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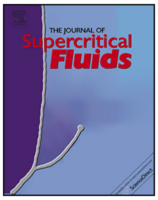

Mesoporous spherical silica encapsulating Pd nanoparticles prepared by CO_2-induced mircoemulsion and catalytic application in Suzuki coupling reaction

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ABSTRACT

The CO_2-in-water (C/W) microemulsion was formed when the pressure of CO_2 was above 4.0 MPa and has been investigated in-situ via high-pressure UV/vis spectra. The spherical mesoporous silica was successfully synthesized in CO_2-induced microemulsion. Uniform spherical silica with a diameter of 102 ± 15 nm can be obtained by using C/W microemulsion as a template. It was observed that the BET area and pore volume of the spherical silica were enlarged with increasing the pressure of CO_2. Moreover, Pd nanoparticles (Pd NPs) were encapsulated inside the spherical mesoporous silica through one-pot approach. Owing to the particular core–shell structure, this catalyst showed excellent recyclability in the Suzuki coupling reaction when compared with conventional Pd/SiO_2 and Pd/C catalysts. The new strategy can be extended as a general approach to prepare other metal nanoparticles encapsulated in spherical mesoporous silica.

1. Introduction

Supercritical carbon dioxide ($ScCO_2$) or compressed CO_2 has been utilized not only in the separation, extraction, chemical reaction, but also in the preparation of organic and inorganic materials [1–5]. Among these materials, mesoporous silica shows high BET area, particular pore structure and also excellent thermal stability, which finds wide application in catalysis. Nowadays using compressed CO_2 to fabricate mesoporous silica is still a challenge [6]. Fortunately, the compressed CO_2 has been shown to be useful for tuning surfactant aggregations, and thus it can adjust the properties of emulsion [7,8]. Nevertheless, there are a few works about synthesizing mesoporous material in CO_2-induced emulsion [9]. On the other hand, CO_2-induced mircoemulsion shows thermodynamical stability and internal phase micro-scale droplets as compared with the CO_2-induced emulsion. Thus much more small size of spherical materials could be achieved by using the CO_2-induced mircoemulsion as a template. Recently, Han and co-workers have constructed CO_2-induced microemulsion to synthesize spherical Au nanoparticles [10]. As far as we known, CO_2-induced mircoemulsion has rarely reported to prepare silica materials.

The spherical mesoporous silica has attracted much attention recently because it exhibits unique textural features which can be used as catalyst supports or as catalyst itself [11]. However, how to control the morphology of mesoporous silica is another huge challenge. The spherical mesoporous silica nanoparticles could be obtained by the hydrothermal method with the addition of the conventional inorganic acid, base or co-solvent [12]. Thus developing an approach to control the morphology of mesostructured silica by the compressed CO_2 as an environmentally benign alternative additive would be highly promising. Usually, tuning the pore size or BET area of the mesoporous silica are achievable by the compressed CO_2 [13], but it is difficult to control the shape of materials simultaneously. Although the spherical silica has been prepared in CO_2-induced emulsion, the particle size is very large (over 5 μm) [14]. Thus CO_2-induced microemulsion could be an excellent alternative to prepare small size of spherical silica and also the core–shell structural nano-catalyst.

Suzuki coupling reaction over different heterogeneous Pd catalysts has been an active investigation field. Corma et al. had developed a heterogeneous Pd-supported catalyst by anchoring 2-dicyclohexylphosphino-2′,6′-dimethoxy-1,1′-biphenyl (SPhos) ligand on different solid supports [15]. In order to obtain ligand-free heterogeneous Pd catalysts, Shimizu et al. had prepared Pd–sepiolite catalyst by ion exchange [16]. In addition, well-dispersed palladium nanoparticles in mesoporous SBA-15 were

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also prepared with sol-gel route, and the resulting nanocomposites exhibit a highly catalytic activity and reused ability for both the Suzuki and Heck coupling reactions [17]. Moreover, core–shell structure materials had also been prepared for the sake of enhancing the catalytic stability [18,19]. Recently, Opanasenko provided an outstanding overview on the heterogeneous Pd catalysts [20]. This review introduced the application of SiO_2-supported Pd catalysts in cross-coupling and other synthetically useful organic reactions. Although various types of heterogeneous Pd catalysts had been reported, the catalyst deactivation might occur due to the leaching of active component or the aggregation of Pd nanoparticles. Therefore, to design a highly stable and active catalyst still remains a huge challenge.

In the previous research, we have embedded gold nanoparticles within silica hollow nanospheres by using the compressed CO_2 [21]. On the basis of the work, we continue on the previous research and attempted to provide an alternative approach for preparing the core–shell mesoporous structured materials in CO_2-induced microemulsion. Currently, much attention has been focused on core–shell or york–shell structured materials because the independent adjustability and functionality in the cores and shells can endow them with great potential for applications in catalysis [22,23]. However, the preparation of catalyst with core–shell or york–shell structures was complicated and normally required at least four consecutive steps, including the synthesis of metal nanoparticles, silica coating, etching and calcination [24]. In this work, the spherical silica with mesoporous structure has been achieved through the CO_2-induced mircoemulsion. Moreover, palladium nanoparticles encapsulated in the spherical mesoporous silica can also be easily realized by compressed CO_2. According to the TEM result, we confirmed that all the Pd nanoparticles have been encapsulated in the spherical mesoporous silica. Besides, the present core–shell structured catalyst shows excellent recyclability in Suzuki coupling reaction compared with Pd/SiO_2 and Pd/C.

