

Controlled synthesis of metal@fullerene nanoarchitectures for catalysis

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ABSTRACT

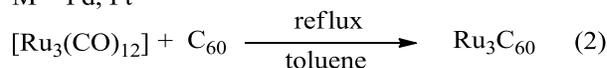
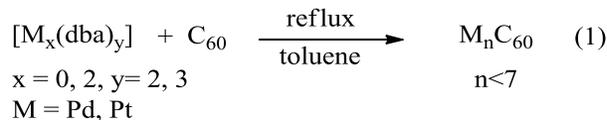
Ru@fullerene C₆₀ nanostructures have been synthesized by decomposition of an organometallic precursor ([Ru(COD)(COT)] (COD= 1, 5 cyclooctadiene, COT= 1, 3, 5-cyclooctatriene)) in the presence of C₆₀ using mild conditions. The nanoarchitectures obtained display small Ru nanoparticles (1.5 nm of mean diameter). The shape of the nanostructures is controlled by the use of different solvents. The Ru@C₆₀ nanoarchitectures have a good catalytic activity and selectivity in the hydrogenation of nitrobenzene.

Keywords: ruthenium nanoparticles, C₆₀ fullerene, nanostructures, catalysis

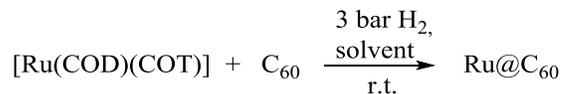
The association of metallic or semi-metallic nanoparticles with carbon materials provides unique materials that are useful in many applications including catalysis, gas storage, sensors, fuel cells and batteries.¹ The use of nano-structured carbon materials to build such assemblies is particularly attractive since they are unique and ideal templates onto which nanoparticles can be grafted, allowing the construction of designed nanoarchitectures.² A plethora of reports therefore exists on the functionalization of nano-structured carbon materials with metal particles. Metallic nanoparticles have been associated to carbon nanotubes,³ graphene,⁴ fullerenes⁵ and even nano-diamonds.⁶ However, the main limitation of these assemblies is the complete absence of a control of their organization, *i.e.* the metallic nanoparticles are randomly distributed on the surface of the nanocarbons. Consequently, it is extremely difficult to achieve a high metal loading with small metal nanoparticle size, which is detrimental to many applications such as fuel cells, sensors or gas storage. Additionally, the distance between nanoparticles being not controlled, their properties are not optimized. Indeed, it has been shown that the proximity of nanoparticles may affect their catalytic performances.⁷

Fullerenes are an important member in the carbon material family, which have been extensively investigated up to now. As far as we know, most of metal nanoparticles@fullerene C₆₀ structures have been synthesized by the following methods: a) deposition of pre-synthesized metal nanoparticles on fullerene C₆₀;⁸ b) thermal decomposition of an organometallic complex in the presence of fullerene C₆₀;⁹ c) co-evaporation of the metal and fullerene C₆₀;¹⁰ and d) electrochemically.¹¹

Fullerene C₆₀ may produce metal polymer fullerenes.¹² The first metal fullerene polymer was described by Nagashima,^{13a} which was synthesized from C₆₀ and [Pd₂(dba)₃] (equation (1)). Pt fullerene polymer has been also synthesized in the same way.^{13b} The polymer presents an amorphous structure and no metal nanoparticles are observed. Metal nanoparticles can be obtained by thermal decomposition of the polymer at 650 K.¹⁴ Ru_nC₆₀ species were prepared by the reaction of [Ru₃(CO)₁₂] and C₆₀ in refluxing toluene (equation (2)).¹⁵ Compared to the Pd-, and Pt-C₆₀ polymers, the amorphous matrix showed small ruthenium particles (2-5 nm mean diameter) in the Ru fullerene compound.



In this context and highly interested in the development of nanostructured hybrid materials, we associate here fullerene C₆₀ with ruthenium. The Ru@C₆₀ nanoarchitectures were synthesized by decomposition of [Ru(COD)(COT)] in the presence of C₆₀ using an organometallic approach.¹⁶ Scheme 1 depicts the procedure of preparation of Ru@C₆₀ nanostructures. [Ru(COD)(COT)] was decomposed by molecular H₂ (3 bar) in the presence of fullerene C₆₀. The solvent used as well as the Ru/C₆₀ ratio play an important role in the synthesized nanostructures.



