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Short Communication

Covalently anchored ruthenium–phosphine complex on mesoporous organosilica: Catalytic applications in hydrogenation reactions

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ABSTRACT

New heterogeneous catalysts for alkene hydrogenation reactions were prepared by the immobilization of trimethoxysilane functionalized triphenylphosphine η^6-*p*-cymene ruthenium complex on mesoporous organosilica (*PMO-Ru*). Characterization techniques confirmed the structural integrity of the organosilica material and proved the successful anchoring of ruthenium complex. Catalytic activity and stability of *PMO-Ru* sample investigated in the hydrogenation of various olefins showed higher activity than a neat and MCM-41 supported ruthenium catalyst. High catalytic activity and stability of organosilica supported ruthenium catalyst are attributed to the hydrophobic environments and to the unique structural features imparted from the presence of organic groups in the framewall positions.

1. Introduction

Liquid-phase hydrogenation of olefins using heterogeneous catalysts is an industrially relevant process [1–3]. Various homogenous complexes were widely used for this transformation; however, separation and recycling of the rather expensive catalyst impart difficulties. Heterogenization of such homogenous catalysts on solid supports can mitigate these problems and attracted much attention on mesoporous solids due to the periodicity in the pore arrangement as well as due to the high surface area and pore sizes [4–6]. For instance, ruthenium complexes bearing ligands such as triphenylphosphine (tpp), [tris(3-sulfonatophenyl)phosphane sodium salt)] (tppms), and (η^2-C_2H_4)$_2$ have been immobilized on various supports [7–9]. Among them, triphenyl phosphine is widely used as a ligand in olefin hydro-genation reactions, because it is a cheap phosphine donor ligand, nucleophilic and has tendency to bind well to most transition metals, especially the middle and late transition metals [10,11]. In a detailed study, Caballero et al. reported the high stability and recyclability of heterogenized ruthenium–phosphine complex on $AlPO_4$ [12]. Zsigmond et al. reported the heterogenization of [{$RuCl_2$(tppms)$_2$}$_2$] and [$RuCl_2(PPh_3)_3$] catalysts, using heteropoly acid (phosphotungstic acid) as an anchoring medium, for the hydrogenation of trans-cinnamaldehyde and crotonaldehyde. These heterogenized catalysts showed comparable activity with their neat counterparts while the selectivity to the hydrogenated product was twofold higher than the corresponding homogeneous counterpart [13]. Recently, some of us have reported the catalytic activity of triphenylphosphine rhodium complex supported on mesoporous SBA-15 for olefin hydrogenation [14,15]. This supported rhodium complex showed high activity and selectivity and is more active than its homogeneous congener under mild reaction conditions. However, the resulting hybrid catalyst takes long reaction time to attain high conversions.

In this context, periodic mesoporous organosilicas (PMOs) represent an exciting class of organic–inorganic hybrid mesoporous material integrating organic groups in the frame wall positions as molecularly bridging ligands. Some important advantages of these mesoporous materials compared to periodic mesoporous silicas are (a) organic moieties are homogeneously dispersed inside the channel walls, (b) these organic parts in the channel walls do not block the pores and (c) the organic precursors can be easily varied to produce a wide range of materials [16–18]. Recent systematic studies also depict a substantial decrease in activity and selectivity of the immobilized catalyst over M41S supports due to their low hydrophobicity and hydrothermal stability [19]. These results showed the significant impact of hydrophobic mesoporous support materials in various catalytic reactions and in general, if the support is hydrophobic and the anchoring is covalent, it can be robust enough to withstand even the harsh conditions of the catalytic reactions. Thus the rational design of various hydrophobic mesoporous materials is relevant for the heterogenization of homogenous catalysts [20,21].

