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Short Communication

Controlled synthesis of highly dispersed semi-embedded ruthenium nanoparticles in porous carbon framework with more exposed active sites

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ABSTRACT

Ordered mesoporous ruthenium containing carbon (Ru-OMC) catalyst with semi-embedded uniform Ru particle distribution was synthesized by using $RuCl_3$/SBA-15 as a hard template. The sucrose both acts as the carbon precursor and Ru^{3+} stabilizer. The use of $RuCl_3$/SBA-15 makes more exposed Ru surface available for reactants. The turnover frequency of the Ru-OMC catalyst for hydrogenation of benzene reaches ca. 35,000 h^{-1} at 4 MPa, 110 °C, which is 12 times improvement compared with that of Ru/OMC catalyst prepared by impregnation. The Ru-OMC catalyst can be recycled more than 9 times without much loss of performance and aggregation of Ru nanoparticles.

1. Introduction

Carbon supports offer many advantages such as mechanical stability, high surface area, ideal porosity, abundant and adjustable surface functional groups which can be used as anchoring sites for noble metal particles [1]. Impregnation is a normally used method to support noble metal catalysts into carbon materials [2]. However, it can be challenging to synthesize nanoscale metal particles less than 3 nm in diameter on porous supports by impregnation because nanoparticles easily undergo sintering through certain thermal treatments, such as calcination and reduction [3].

Recently, the preparation of confined noble metal catalyst has been a hot topic with new mesoporous materials appearing. Improvement in the catalytic properties is derived from the confinement concept resulted from imprisonment of the substrate within the pores of the support, which leads to improved interactions between the active catalyst and the substrate [4]. For example, Ji et al. [5] reported that Ru-containing ordered mesoporous carbon (OMC) through an evaporation-induced multi-constituent co-assembly method exhibits good catalytic activity for benzene hydrogenation. Zhao et al. [6,7] reported that Ru nanoparticles can be semi-embedded in a matrix of porous carbon by a chemical vapor deposition (CVD) method and that these materials display high catalytic activity. They also reported a thermal reduction method to prepare carbon supported Ru catalyst and that OMC can act both as the support and the reducing agent for ruthenium nanoparticles, and the intimate interfacial contact between the Ru nanoparticles and the carbon support was believed to be responsible for the remarkably high activity in the hydrogenation of benzene and toluene [8]. Liu et al. reported a controlled synthesis of highly dispersed platinum and stable PtRu nanoparticles in OMCs by dispersing platinum acetylacetonate in the furfuryl alcohol and trimethylbenzene as the co-feeding carbon and Pt precursor [9,10]. Xiong et al. reported a method by using furfuryl alcohol solution containing $Ru(NO)(NO_3)_3$ for the preparation of stable Ru nanoparticles embedded on the OMC material for applications in Fischer–Tropsch synthesis [11]. Both of them use a mixture of noble metal precursor in organic carbon source to prepare noble metal embedded carbon catalysts. Although the mesostructures of metal-carbon catalysts is uniform by using the mesostructured silica hard templates, most of the metal particles are buried in the carbon framework due to the premixing of metal ions with carbon precursors. The deeply buried status of metal particles caused problems such as less contact metal surface with reactants during reaction. Recently, Liu et al. [12] described a stepwise method for the accurately controlled growth of Pt nanoparticles supported on ordered mesoporous carbons (Pt-OMC) by the nanocasting of carbon and metal precursors in the pore channels of mesoporous silicas functionalized with Si–H groups.

In the present work, we reported a one-pot method for preparation of Ru-OMC catalyst with more exposed active sites by using $RuCl_3$/SBA-15 as a hard template. The catalytic performance of Ru-OMC catalysts was evaluated in the hydrogenation of aromatics, which are important industrial transformations and model hydrogenation reaction for evaluation of supported noble metal catalysts [13,14].

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2. Experimental

2.1. Preparation of the materials

Mesoporous pure-silica SBA-15 was synthesized according to Zhao et al. [15] Ru-OMC was synthesized by using sucrose as the carbon precursor, and $RuCl_3$ as Ru source. A detailed preparation of the Ru-OMC catalyst was given in supporting information. The supported ruthenium catalyst on OMC (donated as Ru/OMC) and SBA-15 silica (donated as Ru/SBA-15) were prepared by a wet impregnation method. The preparation for the above samples are summarized in Fig. 1.

2.2. Measurement of catalytic activities

The evaluation of the catalytic properties of the Ru catalysts for benzene hydrogenation was done in a 100 mL stainless-steel stirred pressure reactor. A given amount of Ru catalyst (0.085 g) and 30 mL of benzene (>99.5%, Aldrich) were placed in the reactor. The reaction pressure was generated by using H_2 at the reaction temperature and kept constant. The reaction was stopped until no uptake of H_2 was observed. The product was analyzed by using an Agilent 7890A gas chromatograph equipped with a DB-1 capillary column with a flame-ionization detector. To investigate the recyclability of the catalyst, the used Ru catalyst was filtered after the reaction and vacuum-dried at 80 °C overnight before the next reaction run.

