



Fluorescence-marked mesoporous silica core–shell nanocatalyst for asymmetric transfer hydrogenation



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ARTICLE INFO

Article history:

Received 26 August 2015
Received in revised form 12 October 2015
Accepted 17 October 2015
Available online 20 October 2015

Keywords:

Fluorescence
Heterogeneous catalyst
Mesoporous silica
Asymmetric transfer hydrogenation

ABSTRACT

Fluorescence-marked core–shell structured nanocatalyst was prepared through co-condensation method. The catalyst exhibits good catalytic efficiency for asymmetric transfer hydrogenation of aromatic ketones and can be recovered and reused several times. The strong fluorescent emission easily tracks the recovery process of the nanocatalyst.

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1. Introduction

Fluorescence, a form of luminescence, is the emission of light by a fluorophore or substance in excited state that is excited by light or other radiation. The fluorescence is very sensitive, which indicates that strong fluorescence would be observed even in the presence of rare fluorophore. Most fluorescent emissions by fluorophores are in the visible region and the fluorescence spectrum is easily measured. Therefore, fluorescent method has attracted much interest and many successful examples in this area, such as fluorescent labelling [1,2], chemical sensors [3–8], and fluorescent lamps [9,10] have been developed.

The increasing demand of optically pure molecules for construction of high value fine chemicals including pharmaceuticals and pesticides has greatly promoted the development of asymmetric catalysis, which has gotten significant achievements in past decades [11–19]. A great amount of asymmetric catalysts are very expensive because of their complicated synthetic processes and the high cost of precious metal [20,21]. These catalysts would also be harmful for environment and pollute the products which may need high purity. Therefore, the recovery and reuse of chiral catalysts, precious metal-based catalysts especially, are significant for the

development of asymmetric catalysis. Supported chiral catalysts have attracted much attention nowadays [22–25]. Since mesoporous silica supports possess large specific surface area and pore volume, tunable pore dimension, well-defined pore arrangement, as well as high thermal and mechanical stability, mesoporous silica-based heterogeneous asymmetric catalysts have led to significant achievements [21,26,27]. Recently, many outstanding mesoporous silica supported chiral catalysts have been developed and they present excellent catalytic efficiency in various asymmetric organic transformation and most of them are easily recovered and reused [28–31]. However, a sensitive and simple method for marking the recovery process of heterogeneous chiral catalysts has not been established so far.

Core–shell structured mesoporous silica spheres possess distinct advantages in several applications, asymmetric catalyst especially, in which the core and shell of silica spheres could be functionalized with different functional molecules, respectively. Several works also demonstrated that the fluorescent nanomaterials showed much higher photostability than traditional organic fluorophores [32,33]. Hence, fluorescence is potential admirable marking for indicating the recovery of the supported chiral catalysts. Herein, we develop a core–shell structured heterogeneous ruthenium catalyst with fluorescence marking for asymmetric transfer hydrogenation of aromatic ketones in aqueous medium. The catalyst exhibits good catalytic efficiency and high fluorescence for self-marked recovery.

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2. Experimental

2.1. Chemicals and instruments

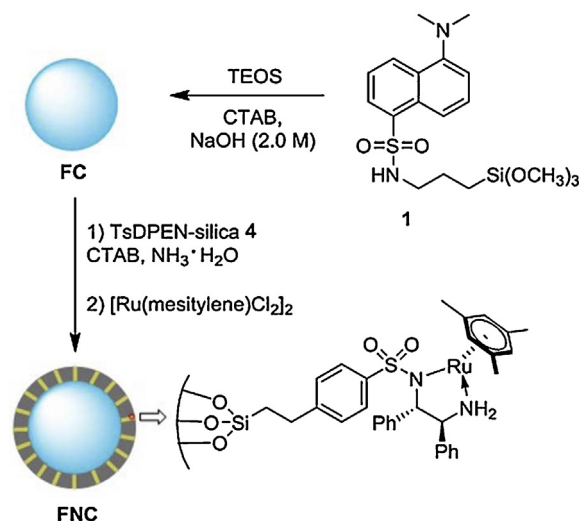
Tetraethoxysilane (TEOS), 3-aminopropyltrimethoxysilane, dansyl chloride, 4-(methylphenylsulfonyl)-1,2-diphenylethylenediamine [(*S,S*)-TsDPEN], the surfactant cetyltrimethylammonium bromide (CTAB), 2-(4-chlorosulfonylphenyl)ethyltrimethoxysilane, and [(mesitylene)RuCl₂]₂ were purchased from Sigma–Aldrich Company Ltd. Compound dansylamide silica source (1) [34] and (*S,S*)-4-((trimethoxysilyl)ethyl)phenylsulfonyl-1,2-diphenylethylenediamine (4) [35] were prepared according to the reported methods. Ru loading amounts in the catalyst were analyzed using an inductively coupled plasma optical emission spectrometer (ICP, Varian VISTA-MPX). Scanning electron microscopy (SEM) images were obtained using a JEOL JSM-6380LV microscope operating at 20 kV. Transmission electron microscopy (TEM) images were performed on a JEOL JEM2010 electron microscope at an acceleration voltage of 220 kV. Nitrogen adsorption isotherms were measured at 77 K with a Quantachrome Nova 4000 analyzer. The samples were measured after being outgassed at 423 K overnight. Pore size distributions were calculated by using the BJH model. The specific surface areas (SBET) of samples were determined from the linear parts of BET plots ($p/p_0 = 0.05–1.00$). Thermal gravimetric analysis (TGA) was performed with a Perkin-Elmer Pyris Diamond TG analyzer under air atmosphere with a heating ramp of 5 K/min.