In the present work, we describe the successful synthesis of a novel ruthenium complex having triphenyl phosphine (tpp) as ligand, *p*-cymene as a supporting ligand, covalently immobilized on an ethane-bridged mesoporous organosilica (PMO-Ru). All these heterogenized

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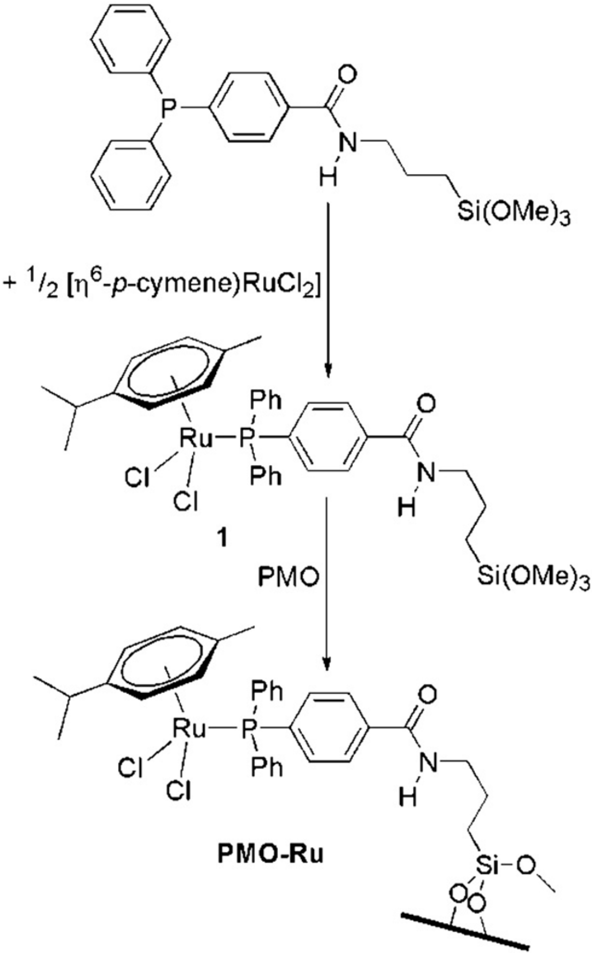
materials were characterized in detail by powder XRD, N_2 adsorption–desorption, FT-IR, XPS, solid-state ^{29}Si, ^{13}C, and ^{31}P MAS NMR spectroscopy and TEM analysis. Catalytic activity and stability of the material were evaluated in the hydrogenation of various olefins and the rates were compared to the corresponding homogeneous catalyst and MCM-41 supported ruthenium complex. Recycling of the heterogenized catalysts and, in particular, the extent of Ru leaching under reaction conditions were also discussed.

2. Experimental

All the solvents, procured from SD Fine Chemicals, India, were of AR grade and were distilled and dried before use. 3-Trimethoxysilylpropyl amine, 4-diphenylphosphinylbenzenecarboxylicacid methyl ester [15], octadecyl trimethylammoniumbromide (C18-TMABr), 1,2-bis(triethoxysilyl)ethane (BTEE), styrene, α-methyl styrene, $[(\eta^6\text{-}p\text{-cymene})\,RuCl_2]_2$, and NaOMe were obtained from Aldrich.

Synthesis of the ruthenium(II) complex **1**: a solution of 0.24 g (0.52 mmol) of 4-diphenylphosphinylbenzenecarboxylicacid-4N-(3-trimethoxysilypropyl)amide in 5 mL of CH_2Cl_2 was added dropwise to a solution of 0.16 g (0.26 mmol) of $[(\eta^6\text{-}p\text{-cymene})RuCl_2]_2$ in 5 mL CH_2Cl_2. After the mixture was stirred at room temperature for 2 h, the solvent was removed in vacuum. The residue was washed with diethylether and dried in vacuum to give the dark red product. Yield: 90%. Anal. calcd. for $C_{35}H_{44}NCl_2O_4PRuSi$ (773.77) C, 54.33; H, 5.73; N, 1.81; found (%) C, 53.90; H, 5.61; N, 1.81.

Anchoring of **1** over the PMO support (Scheme 1): in a typical synthesis, 2.5 g of the PMO [16] was dispersed in 30 mL of toluene containing 0.3 g of **1**. After stirring the mixture at reflux temperature for 6 h under an atmosphere of nitrogen, the resulting solid was isolated by filtration and washed thoroughly with toluene, in successive steps. It was further extracted with toluene in a Soxhlet extractor for 24 h. The obtained organic–inorganic hybrid material is denoted as *PMO-Ru* and contains 0.115 mmol/g of ruthenium by ICP-OES analysis.



