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Biosynthesized ruthenium nanoparticles supported on carbon nanotubes as efficient catalysts for hydrogenation of benzene to cyclohexane: An eco-friendly and economical bioreduction method

Yao Ma, Yangqiang Huang, Youwei Cheng*, Lijun Wang, Xi Li

Department of Chemical and Biological Engineering, Zhejiang University, Hangzhou 310027, PR China

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ABSTRACT

Ru/carbon nanotubes (CNTs) catalysts synthesized by an environmentally benign and economical bioreduction approach were applied to the hydrogenation of benzene to cyclohexane under mild conditions without adding any solvent. The catalysts were characterized by a variety of techniques including BET, TEM, HAADF-STEM -EDX, XRD, XPS, FTIR, TG, and DTG. The effect of various preparation parameters, such as Ru loading, preparation temperature and calcination temperature on the catalytic performance were systematically analyzed and the optimum conditions were found to be 2 wt%, 60 °C, and 500 °C, respectively. In terms of reaction conditions, the combination of reaction temperature at 80 °C under the pressure of 4 MPa, and the time length of 0.5 h proved to be optimum, under which the cycohexane yield of 99.97% along with the TOF value of 6983.09 h^{-1} were achieved. Such results could match or even outweigh those reported in the literature. Furthermore, efforts were also made to probe the stability of catalysts. In a word, the merits of excellent durability, sound productivity and preferable reusability grant the catalysts a promising future in the industrial application.

1. Introduction

With the increasing industrial demands of low-aromatic diesel fuels, the development of effective catalysts for hydrogenation of arenes is of critical importance [1,2]. Poor fuel with high aromatic content produces a low cetane number in diesel fuel and a high smoke point in jet fuel. There is also evidence that particulate emissions in diesel exhaust gases correlate with the aromatic content in the fuel [2]. More and more stringent environmental laws and regulations have been enforced to bring down aromatics content to controllable level, which boosts new catalytic processes for aromatic saturation.

The hydrogenation of benzene to cyclohexane is one of the most important compounds hydrogenation reactions practiced in industry [3–5]. Cyclohexane is a valuable chemical used in the manufacture of nylon 6 and nylon 66, which constitute about 90% of all polyamides. In addition, cyclohexane is an excellent and nontoxic solvent for cellulose ether, wax, asphalt and rubber [6,7]. Nowadays, catalytic benzene hydrogenation to cyclohexane is the dominant production process in industry, although cyclohexane can be obtained from the separation of petroleum distillate [8]. There are lots of researchers [9,10] who use the catalytic benzene hydrogenation reaction to evaluate the performance of the hydrogenation catalysts. The use of homogeneous catalysts will inevitably encounter the separation problems which could be very sophisticated and money-consuming during the production process. Thus, to seek more economical heterogeneous catalysts becomes the primal concern for researchers in this field. The IFP process uses nickel-based heterogeneous catalysts at temperature above 200 °C under 50 bar [11,12]. These forcing conditions will lead to poor life-time performance, additionally, higher temperature will create favorable conditions for the side reactions such as isomerization and hydrocracking which result in selectivity of cyclohexane decline. Recently, several types of noble metals such as Ru, Rh, Pt, Pd, etc. have arose extensive interests and been used extensively as heterogeneous catalysts in the hydrogenation of benzene to cyclohexane [13–15]. In particular, considerable studies have focused on Ru-based catalysts which have extensively been investigated in hydrogenation processes. Nowicki et al. reported new colloidal solutions of Me-CD protected Ru(0) nanoparticles which were prepared by reduction of $RuCl_3$ with sodium borohydride [16]. They found these nanoheterogenous system present

* Corresponding author. Tel.: +86 571 8795 2210; fax: +86 571 8795 1227.
E-mail addresses: ywcheng@zju.edu.cn, uway@163.com (Y. Cheng).

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interesting activity for aromatic ring hydrogenation. Ozkar and coworkers prepared intrazeolite ruthenium(0) nanoclusters catalyst which exhibited excellent catalytic activity in the hydrogenation of benzene to cyclohexane [17].

The deposition-precipitation (DP) technique has long been used to synthesize Ru-based catalysts, which is not only energy intensive (because of numerous stringent conditions) but also hostile to environment (due to the use of toxic solvents or additives such as surfactant stabilizers and auxiliary capping agents). Compared to the conventional methods, bioreduction approach ("green chemistry") based on microorganisms or plants extract [18] is eco-friendly, cost-efficient and can be served as an alternative method to the DP technique to produce Ru nanoparticles. Biosynthesis of noble metal nanoparticles as an intersection of nanotechnology and biotechnology has gathered increasing interests in the last decade. Song and Kim reported the biosynthesis of Ag nanoparticles by using five plant leaf extracts (*Pine*, *Persimmon*, *Ginkgo*, *Magnolia* and *Platanus*) which could be used in various areas closely related with people's daily life such as cosmetics, foods and medical applications [19]. Zhan et al. successfully prepared Au nanoparticles by biogenic fabrication methods and they further immobilized the biosynthesized Au nanoparticles on TS-1 support which can act as bioreduction catalysts in vapor phase propylene epoxidation [20,21]. Although there are fewer attempts to apply the biosysthesized nanoparticles to catalytic system, it has been proved to be a promising approach for the fabrication of novel heterogeneous catalysts.

