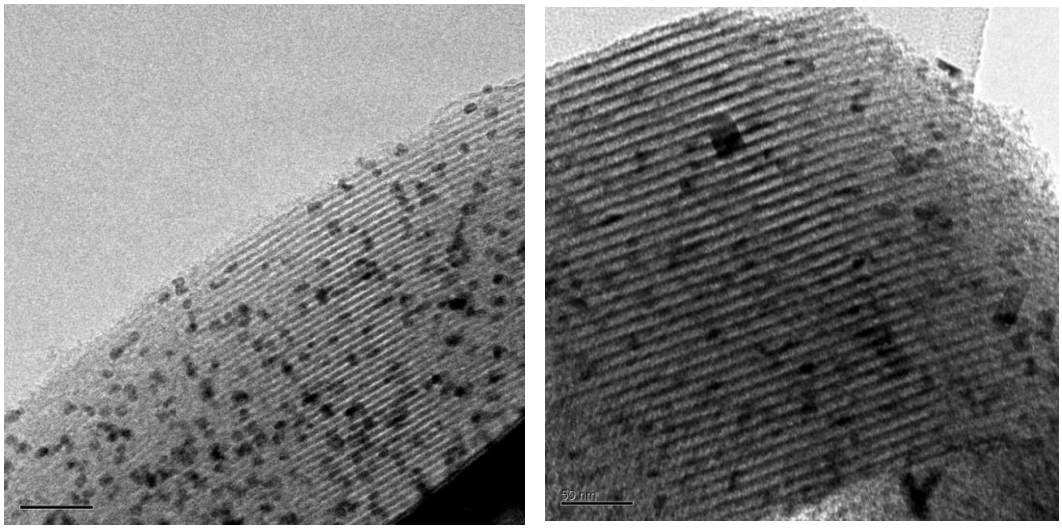

Figure 1. TEM images of (a) Pd and (b) Ru nanoparticles deposited on SiO_2 SBA-15. Scale bars: 50 nm