Multimodal porous silica supports to generate interacting oxide/metal particles and potential catalytic applications

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Small oxide particles have unique physical and chemical properties and understanding them is important for the design of original heterogeneous catalysts. Among oxides, Co_3O_4 is often selected for environmental applications, energy and fine chemicals reactions because of the high mobility of its oxygen atoms. We have used the pores of SBA15 silicas as solid templates to obtain Co-oxide particles of calibrated diameters and shapes. We have selected SBA15 because of their large porous volume (more than 1 cm^3/g) and bimodal porosity (ordered mesopores linked by disordered and smaller pores) in which it is possible to disperse high amount of oxide particles and control their structural defects by heat treatments. Co-nitrate was used as a precursor and deposited inside the pores by the "two solvents" in which dry silica grains are suspended in an organic solvent before the addition of a small amount of water containing the Co-precursor (for 1g of silica, 70 ml of solvent; nitrate, 3 $mol.M^{-1}$, added volume 0.300 μL). The samples that we have prepared are complex and after calcination at 700°C in iar, three distinct Co-species were distinguished based on structural (XRD, SAED) and spectroscopic arguments (UV-visible, ESR). i) spinel oxide particles templated inside the pores, ii) metallic small particles in the silica walls, iii) oxide particles dispersed on the external surface of the silica grains. The last particles, sensitive to external conditions, are difficult to identify definitively after air storage. In situ measurements will be necessary.

Catalytic tests (in particular for the hydrogenation of α,β unsaturated cinnamaldehyde) reveal unusual catalytic properties (an unsaturated alcohol selectivity in the early steps of the reaction) compatible with a reagent adsorption on metallic particles. Arguments in favour of the association between the particles identified outside the silica grains and strong electronic interactions between them and the internal oxide (spinel) particles, acting as nanodots (electron donors) is proposed.