Ru nanoparticles stabilized by organosilanes:
Influence of the initial Si/Ru ratio

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Surface Organo-Metallic Chemistry on Metals (SOMC/M) [1] provides access to a new type of materials. The strategy is to create catalytically active sites which are homogeneously dispersed and uniform in their structure by grafting organometallic precursors on well defined metallic surfaces. For example, tetrabutyltin reacts with the surface of metallic particles supported on silica leading to formation of grafted organometallic fragments on the “host” metal [2]. Unfortunately, for particles in the nanometric range, strong interactions between support and particles lead to undesired inhomogeneity of the active sites.

Our approach is the combination of SOMC/M and synthesis of unsupported nanoparticles via the organometallic route. The use of organic ligands such as amines, alcohols or thiols for the stabilization of metal nanoparticles has been considerably developed to prevent agglomeration and to favor self-assemblies [3]. Consequently, organometallic ligands such as octylsilane have been proposed as stabilizer.

The decomposition of the organometallic precursor [Ru(COD)(COT)] (Ruthenium-1,5-cyclooctadiene-1,3,5-cyclooctatriene) in mild conditions (193 K, 3 bar H₂) in n-pentane leads, in the presence of octylsilane, to the formation of Ru nanoparticles with narrow size distribution. The influence of the initial octylsilane/Ru(COD)(COT) ratio ranging from 0.2 to 2.0 was studied. In all cases stable colloidal solutions containing crystalline nanoparticles have been obtained from which the particles have been extracted by precipitation and washing with n-pentane followed by drying in vacuum. The black powders were fully characterized by elemental analysis, TEM with EDX, IR, solid state ¹³C CP-MAS NMR as well as XRD. These analyses showed that the metal surface is covered by octylsilane groups and that the size of the nanoparticles decreases with increasing initial Si/Ru ratio. The smallest nanoparticles with a size of 1.6 nm were obtained for the lowest initial Si/Ru ratio (0.2). The thermal stability of these nanoparticles (Si/Ru = 1; see Figure: Molecular modeling of the particle covered by a monolayer of ligand) was studied by TPR and TPD reactions. The particles sintered during treatment in H₂ at 400 °C, while their size increases only slightly in inert atmosphere. The amount of grafted ligand could be quantified by analyzing the desorbing gases from the surface during heating.

In conclusion, unsupported Ru particles of controlled size can be synthesized by variation of the amount of added stabilizer. The properties of such well-defined catalysts can be tuned via the noble metal particle size and the nature of the grafted organometallic fragments.