Microporous and Mesoporous Materials 153 (2012) 155–162

Contents lists available at SciVerse ScienceDirect

Microporous and Mesoporous Materials

journal homepage: www.elsevier.com/locate/micromeso

Carbon-supported Ru and Pd nanoparticles: Efficient and recyclable catalysts for the aerobic oxidation of benzyl alcohol in water

Eduardo J. García-Suárez [a,b,c], Mar Tristany [b,c], Ana B. García [a], Vincent Collière [b,c], Karine Philippot [b,c,*]

[a] Instituto Nacional del Carbón (CSIC), Francisco Pintado Fe 26, 33011 Oviedo, Spain
[b] CNRS, LCC (Laboratoire de Chimie de Coordination), 205, Route de Narbonne, F-31077 Toulouse, France
[c] Université de Toulouse, UPS, INPT, LCC, F-317077 Toulouse, France

ARTICLE INFO

Article history:
Received 5 September 2011
Received in revised form 8 December 2011
Accepted 8 December 2011
Available online 16 December 2011

Keywords:
Carbon materials
Heterogeneous catalysis
Metal nanoparticles
Alcohol oxidation
Recyclable catalysts

ABSTRACT

Ru NPs and Pd NPs were firstly synthesized and further supported on mesoporous carbon materials. Spherical and homogenously dispersed MNPs displaying mean sizes in the range 1.2–2.2 nm were thus achieved. The catalytic activity as well as the recyclability of these carbon-supported Ru and Pd NPs in the aerobic oxidation of benzyl alcohol to benzaldehyde in water was investigated, showing excellent conversions and high selectivity to the aldehyde. The selectivity towards aldehyde is particularly relevant since usually the oxidation of primary alcohols in water mainly yields the carboxylic acid. Moreover, these nanocatalysts present good recyclability in terms of conversion with up to eight successive reaction cycles. However, the selectivity to the aldehyde decreased, in some cases significantly, after the third cycle. The catalytic activity of these systems was found to be influenced by the hydrophilicity of the carbon support surface. However, the significance of this influence depends on the ligand used to stabilize the MNPs.

© 2011 Elsevier Inc. All rights reserved.

1. Introduction

In the last years, much attention has been focused on the preparation and application of metal nanoparticles (MNPs) due to their unusual and unique physical and chemical properties [1,2]. The synthesis of MNPs is mainly achieved by chemical or electrochemical reduction of the corresponding precursor (metal salt or organometallic precursor) in the presence of polymers, surfactants or ligands [3].

As metal nanoparticles display much larger surface area than the bulk metals, they are promising materials for application in catalysis [4–6]. However, the widespread use of MNPs as catalysts have been hampered by some drawbacks associated with agglomeration tendency, handling and recovery. Traditionally, these problems have been partially circumvented by supporting the MNPs on solid materials such as mesoporous silica [7], inorganic oxides [8], molecular sieves [9], polymers [10], capsules [11], apatites [12] or activated carbons [13]. Among these solid supports, mesoporous carbon materials offer very interesting advantages such as availability, good mechanical and chemical properties, adequate pore size distribution, high stability and relatively low cost. Furthermore, these materials have a surface chemistry which allows modifications by chemical or thermal treatments to improve the MNPs immobilization.

The selective oxidation of alcohols to aldehydes, carboxylic acids and/or carbonyl compounds is an important reaction in the field of fine chemistry [14]. However, halogenated organic compounds are often employed as solvents, thus leading to the production of large amounts of hazardous or toxic wastes [14b,15]. Besides stoichiometric oxidants in halogenated solvents, the more economically and environmental benign molecular oxygen and air are effective agents to be used in this reaction. Therefore, the development of green, selective, and efficient catalysts for the alcohols oxidation by these agents is a subject of great interest. Thus, the reaction with molecular oxygen using homogeneous catalytic systems (Pd, Cu, Co, Ru complexes) has been extensively studied [16]. Moreover, Au, Pd, Ru, Fe and Pt NPs supported on activated carbon, poly(ethylene glycol), hydroxyapatite, alumina, silica (MCM-41, SBA-16), poly(*N*-vinyl-2-pyrrolidone), zeolite, titania, etc. have also been investigated as heterogeneous catalysts for the aerobic oxidation of alcohols [17]. Among them, those of Ru and Pd NPs with a wider range of catalytic applications have attracted the greatest attention [18].

