



Research paper

Selective hydrogenation of benzoic acid to cyclohexane carboxylic acid over microwave-activated Ni/carbon catalysts



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ARTICLE INFO

Article history:

Received 21 July 2017

Received in revised form 2 October 2017

Accepted 10 October 2017

Keywords:

Selective hydrogenation

Benzoic acid

Cyclohexane carboxylic acids

Ni/carbon catalysts

ABSTRACT

High yields of cyclohexane carboxylic acids were obtained by direct hydrogenation of aromatic carboxylic acids over different Ni/carbon catalysts having distinctive surface properties. The catalysts were characterized by SEM, TEM, H₂-TPR and N₂ adsorption isotherms for the determination of BET surface area and porosity. The hydrogenation reaction was carried out in batch pressure reactor in gas-liquid phase at 200 °C. High selectivity (100%) of cyclohexane carboxylic acids at 86.2 mol% conversion of benzoic acid was achieved over microwave-activated biochar supported non-precious metal Ni catalyst. The 10%Ni/CSC-b catalyst has been investigated for hydrogenation of benzoic acid to cyclohexane carboxylic acids and shown little deactivation in stability test. The effects of Ni loading, high dispersion of Ni species, appropriate power of microwave heating and strong interaction of Ni species with carbon are of benefit to the reaction.

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1. Introduction

Catalytic hydrogenation is an ubiquitous reaction and is used for instance in the synthesis of fine chemicals and fuel upgrading [1–5]. Increasing sustainability demands are now appealed for chemical production to improve catalytic selectivity, to minimize byproduct formation, to circumvent separation/purification operations and to avoid costly clean-up and disposal. Benzoic acid is an inexpensive feedstock [1] that can be hydrogenated to benzaldehyde [6–10], benzyl alcohol [11–13] or cyclohexane carboxylic acid [14–17] as important commercial products. The chemoselective hydrogenation of benzoic acids (BA) to cyclohexane carboxylic acid (CCA) is the most important reaction in the synthesis of caprolactam from toluene, and CCA is also an important organic intermediate for the synthesis of pharmaceutical industries for example praziquantel and ansatrienin [18–20]. So chemoselective hydrogenation of BA to CCA has attracted great interest all over the world [21–24].

The catalytic hydrogenation of carboxylic acids is performed industrially by using heterogeneous catalysts, such as noble metal catalysts, including Pd/C, Rh/C, Pd/Ru, RuPt and platinum

nanowire [25–27], have been widely applied in this transformation, and all exhibit high activities. Due to stability and can be used multiple times, heterogeneous catalysts are the preferred options for most processes in chemical industry [28,29]. In principle, in the case of the supported catalysts, two basic but important issues should be taken into account in order to design and screen suitable supports for catalytic applications. One of which is that the support must show high stability and high surface area; the other is that the support should contain high density of defect sites. There are a variety of materials that suitable as supports [30,31], among which carbons (including activated carbon [32], graphene [33] and carbon nanotubes [34]) are the most frequently used. As carbon materials are mainly composed of carbon and even can be made directly out of biomass, they are obviously “sustainable” support materials for Pd nanoparticles (NPs). However, the agglomeration and leaching of noble metal nanoparticles (such as Pd, Pt, Au) in the catalysts cannot be effectively avoided by simply treating the support using reagents such as nitric acid and hydrogen peroxide due to the weak interaction of surface oxygen groups [35], and also the high price of noble metal catalysts has limited their further application in industry.

Cyclohexanecarboxylic acid is an important organic synthesis intermediate, which itself is a good light curing agent, but also for the synthesis of the drug antiemulsion 392 and praziquantel (treatment of schistosomiasis), its derivatives such as cyclohexyl-

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methyl carbamate and *trans*-4-isopropylcyclohexyl acid are the important intermediates for the synthesis of many chemical products and pharmaceutical. Our previous work reported the selective hydrogenation of aromatic carboxylic acids over basic N-doped mesoporous carbon supported palladium catalysts [14], these N-doping materials showed high catalytic activity for the selective hydrogenation of aromatic ring. The present paper reports a simple microwave-heating preparation method for biocarbon supported Ni NPs (nanoparticles) catalyst and its application in the ring hydrogenation of benzoic acid under mild conditions. The influence of microwave heating power on the dispersion and morphology of Ni and the benzoic acid hydrogenation is discussed.

2. Experimental

2.1. Preparation of catalysts

All chemicals were purchased from were purchased from Shanghai Aladdin Chemical Co. The 10%Ni/CSC-a catalyst was prepared through conventional impregnation method, as described in our previously published articles [36].

An aqueous solution of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was impregnated onto various carbon supports like coconut shell charcoal (CSC), activated carbon (AC) and graphite (G). Typically, 1.0 g carbon was dispersed in 50 mL deionized water consisted of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.493 g). Then, the resulting mixture was heated to 90 °C while stirring and heating in microwave reactor. Afterwards, the composite catalyst precursors were obtained by evaporating the water under rotary evaporator at 70 °C and dried in a vacuum oven at 120 °C for 8 h, followed by reduction with H_2 at 400 °C (with a rate of 5 °C/min H_2) for 3 h in a tubular reactor. The resultant catalyst was designated as 10%Ni/CSC-b, 10%Ni/AC-b, 10%Ni/G-b. Other two different samples with the same nominal loading of 10 wt% (weight percent) were prepared by using SiO_2 and Al_2O_3 as supports and designated as 10%Ni/ SiO_2 -b and 10%Ni/ Al_2O_3 -b.

