



Rhodium nanoparticles stabilized by sulfonic acid functionalized metal-organic framework for the selective hydrogenation of phenol to cyclohexanone



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ABSTRACT

Rhodium(0) nanoparticles stabilized by sulfonic acid functionalized metal-organic framework (Rh@S-MIL-101) were prepared, for the first time, by using a direct cationic exchange approach and subsequent reduction with sodium borohydride at room temperature. The characterization of the resulting Rh@S-MIL-101 material was done by using multi pronged analyses including ICP-OES, EA, P-XRD, XPS, DR-UV-vis, BFTEM, HRTEM, STEM-EDX and N₂-adsorption-desorption technique, which revealed that the formation of rhodium(0) nanoparticles (2.35 ± 0.9 nm) stabilized by the framework of S-MIL-101 by keeping the host framework intact (Rh@S-MIL-101). The catalytic performance of Rh@S-MIL-101 in terms of activity, selectivity and stability was demonstrated in the hydrogenation of phenol under mild conditions (at 50 °C and 5 bar initial H₂ pressure). We found that Rh@S-MIL-101 catalyst selectively hydrogenated phenol to cyclohexanone with high activity (initial TOF = 78 mol cyclohexanone/mol Rh × h) and selectivity (>92%) at almost complete conversion (>95%). Moreover, the resulting rhodium nanoparticles were found to be highly stable against leaching and sintering, which makes Rh@S-MIL-101 reusable heterogeneous catalyst without losing of significant activity and selectivity.

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1. Introduction

In recent years, metal nanoparticles have been broadly explored in the search of enhanced catalytic performances as compared to their bulk-counterparts metal nanoparticles have much higher surface-to-volume ratio, thus, larger fraction of catalytically active atoms exist on their surface [1,2]. Because of high surface energies and large surface areas, metal nanoparticles are considered as thermodynamically unstable against to agglomeration into bulk form and therefore protecting ligands, polymers or capping agents must be used to stabilize them in their synthesis [3]. However, the aggregation of nanoparticles ultimately to the bulk metal despite using the best stabilizing agents [4,5] is still the most important problem that should be overcome in their catalytic applications. Additionally, it is another critical issue to obtain pure active metal surfaces by avoiding surface contamination from surface protecting groups, which often leads to a decrease in catalytic activities. In this context, the use of porous solid matrices as host material for guest

metal nanoparticles immobilization allows the generation of specific surfactant-free active sites with the advantages of preventing particle aggregation [1–5].

In this context, porous materials like zeolites [6,7], carbonaceous materials [8,9], and minerals [10,11] have been widely used for fabricating metal nanoparticles within their porous matrices [12]. In addition to these porous materials, more recent studies [13–15] have also shown that metal-organic frameworks (MOFs), which are highly crystalline hybrid materials that combine metal ions with rigid organic ligands [16], can also be considered as suitable host materials to stabilize ligand-free guest metal nanoparticles. Indeed, MOFs can act as more suitable support material for metal nanoparticles with respect to other porous solids as they allow more flexible and systematic modification of the pore structure by the proper selection of the structural subunits and their connected ways [13–16]. Moreover, the stabilization of metal nanoparticles within the structure of MOFs can help us in the kinetic controlling of the catalytic reactions. The correct choosing of MOF's type under experimental conditions is the most critical step for the employment of MOFs as supports for metal nanoparticle immobilization as only a few MOFs with suitable pore structures are presently known for their thermal/chemical stability. The results of recent studies

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are showing that chromium(III) terephthalate framework; MIL-101 ($[\text{Cr}_3\text{F}(\text{H}_2\text{O})_2\text{O}\{\text{O}_2\text{CC}_6\text{H}_4(\text{CO}_2)\}_3 \cdot n\text{H}_2\text{O}]$; MIL:Materials Institut Lavosier), which was first reported in 2005 by Férey et al. [17], can be used in the stabilization of metal nanoparticles as it is stable in water even under very acidic conditions and can show thermal stability up to 300 °C under air [18]. MIL-101 has very high surface area ($\sim 4100 \text{ m}^2/\text{g}$) and contains two types of cages with diameters of 29 and 34 Å, which have pore apertures of 12 and 16 Å, respectively. These unique features of MIL-101 prompted us to focus on the use of the MIL-101 matrix in the stabilization of metal nanoparticles.