2. Experiment section

2.1. Materials

Tetraethoxysilane (TEOS), dimethyl sulfoxide (DMSO), toluene, pyridine, hydrazine hydrate, iodobenzene, palladium chloride, Sudan III and ethanol were obtained from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). Dodecylamine (DDA) and triphenylphosphine (PPh_3) were purchased from Aladdin Industrial Corporation. Phenylboronic acid, 4-*tert*-butylphenylboronic acid and *n*-octyltrimethoxysilane were obtained from Adamas Reagent Co., Ltd. Pd/C (5 wt%) catalyst was purchased from Aldrich. Silica gel (SiO_2) was obtained from Qingdao Marine Chemical Co., Ltd., China. CO_2 was supplied by Shanghai Shangnong Gas Factory with a purity of >99.995%. Deionized water with a resistivity of 18 MΩ cm was used in all experiments. All materials are of analytical grade and used as received without any further purification.

2.2. Preparation of mesoporous silica nanospheres

In a typical synthesis, 0.122 g DDA was mixed with 1.0 ml ethanol and 9.0 ml H_2O at ambient temperature and then 0.816 g TEOS was added to the mixture under vigorous stirring. The mixture was sealed in a 100 ml stainless steel autoclave and then pressurized with CO_2 by high-pressure pump. The amount of CO_2 added to the autoclave was determined by weighing. For example, when the pressure was 13.6 MPa, the mass ratio of CO_2 and TEOS was about 71. After stirring 20 h at 40 °C, the autoclave was cooled in ice-bath for 0.5 h and then depressurized slowly. The resultant solid was separated by filtering, washed with deionized water and ethanol several times, and then dried at 90 °C overnight. Calcination of the samples was performed at 550 °C in air for 5 h with the ramp rate of 1 °C/min to obtain white powders as SiO_2–CO_2-*x*, where *x* represented the pressure of CO_2 at 40 °C. Normally, the yield of the as-prepared silica materials was over 85%. Similarly, SiO_2–air material was synthesized under air atmosphere.

2.3. Synthesis of Pd nanoparticles encapsulated in the spherical silica

First, Tetrakis(triphenylphosphine) palladium(0) ($Pd(PPh_3)_4$) was prepared following the literature procedure [25]. Second, the synthesis procedures were similar to that of silica nanospheres described above except that $Pd(PPh_3)_4$ was introduced initially. A mixed solution containing DDA (0.122 g), ethanol (1.0 ml), water (9.0 ml), TEOS (0.816 g) and $Pd(PPh_3)_4$ (0.002 g) was sealed in a 100 ml stainless steel autoclave and then pressurized with CO_2 by high-pressure pump. When temperature reached 40 °C, the autoclave was pressurized with CO_2 up to 13.6 MPa. After stirring 20 h at 40 °C, the resultant solid was separated by filtering, washed with deionized water and ethanol several times, and dried at 90 °C overnight. Calcination of the sample was performed at 550 °C in air for 5 h with the ramp rate of 1 °C/min. The solid was then reduced at 300 °C for 1 h in flowing N_2/H_2 gas mixture (20:1) prior to use. 0.11 wt% of Pd was found by ICP–AES analysis (0.1 wt% Pd@SiO_2–CO_2-13.6). Moreover, 0.4 wt% and 1% Pd@SiO_2–CO_2-13.6 catalysts were also prepared in a similar method.

For the sake of comparison, 0.1 wt% Pd/SiO_2 was prepared by impregnating corresponding supports (0.85 g) with the 1.0 mol l^{-1} HCl solution of $PdCl_2$ (2 ml, 17 mg in 20 ml distilled water), followed by drying at 90 °C for 12 h. After drying, the solid products were then reduced at 300 °C for 1 h in flowing N_2/H_2 gas mixture (20:1). 0.09 wt% of Pd was found by ICP–AES analysis.

2.4. The silylation of Pd@SiO_2–CO_2-13.6

0.4 mmol of *n*-octyltrimethoxysilane and 0.2 mmol of pyridine were dissolved in 1.6 ml of dried toluene. 0.1 g of dry Pd@SiO_2–CO_2-13.6 was added into the above solution. After stirring for 24 h at 110 °C under N_2 atmosphere, the solid was isolated through centrifugation, thoroughly washed with toluene and ethanol and dried under vacuum. This sample was denoted as Pd@SiO_2–CO_2-13.6-C8.

2.5. Typical procedure for Suzuki coupling reaction

Iodobenzene (0.25 mmol), phenylboronic acid (0.33 mmol), Cs_2CO_3 (0.49 mmol), ethanol (10 ml), water (0.4 ml) and catalyst (0.001 mmol Pd) were mixed together. The mixture was then stirred for 24 h at 298 K. After the reaction, the reaction products were analyzed by GC-MS (Agilent-6890GC-5973MS, HP-5MS, 30 m × 0.25 mm × 0.25 μm) and GC (Shimadzu GC-2014, KB-50 capillary column, 30 m × 0.32 mm × 0.50 μm). For the recycling procedure, the catalyst was separated from the reaction mixture by filtration and then washed with copious amounts of EtOAc and H_2O to remove residual organics and salts.

2.6. Characterization

X-ray diffraction (XRD) patterns were collected on a D/MAX 2550 VB/PC diffractometer with Cu K radiation. N_2 adsorption and desorption isotherms were measured using a Micromeritcs ASAP 2020 M system. The samples were degassed for 10 h at 200 °C before the measurement. Scanning electron microscopy (SEM) experiments were performed on JSM electron microscopes (JEOL JSM-6360LV, Japan). Transmission electron microscopy (TEM) experiments were performed on a JEOL JEM 2100 transmission

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