Owning to their unique properties and surfaces, Carbon nanotubes (CNTs) are suitable for many potential applications as promising carbon materials and solid supports for heterogeneous catalysts [22–25]. CNT-supported metallic nanoparticles exhibit remarkably high catalytic activities for hydrogenation of aromatic compounds. Pan and Wai developed a simple one-pot sonochemical method for the preparation of rhodium catalysts supported on CNTs which exhibited high catalytic activity of benzene and its derivatives hydrogenation without solvent under mild conditions [26]. Guo et al. reported Pt-based mono and bimetallic catalysts supported on CNTs by microwave-assisted polyol reduction method (MAPR) [27]. These catalysts were successfully applied to the selective hydrogenation of cinnamaldehyde to cinnamal alcohol. Effective dispersion of the nanocatalysts in organic solvents is one obvious reason favoring the CNT-supported metallic nanoparticles for catalytic hydrogenation reactions [25]. It becomes clear that, carbon nanotubes possess specific characteristics such as remarkable electronic properties, particular adsorption properties and high resistance to abrasion, all of which usher in a brighter prospect for such materials.

Hydrogenation of benzene to cyclohexane under mild conditions is also worthy of discussion from the perspective of energy and environmental considerations. In this paper, we probe into the biosynthesis of the Ru nanoparticles using the *Cacumen Platycladi* (*CP*) extract, which plays a dual role in reducing and protecting agent without any other additive and the immobilization of Ru nanoparticles on the nanoscale materials carbon nanotubes. The prepared catalysts were characterized by different techniques, including low temperature N_2 physisorption, transmission electron microscopy (TEM), high-angle annular dark field-scanning transmission electron microscopy (HAADF-STEM) with energy dispersive X-ray spectroscopy (EDX), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), fourier transform infrared spectroscopy (FTIR), thermogravimetric (TG), and differential thermogravimetric (DTG). The performance of the bioreduction Ru-based CNTs catalysts was evaluated by the hydrogenation of benzene to cyclohexane without any solvents under mild conditions. In order to optimize the reaction parameters for maximum yield of cyclohexane and TOF value, the effect of various preparation and reaction conditions on the reaction was also included.

2. Experimental details

2.1. Materials

Carbon nanotubes (CNTs) were purchased from Bema Environmental Science and Technology Co. Ltd., *Cacumen Platycladi* (*CP*) was obtained from Zhejiang university hospital and other chemical reagents mentioned were analytic grade from Sinopharm Chemical Reagent Co. Ltd. and used directly without pretreatment.

2.2. Catalyst preparation

A series of Ru-based catalysts were prepared by the adsorption-reduction (AR) technique employing plant biomass extract [28]. Firstly, to obtain the *CP* leaf extract, screened powder *CP* leaf of 1 g dosage was dispersed in 100 mL deionized water under stirring for 4 h. The extract was then filtrated and used for the synthesis of RuNPs. In a typical catalyst preparation procedure, an appropriate amount of dried CNTs were immersed in aqueous $RuCl_3$ solution (50 mL, 2.2 mM) for 1 h in an oil bath (60 °C) under magnetic stirring. Afterward, 30 mL *CP* extract was added immediately into the mixture solution under stirring. After another 5 h, the products were filtered, washed thoroughly with deionized water, dried at 60 °C overnight in a vacuum oven, and then calcined at 500 °C for 3 h in the atmosphere of nitrogen. To investigate the influence of preparation parameters, different preparation conditions (Ru loading, 0.5–3.0 wt%; preparation temperature, 30–90 °C; calcination temperature, 200–700 °C) were implemented. To meet the needs of the characterization, the Ru nanoparticles (RuNPs) were prepared by reducing the metal precursor with the *CP* leaf extract free of the supports.

2.3. Catalyst characterization

Brunauer–Emmet–Teller (BET) specific surface areas were measured by N_2 adsorption at liquid N_2 temperature in an ASAP 2020 analyzer. Transmission electron microscopy (TEM), high-resolution transmission electron microscopy (HRTEM) and high-angle annular dark field-scanning transmission electron microscopy (HAADF-STEM) with energy dispersive X-ray spectroscopy (EDX) images were obtained with a FEI Tecnai G2 F20 S-TWIN microscope operated at 200 kV. The specimens were prepared by ultrasonically suspending the sample in ethanol for 0.5 h. Size distribution of the resulting NPs was estimated on the basis of TEM micrographs with the assistance of SigmaScan Pro software (SPSS Inc., Version 4.01.003). The X-ray diffraction (XRD) analyses were performed on a Shimadzu powder X-ray diffractometer with Cu Kα radiation at 40 kV and 30 mA using the scanning angle 2θ from 10° to 90°, at a step of 0.02° and rate of 2° min^{-1}. XPS experiments were performed on a VG ESCALAB MARK II equipment. Monochromatic radiation from an Mg Kα (BE = 1253.6 eV) X-ray source was used for excitation. FTIR spectra were recorded on a Nicolet 5700, where the samples were ground with KBr and pressed into the wafer. Thermogravimetric (TG) and differential thermogravimetric (DTG) analysis were measured with a METTLER TGA/SDTA 851^e thermobalance. The sample was heated from room temperature to 900 °C at a heating rate of 10 °C/min under a high purity nitrogen flow of 100 mL/min.

2.4. Catalyst evaluation

The hydrogenation of benzene to cyclohexane was carried out in a magnetically stirred 100 mL stainless steel high pressure