2.3. Characterizations

Powder X-ray diffraction (XRD) patterns were recorded on a Rigaku D/Max-2500/pc powder diffraction system using Cu Kα radiation (40 kV and 100 mA) over the range $0.5° \leq 2\theta \leq 10°$ (low angle) and $10° \leq 2\theta \leq 80°$ (high angle). Nitrogen adsorption isotherms were determined at −196 °C on a Micromeritics ASAP 2020 system in static measurement mode. The samples were outgassed at 350 °C for 10 h before adsorption measurement. The Brunauer–Emmett–Teller (BET) method was used to calculate the specific surface area. High resolution transmission electron microscopy (HRTEM) and scanning transmission electron microscope (STEM) images of the samples were obtained by a FEI Tecnai G20 instrument. Energy-dispersive X-ray spectroscopy (EDS) and inductively coupled plasma plasma emission spectrometry mass spectrometry (ICP-MS) was conducted for the analysis of sample composition. The dispersion of Ru was obtained by CO chemisorption method, which was carried out at 40 °C on a Quantachrome Autosorb-1/C chemisorb apparatus. Prior to measurements, the pre-reduced catalysts were reduced in situ for 2 h at 450 °C in H_2. The metal dispersion and particle size were estimated based on assumption of a spherical geometry of the particles and an adsorption stoichiometry of one CO molecule on one Ru surface atom.

3. Results and discussion

3.1. Texture properties

The low-angle XRD patterns of various Ru catalysts and supports are given in Fig. 2-a. A remarkable diffraction peak at $2\theta = 0.5$–$1.0°$ is observed for Ru/SBA-15, Ru-OMC, OMC and SBA-15, indicating the ordered mesoporous structures of these samples. The existence of the Ru metal leads to decreasing of the intensity of the characteristic peaks of the SBA-15 and shrinkage of cell parameter (Table 1). This should be attributed to the pore-filling effects that can reduce the scattering contrast between the pores and the framework of the SBA-15. Similar results have been reported previously [16,17]. In contrast, this peak disappears for Ru/OMC, implying the Ru metal particles is blocking the pore or the ordered mesostructure is somewhat destroyed.

The porosity of the SBA-15, Ru/SBA-15, OMC, Ru-OMC, Ru/OMC and Ru-Carbon was measured by N_2 sorption. Fig. 3 gives the isotherms (a) and pore size distributions (b) of various samples. For the sample SBA-15 and Ru/SBA-15, the isotherms are typical type-IV with an H1 hysteresis loop, which is a typical characteristic for mesoporous materials with 2D-hexagonal structure. The specific surface area of SBA-15 decreases from 904 to 645 m^2/g and pore size decreases from 6.4 to 5.6 nm (calculated from the desorption branch of the isotherm) after Ru metal was supported (Table 1). This indicates that the impregnation of Ru metal blocks parts of the pores of SBA-15 support. The isotherms of Ru-OMC and OMC are typical type-IV with an H2 hysteresis loop, which is a typical adsorption for OMC materials with an ordered mesoporous structure [18]. Nevertheless, the isotherm of the Ru/OMC shows an obvious

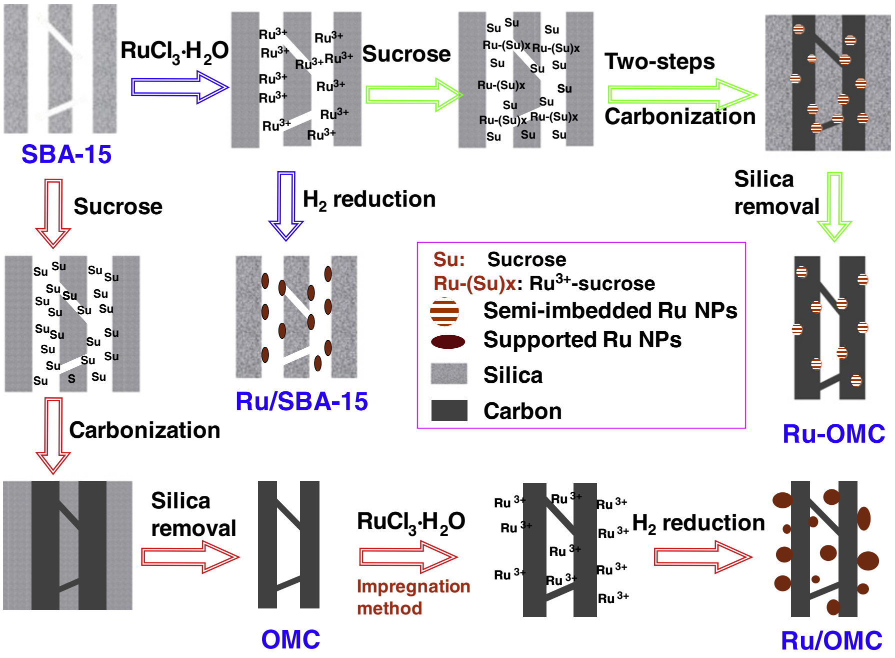

Fig. 1. The preparation for Ru-OMC, Ru/OMC and Ru/SBA-15.