Herein, Ru NPs and Pd NPs were firstly synthesized and subsequently supported on different mesoporous carbon materials. It should be remarked that these systems were prepared for the first time by direct impregnation of the solid support with a suspension of the MNPs previously obtained by the organometallic method

---

* Corresponding author at: CNRS, LCC (Laboratoire de Chimie de Coordination), 205, Route de Narbonne, F-31077 Toulouse, France.
E-mail address: karine.philippot@lcc-toulouse.fr (K. Philippot).

1387-1811/$ - see front matter © 2011 Elsevier Inc. All rights reserved.
doi:10.1016/j.micromeso.2011.12.023

[19,20]. Besides of mild reaction conditions as regards to temperature and pressure, this method avoids the use of chemicals such as $NaBH_4$ which are commonly employed in other reported procedures for the synthesis of NPs [21]. The catalytic activity as well as the recyclability of the carbon-supported Ru and Pd NPs in the oxidation of benzyl alcohol to benzaldehyde in water under aerobic conditions was studied. Moreover, the influence of the textural and chemical properties of the carbon materials on the catalytic activity of the supported MNPs is also discussed.

2. Experimental

2.1. Chemical reagents and solvents

(1,5-Cycloctadiene)(1,3,5-cycloctatriene)ruthenium (0) complex [Ru(COD)(COT)] from Nanomeps-Toulouse, tris(dibenzylideneacetone)dipalladium (0) complex [$Pd_2(dba)_3$] from Strem Chemicals, 4-(3-phenylpropyl)pyridine (PPP) from Acros Organics, benzyl alcohol, triphenylphosphine (TPP) and trioctylphosphine (TOP) from Sigma–Aldrich were used without any further purification. THF and pentane solvents (from SDS) were, respectively, distilled over sodium-benzophenone and dried in a purification column. Reagents and solvents were degassed before using by means of three freeze–pump–thaw cycles.

2.2. Carbon supports

Mesoporous carbon beads (MB) of particle size in the range 0.5–1.0 mm with spherical shape were used as starting support. They are commercially available phenolic resin-based activated carbon with a bi-modal pore texture [22]. MB carbon material was heated at 1500 °C for 1 h in a graphite electrical furnace, at a heating rate of 10 °C min^{-1} in Ar flow. The new material prepared was named MB-1500. Oxidation of MB was carried out by treatment with hydrogen peroxide (30 wt.%) at 50 °C during 16 h followed by washing with distilled water, thus obtaining a carbon material denoted as MB-H_2O_2.

2.3. Ru and Pd NPs synthesis

Ru nanoparticles were prepared in the presence of 4(3-phenylpropyl)pyridine (PPP) as stabilizing ligand by a previously described procedure [23]. In a typical experiment, 0.8 mmol of the Ru precursor [Ru(COD)(COT)] were dissolved in 190 ml of THF in a Fischer–Porter reactor. Pd nanoparticles were also prepared by the organometallic method [20] using triphenylphosphine (TPP) or trioctylphosphine (TOP) as stabilizing ligands. In this case, 0.084 mmol of the Pd precursor [$Pd_2(dba)_3$] were dissolved in 40 mL of THF in a Fischer–Porter. Then, the corresponding ligand (PPP, TPP or TOP in 10 ml of THF) was added to the solution in a ligand/metal molar ratio of 0.5 at −30 °C. The mixture was pressurized with 3 bar of H_2 and stirred overnight at room temperature. The Fischer–Porter was afterwards degassed and the solvent evaporated to a volume of ca. 2 ml. Ru or Pd NPs were then precipitated, washed with pentane and dried under vacuum overnight to obtain powders that were kept in a glove-box (Ar, H_2O <1 ppm) until their use.