Scheme 1. Synthesis of Ru@C₆₀ nanoarchitectures.

The effect of different solvents (toluene, chlorobenzene, *o*-dichlorobenzene, dichloromethane, and decalin) was investigated first with a Ru/C₆₀ ratio of 2. TEM images (Figure 1) show that several structures can be obtained depending on the solvent used. Chlorinated solvents produced Ru@C₆₀ polymeric particles with mean size of: 285 ± 3 nm for chlorobenzene, 200 ± 3 nm for *o*-dichlorobenzene and 39.6 ± 0.7 nm for dichloromethane. On the other hand, decalin and toluene produced amorphous structures. In addition, non coordinating solvents such as decalin and dichloromethane

allowed to obtain organometallic polymers decorated with Ru nanoparticles.

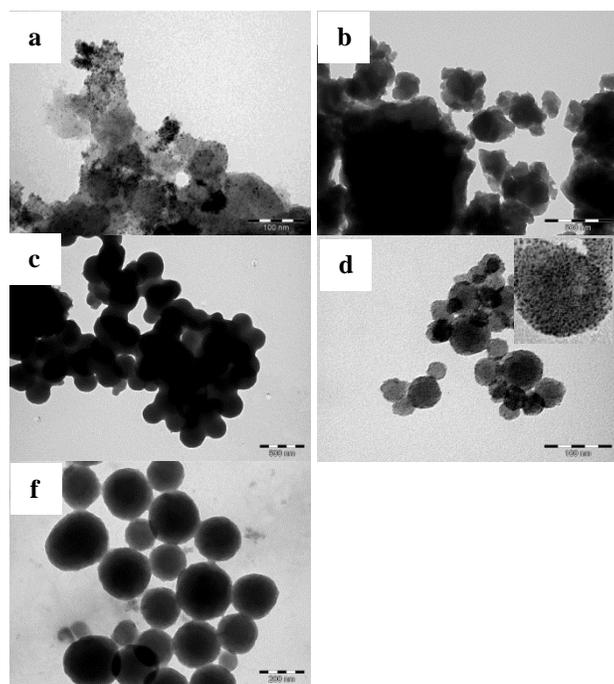


Figure 1. TEM images of Ru/C₆₀=2/1 synthesized in different solvents: a) decalin (scale bar 100 nm), b) toluene (scale bar 500 nm), c) chlorobenzene (scale bar 500 nm), d) dichloromethane (scale bar 100 nm), and (f) *o*-dichlorobenzene (scale bar 200 nm).

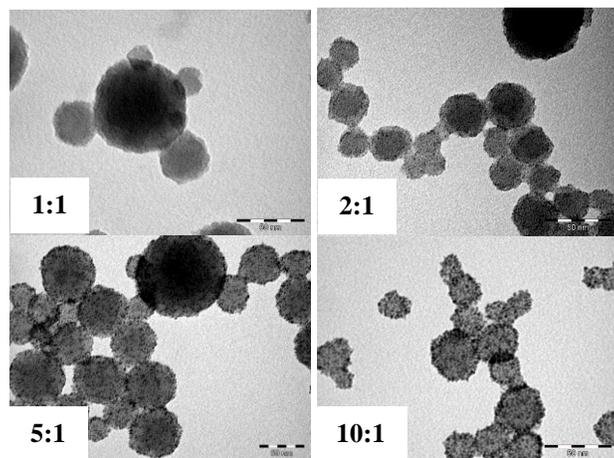


Figure 2. TEM images of nanostructures produced in dichloromethane using different Ru/C₆₀ ratio, scale bar are 50 nm.

Using dichloromethane as solvent, which allow to obtain well defined polymeric nanospheres, we examined the effect of the Ru/C₆₀ ratio (Figure 2). Ru/C₆₀=1/1 display polymeric nanospheres (37.8 ± 1.0 nm) with no Ru nanoparticles. The increase of Ru content allow to obtain polymeric nanospheres decorated with Ru nanoparticles. The size

of the nanospheres being constant and the Ru nanoparticles size showing a narrow distribution (1 nm).

