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Hydroformylation of 1-octene in Pickering emulsion constructed by amphiphilic mesoporous silica nanoparticles

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ABSTRACT

An efficient and stable oil/water Pickering emulsion system was constructed for hydroformylation of 1-octene with surface modified mesoporous silica nanospheres as stabilizer and Rh-TPPTS as catalyst. Compared to the neat water–oil biphasic system, the Pickering emulsion system exhibits much higher activity (TOF: 392 h^{-1} versus 56 h^{-1}) and aldehyde selectivity (79.0% versus 45.7%) in hydroformylation of 1-octene under non-stirring conditions due to the greatly increased interface area. It was found that dimethyloctadecylammonium group is more efficient than octadecyl group for emulsion catalytic system, which is mainly attributed to its enrichment effect for anionic Rh-TPPTS on the interface of two phases. The higher activity and aldehyde selectivity were obtained with mesoporous silica as stabilizer than with nonporous silica, which is attributed to the enhanced diffusion rate of the reactants by the mesopore and uniform distribution of Rh-TPPTS in the mesopore. The Pickering emulsion system could be easily recycled without obvious loss of activity and aldehyde selectivity.

1. Introduction

The hydroformylation of olefins represents one of the largest homogeneously catalyzed reactions in industry. This is an atom-economical and clean process, which has been applied for the production of aldehydes, important raw materials for alcohols, esters, and amines. Though various catalysts for olefin hydroformylation have been developed, rhodium complexes are still among the most efficient catalysts under mild conditions [1–6]. However, the application of homogeneous catalytic system confronts problems of high cost of noble metals and the difficulty in separation of thermally sensitive rhodium complexes from the low volatilized products [6]. Therefore, the development of heterogeneous catalytic system for hydroformylation with advantages of easy separation and reuse of expensive metal catalysts became an active area of academic and industrial research [7–10].

The two-phase catalytic systems constitute a well established method for heterogeneous catalysis by dissolving catalysts and reactants in different phases [3,11–19]. The aqueous two-phase Ruhrchemie/Rhone-Poulenc (RCH/RP) process with water-soluble Rh-tris(m-sulfonatophenyl) phosphine (Rh-TPPTS) complexes as catalysts has been successfully employed in industry for the hydroformylation of C3–C4 olefins [15–18]. Unfortunately, it is difficult to apply this catalytic process for the hydroformylation of long-chain olefins due to the low reaction rates because of phase-transfer limitations caused by low substrate solubility in water. Therefore extensive efforts have been devoted either to develop novel ligands or to improve the miscibility and solubility of reactants, mainly by using amphiphilic ligands, co-solvents, surfactants, co-ligands and cyclodextrins [3]. Although the above strategies indeed are able to improve the catalytic efficiency, the extra additives and the amphiphilic ligands often cause the difficulty in separating and purifying of the final products and the extra organic synthesis operations. Davis et al. reported the hydroformylation of long-chain olefins by supported aqueous-phase catalysts (SAPCs) formed by subtly adsorbing a thin aqueous layer containing a water-soluble catalyst onto a hydrophilic solid with a large surface area [20]. Due to increasing the interfacial area between aqueous and organic phase, the hydroformylation rate of long-chain olefins could be efficiently increased. However, the SAPCs are often too sensitive to the content of water in substrates, and therefore its stability in long-term operation is not satisfactory [3].

Pickering emulsion is surfactant-free dispersions of two immiscible fluids that are kinetically stabilized by amphiphilic nanoparticles adsorbing onto the biphasic interface, which exhibits promising application in the field of materials fabrication, drug delivery and so on due to its excellent properties including the

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reduction of foaming problem, easy recovery, environment-friendly and low cost [21–23]. Recently, it has also been used as an attractive platform for designing biphasic catalytic systems [24,25]. Resasco et al. reported biphasic hydrodeoxygenation and condensation of 5-methylfurfural and acetone in water/oil biphase systems using carbon nanotube-inorganic oxide supported palladium as both catalyst and stabilizer [26]. Qu et al. utilized individually encapsulated bacteria cells as robust Pickering interfacial biocatalysts to successfully realize whole-cell-based long-term and resistance-minimized biphase biocatalysis [27]. Yang and coworkers constructed an emulsion catalytic system able to separately compartmentalize incompatible or opposing reagents to avoid mutual destruction, which was successfully applied to several cascade reactions [28].

Despite the above developments, the application of Pickering emulsions in two-phase catalytic hydroformylation of olefins is rare. Hapiot et al. developed Pickering emulsion catalytic system for hydroformylation of long-chain olefins with supramolecular hydrogels as stabilizer and Rh-TPPTS as catalyst [29–31]. They observed an obvious enhancement in catalytic activity comparing to neat biphase conditions. However, large amounts of solid particles strongly adsorbed at the interface could inhibit mass transfer between the two phases. Compared with supramolecular hydrogels, mesoporous silica nanospheres have the following advantages: (1) the particle size and porous structure could be finely adjusted; (2) the mesopore allows the fast diffusion of reactants and products through the interfaces; and (3) the mesoporous silica is safe, environmentally friendly and more mechanically and thermally stable [32]. Thus, the Pickering emulsion system stabilized by mesoporous silica nanospheres could be more practical.