2.2. Preparation of catalyst FNC

To a solution of the structure-directing agent cetyltrimethylammonium bromide (CTAB, 0.10 g) and NaOH (350 μ L, 2.0 M) in the deionized water (45 mL), TEOS (460 μ L) and 1 (0.4 mmol) were added dropwise, respectively. The mixture was stirred mechanically at 80 °C for 2 h to give the FC. After cooling down to 38 °C, deionized water (80 mL), ethanol (51 mL), CTAB (0.3 g), and ammonium hydroxide (1 mL, 25 wt%) were added into the flask, which was stirred for another 0.5 h. Then, 1,2-bis(triethoxysilyl)ethane (260 μ L, 0.7 mmol) was then slowly added, in which the mechanical stirring speed is 520 r/min for 15 min. After that, TsDPEN-silica (0.8 mmol) was slowly added. The mixture was stirred mechanically (430 r/min) at 40 °C for another 1.5 h. After cooling down to the room temperature, the white solids were collected by filter. The surfactant template was removed by refluxing in ethanol (120 mL per gram) with ammonium nitrate (80 mg per gram) for 24 h. The solids was separated by filter and washed with excess water and ethanol several times. The collected TsDPEN-functionalized solids were used in next step. In this step, to a stirred suspension of above collected TsDPEN-functionalized solids (0.50 g) in 20 mL dry CH₂Cl₂ was added [(mesitylene)RuCl₂]₂ (47.0 mg, 0.08 mmol) at room temperature. The resulting mixture was stirred at room temperature for 12.0 h. The mixture was then separated by filter. After Soxhlet extraction in CH₂Cl₂ solvent to remove the starting materials for 24.0 h, the solid was dried at 60 °C *in vacuum* overnight to afford the catalyst FNC as a light yellow powder. ICP analysis shows that the Ru loading-amount is 2.108 mg (20.8 μ mol) per gram catalyst.

2.3. General procedure for asymmetric transfer hydrogenation

Catalyst FNC (24.0 mg, 0.5 μ mol of Ru based on ICP analysis), HCO₂Na (136 mg, 2 mmol), ketone (0.2 mmol) and 2.0 mL mixed solvents (H₂O/*i*-PrOH $v/v = 1/3$) were added in a 10 mL round-bottom flask in turn. The mixture was allowed to react at 40 °C for 2–10 h. During that time, the reaction was monitored constantly by TLC. After completion of the reaction, the catalyst was separated by centrifuge and collected for the recycle experiment. The



Scheme 1. Preparation of fluorescence-marked core-shell structured nanocatalyst FNC.

aqueous solution was extracted by Et₂O (3 × 3.0 mL). The combined Et₂O was washed with brine twice and dehydrated with Na₂SO₄. After the evaporation of Et₂O, the residue was purified by silica gel flash column chromatography to afford the desired product. The conversion was determined through above method and the enantiomeric excess was determined by a Daicel AD-H or OJ-H chiralcel columns ($\Phi 0.46$ cm × 25 cm).

3. Results and discussion

3.1. Synthesis and structural characterization of the catalyst FNC

The bifunctional core-shell structured mesoporous silica spheres with (*S,S*)-TsDPENRu(mesitylene) (TsDPEN = 4-methylphenylsulfonyl-1,2-diphenylethylenediamine) were prepared by similar previously reported method [35] as outline in Scheme 1. The fluorescent core (FC) was obtained by co-condensation of dansylamide silica source 1 and tetraethoxysilane (TEOS). Then 1,2-bis(triethoxysilyl)ethane and chiral TsDPEN silica source were added in the suspension, and the external shell was formed by continuous growth in the presence of CTAB (hexadecyltrimethylammonium bromide) and ammonium hydroxide, which led to high nucleation and the slow growth of the generated seeds resulting functional mesoporous silica shell. Finally, the fluorescence-marked nanocatalyst (FNC) was successfully prepared through direct complexation with [(mesitylene)RuCl₂]₂ followed by the trimming of the nanopore using Soxhlet extraction.

The ¹³C CP/MAS NMR spectrum (Fig. 1) of the support exhibited the signals at $\delta = 6.0, 29.2, 61.6,$ and 127.9 ppm indicating that dansylamide and TsDPEN were immobilized on the support. Whilst catalyst FNC produced carbon signals at $\delta = 20.6$ and 102.2 ppm are corresponding to the carbon atoms of arene group and the CH₃ groups attached to the arene group [36], demonstrating that catalyst FNC was successfully prepared. As shown in Fig. 2, the nitrogen adsorption/desorption isotherms display a typical type IV isotherm, which reveals that the catalyst FNC was mesoporous. The pore size is about 4 nm calculated using the BJH method. The SEM image (Fig. 3a) indicates clearly that FNC possesses very uniform size about an average diameter of around 200 nm. The core-shell structure is obviously observed according to the TEM image (Fig. 3b), in which chiral catalyst functionalized silica shell is about 35 nm in thickness. The Ru loading was measured by inductively coupled

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