To date it has already been demonstrated that MIL-101 can act as a suitable host material for Pt [19], Pd [20–22], AuNi [23], AuPd [24], AgPd [25] and PdNi [26] nanoparticles. Xu et al. used “double-solvents” method to produce MIL-101 encapsulated Pt [19], AuNi [23], and AgPd [25] nanoparticles, which were found to be active catalysts in the hydrolysis of ammonia-borane [19,23] and one-pot cascade reactions [25]. Hermannsdörfer et al. achieved the synthesis of bimetallic PdNi nanoparticles within the cavities of MIL-101 by gas phase infiltration of $[(\text{C}_5\text{H}_5)\text{Pd}(\text{C}_3\text{H}_5)]$ and $[(\text{C}_5\text{H}_5)_2\text{Ni}]$ followed by their dihydrogen reduction. The resulting PdNi@MIL-101 material acted as active catalyst in the reduction of 3-heptanone under mild conditions [26]. El-Shall et al. developed an effective microwave-assisted chemical reduction approach to incorporating Pd nanoparticles into MIL-101, and compared their activity toward CO oxidation of embedded Pd nanoparticles with those loaded on the outer surface [22]. Hwang et al. have realized more effective Pd encapsulation into MIL-101 by pre-grafting ethylenediamine (ED) on its coordinatively unsaturated Cr(III) centers. After treatment of the surface amine groups with an aqueous HCl solution, the positively charged ammonium groups undergo ionic reactions with anionic $[\text{PdCl}_4]^{2-}$ salt by anionic exchange of the chloride anions and are finally reduced by sodium borohydride [20]. This methodology yields well-dispersed Pd nanoparticles stabilized by MIL-101 and they can act as active catalyst in the Heck type coupling reactions. Of particular importance, Zhu et al. have recently reported that the preparation of sulfonic acid functionalized MIL-101 by the post-modification of the organic linkers under mild conditions [27]. The resulting sulfonic acid functionalized MIL-101 was found to be an efficient catalytic material that provides high conversions and activities in the esterification of monocarboxylic acids with monohydric alcohols. This study encouraged us to prepare MIL-101 confined metal nanoparticles in a new synthesis protocol that comprises of the neutralization of sulfonic acid with NaOH, then the ion-exchange between Na^+ cations and M^{n+} cations followed by their borohydride reduction within the cages of MIL-101 under mild conditions.

Along this line, herein, we report the preparation and characterization of rhodium(0) nanoparticles stabilized by sulfonic acid functionalized MIL-101, hereafter referred to as Rh@S-MIL-101. As previously mentioned Rh@S-MIL-101 catalyst was reproducibly prepared by using a direct cationic exchange approach and subsequent reduction with sodium borohydride and characterized by inductively coupled plasma optical emission spectroscopy (ICP-OES), elemental analysis (EA), powder X-ray diffraction (P-XRD), X-ray photoelectron spectroscopy (XPS), diffuse reflectance UV–visible spectroscopy (DR-UV-VIS), bright-field transmission electron microscopy (BFTEM), scanning transmission electron microscope–energy dispersive X-ray spectroscopy (STEM-EDX), high resolution-TEM (HRTEM) and N_2 -adsorption–desorption technique. The catalytic performance of these new rhodium(0) nanoparticles in terms of activity, selectivity and reusability was demonstrated in the aqueous phase phenol hydrogenation under mild reaction conditions.