Herein, we report the construction of Pickering emulsion system for catalytic hydroformylation of 1-octene with octadecyl- or dimethyloctadecylammonium chloride- modified MCM-41 silica nanospheres (particle size: ~100 nm) as stabilizer and water soluble Rh-TPPTS as catalyst. Moreover, the influence of the porous structure on the catalytic performance of the emulsion system was investigated using nonporous silica as a control sample.

2. Experimental

2.1. Chemicals and reagents

All chemicals were used as received unless otherwise stated. Tetraethylorthosilicate (TEOS, AR) and CTAB (hexadecyltrimethylammonium bromide) were purchased from Shanghai Chemical Reagent Company of the Chinese Medicine Group. Metal precursor $Rh(acac)(CO)_2$ (acac = acetylacetonato) was purchased from Energy Chemical Company. Tris(3-sulfophenyl)phosphine trisodium salt (TPPTS) was purchased from J&K Chemicals. Dimethyloctadecyl[3-(trimethoxysilyl)propyl]ammonium chloride (C18N) 60% in MeOH and octadecyl trimethoxysilane (C18) was purchased from Acros Company. 1-Octene, decane and *n*-dodecane were purchased from Aladdin-reagent Company. Toluene and Et_3N were distilled from sodium under argon atmosphere. MCM-41 and non-porous SiO_2 nanospheres with diameter of ~100 nm were synthesized according to the reported method [33,34].

2.2. Preparation of organo-modified silica nanoparticles

After vacuum degassing at 120 °C for 3 h, MCM-41 or SiO_2 nanoparticles (1 g) was added to a schlenk flask charged with 30 ml of toluene and 1.2 ml of Et_3N under Ar atmosphere. Then, desired amount of dimethyloctadecyl[3-(trimethoxysilyl)propyl]ammonium chloride (C18N) and octadecyl trimethoxysilane (C18) was added and the resulting mixture was refluxed at 110 °C for 12 h. After cooling down to room temperature, the solid materials were filtrated, thoroughly washed with methanol and dried under vacuum at room temperature. The materials synthesized with MCM-41 and non-porous silica were denoted as MCM-X-*n* and SiO_2-X-*n*, where X refers to the type of organosilane precursor and n refers to the mmol of organosilane precursor used for 1.0 g of silica material during the grafting process. For example, MCM-C18N-1.8 represents the material synthesized with 1.0 g of MCM-41 nanosphere and 1.8 mmol of C18N.

2.3. Characterization

Thermogravimetric analysis (TGA) was performed under an air atmosphere with a heating rate of 5 °C/min by using a NETZSCH STA-449F3 thermogravimetric analyzer. Nitrogen physical adsorption measurement was carried out on micromeritics ASAP2020 volumetric adsorption analyzer. Before the measurements, the samples were degassed at 393 K for 5 h. The BET surface area was evaluated from the data in the relative pressure range P/P_0 of 0.05 to 0.25. The total pore volume was estimated from the amount adsorbed at the P/P_0 value of 0.99. The pore diameter was determined from the adsorption branch by the BJH method. Transmission electron microscopy (TEM) was performed using an FEI Tecnai G2 Spirit at an acceleration voltage of 120 kV. UV–Vis spectra were recorded on a SHIMADZU UV–Vis 2550 spectrophotometer. The content of rhodium in organic phase was determined by ICP-MS analysis. FT-IR spectra were collected with a Nicolet Nexus 470 IR spectrometer with KBr pellet.

2.4. Catalytic reactions

The rhodium precursor $Rh(acac)(CO)_2$ (6.0 mg) and a certain amount of TPPTS were dissolved in 1.0 ml of degassed H_2O for the preparation of a catalyst solution stock with P/Rh ratio of 5, 15 and 25. The surface modified MCM-41 or non-porous silica nanospheres (20 mg) and degassed water (2.5 ml) containing Rh-TPPTS catalyst (Rh: 7.5×10^{-4} mmol) were added to a vial (5 ml) and the mixture was ultrasonicated at room temperature for 1 min to ensure proper wetting of the silica nanospheres. Later on, 0.5 ml of decane solution containing desired amount of 1-octene and dodecane (internal standard) was added to the above mixture. After ultrasonication for 2 min at room temperature, a stable Pickering emulsion was formed. The vial was then placed in an autoclave (100 ml). After being purged three times with CO/H_2 (1/1, mol ratio), the CO/H_2 atmosphere was elevated to 40 bar. The autoclave was heated with an oil bath at 80 °C. After reaction, CO/H_2 pressure was released and the Pickering emulsion was centrifuged for demulsification. The oil phase was extracted by hexane (5 × 3 ml). The conversion and aldehyde selectivity were analyzed by gas chromatography using a HP-5 capillary column (30 m × 0.32 mm × 0.25 mm).

For the catalyst recycling, the water phase containing catalyst obtained after centrifugation and washing with hexane for 3 times was used directly for the next catalytic reaction.

3. Results and discussion

3.1. Synthesis and characterization

Silica nanospheres have been widely employed as stabilizer in Pickering emulsion due to its high stability and easy surface-modification. However, the influence of the meso-structure of silica on the catalytic performance of Pickering emulsion has rarely been reported. In this work, we chose mesoporous MCM-41 nanospheres with a diameter of ~100 nm for constructing Pickering