2.2. Characterizations

X-ray diffraction (XRD) measurements were performed on a Bruker D8A25 diffractometer with $\text{Cu K}\alpha$ radiation. The tube voltage was 30 kV, and the current was 25 mA. The XRD diffraction patterns were taken in a range of 5–65° 2 θ . Quantachrome iQ-MP was used to determine N_2 adsorption–desorption properties of the samples. The specific surface area was calculated by using the Brunauer–Emmett–Teller (BET) method, and the pore size distributions were measured by using Barrett–Joyner–Halenda (BJH) analysis from the desorption branch of the isotherms. The Scanning Electron Microscope (SEM) has been used a JEOL JSM-6510A to detect the morphology and size of crystals. Transmission electron microscope (TEM) (JEOL-135 2010F, operating at 200 kV) was used to investigate morphology and size of the particles. The samples for TEM were prepared by dispersing the material in ethanol and drop-drying onto a Formvar resin coated copper grid. The X-ray photoelectron spectroscopy (XPS) analysis was performed on a Perkin-Elmer PHI ESCA system with 0.1 eV per step for detail scan, and the X-ray source was standard Mg anode at 12 kV and 300 W. The TPR (temperature programmed H_2 reduction) experiments were performed with 10 vol% hydrogen in N_2 (50 mL/min) at a heating rate of 10 °C/min, the hydrogen consumption being measured by a TCD detector. All TPR profiles were normalized for the same catalyst mass.

2.3. Catalytic tests

Hydrogenation of benzoic acid and derivatives was carried out using the as-prepared 10%Ni/CSC-a as the catalyst. Other nickel

supported catalysts were also applied in the hydrogenation of benzoic acid for comparison. In a typical process, 4 mmol benzoic acid and a certain amount of catalyst were put into a 100 mL stainless autoclave, and 10 mL solvent was employed as green solvent. The hydrogenation of benzoic acid was carried out at desired temperature with magnetic stirring at a speed of 1000 rpm. After reaction, the filtrate was analyzed by GC-FID with a 30 m capillary column (Rtx@-5). The catalyst was recovered by centrifugation and then washed several times with THF. The separated catalyst was washed several times with THF and dried overnight in a vacuum oven at 80 °C for use in the next run.

3. Results and discussion

3.1. Structural characterizations

Fig. S1 presents the XRD patterns of the samples with different Ni contents. The characteristic peaks of CSC ($2\theta = 23.3^\circ$) and Ni metal ($2\theta = 45.3, 51.5$ and 76.2°) are observed for all the Ni/carbon catalysts with the carrier is CSC, AC and G, respectively, in which three peaks at $45.3^\circ, 51.5^\circ$ and 76.2° are attributed to [111], [200] and [220] diffraction peaks of Ni. The micropore structure of the 10%Ni/CSC catalysts were identified by nitrogen adsorption/desorption isotherms (Fig. 1). The results clearly show BET surface area of 10%Ni/CSC-a is $599.6 \text{ m}^2/\text{g}$, smaller than $678.2 \text{ m}^2/\text{g}$ of 10%Ni/CSC-b (prepared by microwave-heating). The support CSC still retained its microporosity well after the loading of Ni nanoparticle. Table S1 presents the BET surface areas and total pore volumes of various catalysts determined by the BET analysis. Very clearly, the support G and the catalyst 10%Ni/G-b have the smallest BET surface areas and the pore volumes. Both values of the catalyst 10%Ni/AC-b (activated carbon as the support) are the largest.

Usually, SEM is used to determine the particle size and particle morphology of the synthesized sample. The SEM backscattered composition images of the monometallic Ni/carbon samples are given in Fig. 2, inclusive of 10%Ni/CSC-a, 10%Ni/CSC-b, 10%Ni/AC-b and 10%Ni/G-b. Apparently, SEM images of four samples exhibit irregular spherical morphologies, and it is clear that most of the catalyst particles are in good dispersion. TEM images of metal particle size distribution of 10%Ni/CSC-a, 10%Ni/CSC-b, 10%Ni/AC-b and 10%Ni/G-b are shown in Fig. 3. For 10%Ni/CSC-a, a wide particle size distribution is observed and the metal particle size is varied from 6.3 to 39.9 nm with an average value of 13.2 nm (Table 1). The particle sizes of Ni metal supported on AC and G are determined to be 17.7 and 12.7 nm, respectively. For 10%Ni/CSC-b, highly dispersed Ni nanoparticles are found to evolve and distribute throughout the CSC-b. The mean diameter is estimated to be 9.4 nm. This demonstrates that the microwave-heating plays an important role in the dispersion of metallic species over the CSC support.

Fig. 4 shows TEM images of 10%Ni/CSC-b, in which particle size and dispersion on catalysts are affected by microwave-heating power. When the microwave heating power is 400 W, the mean particle size of Ni on 10%Ni/CSC-b is 14.7 nm. As the microwave power increases to 500 W, the 10%Ni/CSC-b shows the presence of uniformly well-dispersed Ni on CSC, and the mean diameter is estimated to be 9.4 nm. The mean particle size of Ni is decreased to 7.9 nm on 10%Ni/CSC-b (600 W). When the catalyst 10%Ni/CSC-b (700 W) is prepared by 700 W microwave-heating power, the mean particle size of Ni nanoparticles on the CSC support is reduced to 7.7 nm with a wide distribution. However, the hydrogenation activity of the catalysts shows that the microwave-heating power of 500 W is optimal for the preparation of the catalyst.

X-ray photoelectron spectroscopy is a convenient method of studying supported nickel catalysts. The reducibility and interactions between metal and support are further studied by H_2 -TPR, as

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