2. Experimental

2.1. Materials

Chromium(III) nitrate nonahydrate ($\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$), terephthalic acid ($\text{C}_8\text{H}_6\text{O}_4$), dimethylformamide ($\text{HCON}(\text{CH}_3)_2$), methanol (CH_3OH), acetone (CH_3COCH_3), trifluoromethanesulfonic acid ($\text{CF}_3\text{SO}_3\text{H}$), sulfuric acid (H_2SO_4), sodium borohydride (NaBH_4), rhodium(III) chloride trihydrate ($\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$), nitromethane (CH_3NO_2), phenol ($\text{C}_6\text{H}_5\text{OH}$), cyclohexanone ($\text{C}_6\text{H}_{10}\text{O}$), cyclohexanol ($\text{C}_6\text{H}_{11}\text{OH}$), ethanol ($\text{C}_2\text{H}_5\text{OH}$), dichloromethane (CH_2Cl_2), tetrahydrofuran ($\text{C}_4\text{H}_8\text{O}$), activated carbon (C), titanium(IV) oxide (TiO_2), nano-aluminum oxide (Al_2O_3) and silica (SiO_2) were purchased from Sigma-Aldrich. Deionized water was distilled by water purification system (Milli-Q Water Purification System). All glassware and Teflon coated magnetic stir bars were cleaned with acetone, followed by copious rinsing with distilled water before drying in an oven at 150 °C.

2.2. Characterization

The amount of rhodium loaded on S-MIL-101 and leached into the solution was determined by inductively couple plasma optical emission spectroscopy (ICP-OES) by using Perkin Elmer DRC II model (detection limit is 16 ppb for Rh). Elemental analyses were performed on LECO, CHNS-932 model. The powder X-ray diffraction (P-XRD) analyses were carried out on Rigaku Ultima-IV by using $\text{Cu-K}\alpha$ radiation (wavelength 1.54 Å, 40 kV, 55 mA). BFTEM and HRTEM samples were prepared by dropping one drop of dilute suspension on copper coated carbon TEM grid and the solvent was then dried. BFTEM was carried out on a JEOL JEM-200CX transmission electron microscopes operating at 120 kV. HRTEM analyses were run on a JEOL JEM-2010F transmission electron microscope operating at 200 kV. The XPS analyses were performed on a Physical Electronics 5800 spectrometer equipped with a hemispherical analyzer and using monochromatic Al-K α radiation (1486.6 eV, the X-ray tube working at 15 kV and 350 W, and pass energy of 23.5 eV). DR-UV–vis analyses were performed on Shimadzu UV-3600 modulated with integrating sphere attachment. The nitrogen adsorption–desorption experiment was carried out at 77 K using a NOVA3000 series instrument (Quantachrome Instruments). The sample was out-gassed under vacuum at 473 K for 3 h before the adsorption of nitrogen. The percent of exposed surface Rh atoms were obtained as 28, 38, 42, 34, 30 and 32% of the total Rh atoms for Rh@S-MIL-101, Rh@MIL-101, Rh@C, Rh@SiO₂, Rh@TiO₂ and Rh@Al₂O₃ catalysts by CO chemisorption performed by Micromeritics 2010C instrument with the usual 1/1 (CO/Rh) stoichiometry [28].

2.3. Synthesis and purification of MIL-101

MIL-101 was synthesized by following the slightly modified procedure given in the literature [29]. In a typical synthesis, $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (2.0 g, 5 mmol), terephthalic acid (0.83 g, 5 mmol) and deionized water (20.0 mL) were mixed and homogenized by sonication at room temperature. Then, dark blue-colored suspension was placed in a Teflon-lined autoclave bomb and kept in oven at 220 °C. After the synthesis MIL-101 solids were separated from water using a centrifuge (5000 rpm, 10 min) and washed with water, methanol and acetone. The final suspension in acetone was centrifuged and separated solid was placed in DMF (20.0 mL) and the suspension was sonicated for 10 min and kept at 70 °C for 12 h. The resulting solid powder was separated by centrifugation repeatedly washed with methanol and acetone, activated by drying at 150 °C for 12 h under vacuum (10^{-3} Torr). The yield of dried MIL-

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