Table 1. Hydrogenation of nitrobenzene using Ru@C₆₀.^a

1	2	3
Ru/C ₆₀	Conversion (selectivity)% ^b , Time	Conversion (selectivity)% ^b , Time
1:1	21(84), 24h	n. d., 48h
2:1	39(6), 24h	Trace, 48h
5:1	98 (96), 24h	Trace, 48h
10:1	91(92), 4h	81 (80), 3h

^a Reaction conditions: 5.0 mg of catalyst, 4.07mmol of PhNO₂, 0.58 mmol of dodecane as internal standard, 30 mL of EtOH, 30bar of H₂ at 80°C. ^b Conversion was determined by GC-MS using dodecane as internal standard. n.d.= not detected.

The Ru@C₆₀ nanoarchitectures, were tested as catalyst in the hydrogenation of nitrobenzene (Table 1). Ru/C₆₀ polymer show a low conversion to aniline (**2**) after 24 h of reaction, however, increasing the ruthenium content (*i.e.* the nanoparticles on the nanosphere surface) the catalysts were more active reaching total conversion to aniline in 4h with Ru/C₆₀=10/1 nanocatalyst. Furthermore, cyclohexylamine (**3**) was produced in high yields with Ru/C₆₀=10/1 catalyst under mild conditions. Indeed, only a few papers report the direct synthesis of cyclohexylamine from nitrobenzene,¹⁷ always using harsh conditions (170 °C).

In summary, this work presents the synthesis of well defined nanoarchitectures Ru@C₆₀ through decomposition of an organometallic complex [Ru(COD)(COT)] in the presence of C₆₀ at room temperature. According to the experiment data, the solvent is the key to control the nanostructures, and different Ru@C₆₀ composites were obtained controlling the Ru@C₆₀ ratio. It is also revealed that the Ru@C₆₀ nanoarchitecture exhibited high catalytic activity in the hydrogenation of nitrobenzene. We foresee that our method would open the way to design special morphologies and structures of metal@C₆₀ nanostructure, which could find use in various applications.

EXPERIMENT SECTION

General methods

All operations were carried out under argon atmosphere using standard Schlenk techniques or in an MBraun glovebox. Solvents were purified by an MBraun SPS-800 solvent purification system. [Ru(COD)(COT)] was purchased from Nanomeps (Toulouse) and fullerene C₆₀ from Aldrich.

All Ru@C₆₀ nanostructures were synthesised using the same procedure. We describe here a typical experiment:

Synthesis of the Ru/C₆₀ = 2/1. [Ru(COD)(COT)] (20 mg, 0.0635 mmol) was introduced in a Fischer-Porter bottle in the glovebox. A solution of C₆₀ (23 mg, 0.0317 mmol) in 50 mL CH₂Cl₂, was then canulated to the Fischer-Porter bottle. The resulting purple solution was stirred for 30 min at room temperature, after which the bottle was pressurized under 3 bar of H₂. A black precipitate formed quickly indicating ruthenium particles were produced, then the solution was allowed to react for 12 h. After elimination of excess H₂, the resulting solution was reduced to 15 mL, after which addition of 30 mL pentane led to a dark precipitate. The solid was filtered, washed with pentane three times, and dried in vacuum pump.

General method for hydrogenation of nitrobenzene:

Ru/C₆₀ catalyst (5 mg), dodecane (100 mg) and nitrobenzene were added to a schlenked tube (100 mL) with 30 mL of degased ethanol in the glovebox. The resulting dispersion was ultrasonicated for 15 min and then introduced to the autoclave. After, the mixture was heated to the desired temperature (80°C) and autoclave pressurized to 30 bar of H₂ pressure. Samples of the liquid phase were taken during the reaction and analyzed by GC-MS.

Characterization

The TEM specimens were prepared by slow evaporation in a glovebox of droplets of diluted solutions of the different colloids deposited on a high-resolution carbon-supported copper grid. TEM analyses were performed at the *Centre de microcaracterisation Raimond Castaing*, UMS 3623, Toulouse by using a JEOL JEM 1011 CX-T electron microscope operating at 100 kV with a point resolution of 4.5 Å or a JEOL JEM 1400 electron microscope operating at 120 kV. The approximation of the particles mean size was made through a manual analysis of enlarged micrographs by measuring at least 200 particles on a given grid. The ruthenium content was established by inductively coupled plasma optical emission spectroscopy (ICP-OES) performed in a Thermo Scientific ICAP 6300. GC-MS samples were detected using instrument of Perkin Elmer Clarus 500 MS.

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