Scheme 1. Synthesis of *PMO-Ru*.

Anchoring of **1** over MCM-41: *MCM-41-Ru* was synthesized by the same procedure described above for PMO-Ru. In this case, MCM-41 was used as a support instead of PMO. MCM-41-Ru contains 0.10 mmol/g of ruthenium by ICP-OES analysis.

Elemental analysis (C, H and N) was performed on a Carlo Erba (Model EA 1108) elemental analyzer. The ruthenium content in the material was determined by inductively coupled plasma-optical emission spectrometer (ICP-OES) on a Thermo IRIS Intrepid II XSP after solubilization of the samples in HF/HCl solutions. Powder X-ray diffraction (XRD) patterns were measured on a Philips D MAX III VC diffraction system using Ni-filtered CuKα radiation over the range 0.5–5° 2θ, with a scan speed of 1° per min. Nitrogen adsorption–desorption isotherms were measured in a Quantachrome NOVA 1200, surface area analyzer. Before analysis the samples were degassed in vacuum at 120 °C for 24 h. Magic angle spinning (MAS) NMR spectra for ^{29}Si, ^{13}C nuclei were recorded on BRUKER DSX300 spectrometer at 7.05 T (resonance frequencies 59.63 MHz, rotor speed 4000 Hz, number of scans 5275, external reference $Si(OCH_3)_4$ and 78.19 MHz, rotor speed 6000 Hz, number of scans 2800). The ^{31}P MAS NMR spectra were recorded using a Bruker DSX-300 spectrometer at 121.5 MHz with high power decoupling with a Bruker 4 mm probe head. The spinning rate was 10 kHz and the delay between two pulses was varied between 1 and 30 s to ensure the complete relaxation of the ^{31}P nuclei occurred. The chemical shifts are given relative to external 85% H_3PO_4. XPS measurements were performed on a VG Microtech ESCA 3000 instrument, using non-monochromatized MgKα radiation at a pass energy of 50 eV and an electron takeoff angle of 60°. The correction of binding energy was performed by using the C1s peak of carbon at 287 eV, as reference. Scanning electron microscopy (SEM) images were recorded on a Leica Stereoscan 440 instrument, while transmission electron micrographs (TEM) were obtained on a JEOL JEM 1200 EX instrument.

In a typical liquid-phase hydrogenation reaction, 1.0 g of olefin, 50 mL of methanol or 50 mL of toluene, and 0.025 g of the catalyst were placed in a 100 mL Parr autoclave (Parr Inst. Co., Mod. 3911), pressurized with hydrogen (150 psi) and stirred at room temperature for a specific time. Samples were periodically withdrawn from the reaction mixture, filtered off, and analyzed. Olefin conversion and selectivity were determined by using gas chromatography (HP 6890) equipped with a flame ionization detector (FID) and a capillary column (5 μm cross-linked methyl silicone gum, 0.2 mm × 50 m). Before GC analysis, the samples were centrifuged for 5 min at 4000 rpm. Gas chromatography in combination with mass spectrometry (GC–MS; Varian CP-3800 GC coupled to a Varian Saturn-2200 MS) was used to identify the reaction products.

3. Results and discussion

Powder X-ray diffraction patterns of PMO, MCM-41, *PMO-Ru* and *MCM-41-Ru* are shown in Fig. 1. Pristine PMO and MCM-41 samples exhibit a high intense (100) reflection along with (110) and (200) diffraction peaks, characteristic of mesoporous materials having long range periodic pore arrangements. After immobilization of the ruthenium(II) complex **1**, the two dimensional hexagonal pore structures are preserved, however an intensity loss of the characteristic peaks is observed due to partial filling of the void space by the anchored metal complexes. The N_2 adsorption–desorption isotherm and pore size distribution of PMO and *PMO-Ru* shown in Fig. 2 supported this conclusion. PMO and *PMO-Ru* exhibited type IV isotherms with a hysteresis typical for the characteristic capillary condensation, indicating the uniformity in mesopore-size distribution [21]. The BET surface area, the total pore volume, and the BJH pore size of all