2.4. MNPs/Carbon material catalysts preparation

The Ru and Pd NPs were dispersed in distilled THF, 14 ml or 12 ml, respectively. The suspension was divided in two equal portions and each of them was added to a Schlenk flask containing 200 mg of MB-H_2O_2 or MB-1500 carbon supports. The mixtures were stirred for 3 h at room temperature followed by a careful removal of the solvent under vacuum at room temperature. Then, the MNPs/carbon materials catalysts were dried under vacuum overnight. The catalysts were denoted by the metal, the ligand and the carbon material support such as Ru(PPP)/MB-1500 or Pd(TOP)/MB-H_2O_2.

2.5. Characterization techniques

The surface area and pore size distribution of the carbon supports were derived from the N_2 adsorption–desorption isotherms performed at −196 °C in a Micromeritics ASAP 2420 volumetric adsorption system. Prior to measurement, samples were degassed overnight by heating at 250 °C under vacuum. Specific surface areas (S_{BET}) were calculated using the Brunauer–Emmett–Tellet (BET) method, taking 16.2 nm^2 for the cross-sectional area of the nitrogen-adsorbed molecule. Total micropore volumes (VDR_{N2}) were assessed by applying the Dubinin–Radushkevich (DR) equation to the suitable adsorption data. Total pore volumes (V_t) were determined by the amount of N_2 adsorbed at $P/P_0 = 0.99$. Pore size distributions were obtained by applying the DFT (Density Functional Theory) method to the N_2 adsorption isotherms and they are given as Supplementary material (Fig. S1).

XPS surface chemical analysis of the carbon supports were carried out in a SPECS Phoibos 100 analyser using Mg Kα X-rays (1486.6 eV) at a power of 120 W and in a residual vacuum of 10^{-13} bar. Measurements were made with the analyser in fixed transmission mode and normal to the plane of the sample. Analyser pass energy of 80 eV has been used to collect broad scan spectra (0–1100 eV). The total atomic percentages of the different elements present in the ~10 nm upper layers were calculated from the survey spectra by considering the integrated areas of the main XPS peaks. The oxygen distribution in different functional groups was determined by considering the integrated areas of the C1s peaks and their sensitivity factors (see Figs. S2 and S3 in the Supplementary material data). Corel level curve fitting was performed using a Shirley background and a standard least square algorithm. Each component was fitted to a deconvolution of a Gaussian and a Lorentzian functions (80:20).

TEM images of the MNPs colloidal solutions were obtained in a JEOL 1011 microscope operating at 100 kV with a resolution point of 0.45 nm after deposition of a solution drop on a copper grid, previously covered by a holey amorphous carbon film. HR-TEM of the MNPs/carbon material catalysts was carried out with a JEOL JEM 2010 microscope working at 200 kV with a resolution point of 0.235 nm. The samples were prepared using ultramicrotomy technique. Thin slices were obtained by cutting down the middle of catalyst carbon spheres. They were deposited on carbon copper grids for the analysis. Statistical size distributions and mean sizes of both the MNPs colloidal suspensions and after being supported on the carbon materials were carried out manually by measuring ca. 300 particles on enlarged TEM micrographs.

Ru and Pd contents in the MNPs/carbon material catalysts were determined by Atomic Absorption Spectroscopy (AAS) in an AA-6300 Shimadzu spectrofotometer and by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS), respectively. All samples were dissolved in H_2O_2, HNO_3 and HCl before analyses.

2.6. Oxidation reactions

In a typical experiment, the corresponding amount of the MNPs/carbon material catalyst (10.3 mg of Ru(PPP)/MB-H_2O_2, 13.0 mg of Ru(PPP)/MB-1500, 58.0 mg of Pd(TPP)/MB-H_2O_2, 65.6 mg of Pd(TPP)/MB-1500, 31.0 mg of Pd(TOP)/MB-H_2O_2, 39.8 mg of Pd(TOP)/MB-1500) having 3 mol% of metal (metal/substrate molar ratio is 3/100) was introduced in a 10 ml Fischer–Porter bottle and it was purged with oxygen by eight times. Then, 1 ml of a solution of benzyl

Download English Version:

https://daneshyari.com/en/article/74128

Download Persian Version:

https://daneshyari.com/article/74128

Daneshyari.com