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Preparation of Ni/CNTs catalyst with high reducibility and their superior catalytic performance in benzene hydrogenation

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ABSTRACT

A facile synthesis of Ni/CNTs catalyst with high reducibility has been performed. The as-prepared Ni/CNTs sample exhibited excellent catalytic performance for benzene hydrogenation even without pretreatment by H_2. The results indicated that using carbon nanotubes (CNTs) as support in presence of ethylene glycol (EG) may result in the formation of a small amount of metallic Ni. These metallic Ni would induce to produce more metallic Ni and maintain the high activity during catalytic process. The synergy between CNTs and EG has been investigated in detail. The proposed preparation method and the promotion mechanism for catalytic hydrogenation provided a new convenient approach for the research and practical application of CNTs.

1. Introduction

The hydrogenation of benzene to cyclohexane is of particular importance both for environmental protection and industrial processes. Cyclohexane is a valuable chemical intermediate for the manufacture of Nylon-6 and Nylon-66, as well as an excellent and nontoxic solvent. Until now, cyclohexane has been mainly produced by the hydrogenation of benzene [1–3]. Recently, the hydrogenation of benzene has attracted renewed attention due to the increasing demand for the reduction of the aromatic content in petroleum fuels [4,5]. Considerable studies have focused on Ni-based catalysts due to its availability and reasonable cost compared to noble metal catalysts. In order to promote the dispersion of nickel species and to prevent active sites from aggregation during catalytic reaction process, various supports including Al_2O_3, SiO_2, clay and mesoporous molecular sieves have been employed in the benzene hydrogenation reaction [6–10]. It is accepted that the reduced state nickel species are the active sites for hydrogenation reaction because the molecular hydrogen can be effectively dissociated over metallic Ni [11,12], and so the prepared catalysts are generally pretreated by hydrogen gas just before reaction, and found that the greater the reduction extent of nickel species, the higher is the catalytic activity [13–15]. Hence, how to improve the dispersion and reduction degree of nickel catalyst has become a new challenge for benzene hydrogenation.

Carbon nanotubes (CNTs), as a novel nanostructured carbon materials, possess unique characteristics such as large specific surface areas, nanometer-sized channel, high mechanical strength, remarkable electrical and thermal properties and high adsorption capacity for hydrogen [11,16,17]. Studies demonstrated that CNTs-supported metal catalysts exhibit superior catalytic activities for hydrogenation of aromatic compounds due to enhanced dispersion and the interaction with nanoparticles [18–20]. Recently it is found that the high valence metal ions in liquid phase can be reduced into intermediate valence state at room temperature under the spontaneous redox of CNTs. Further found the high temperature also can promote the formation of part of metallic Ni in the presence of CNTs. The research found that these reduced states of metal species are the main reasons for the promotion of catalytic reaction [21,22].

Ethylene glycol (EG) as an environmentally benign solvent has currently aroused great interest for synthesis of carbonaceous material [23,24]. It is also usually used as additive to increase dispersion of activated component on support [25]. On the other hand it is also a weak reducing agent widely used for the reduction of metallic ions such as Pt, Co, and Ag etc [26–30]. We expect to utilize simultaneously these properties of EG, combined with the spontaneous redox of CNTs, to promote the reduction of metal oxides and thereby improve the hydrogenation performance of the catalyst.

Herein, an attempt has been made to synthesize Ni/CNTs catalyst with high catalytic activity for benzene hydrogenation. The using of CNTs in presence of EG may promote the reduction of

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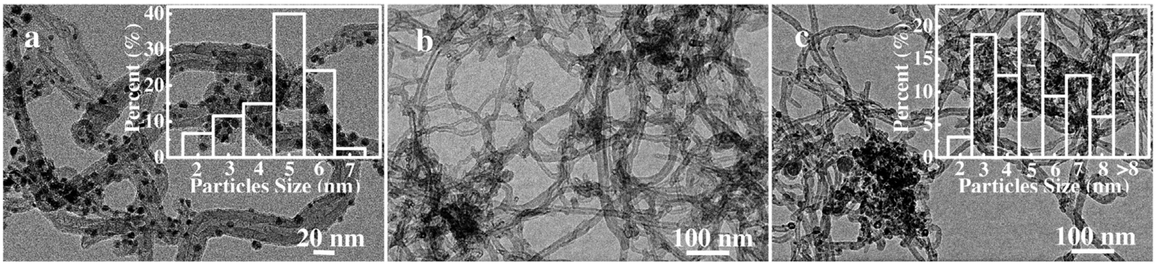

Fig. 1. TEM images of Ni/CNTs-E(a), Ni/CNTs-N(b) and Ni/CNTs-H(c).

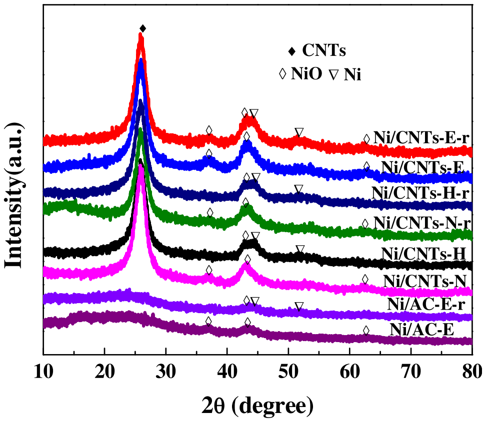

Fig. 2. XRD patterns of different samples before and after reaction.

nickel oxides to form metallic Ni due to the synergy of CNTs and EG. These metallic Ni can induce to produce more metallic Ni in hydrogen atmosphere during catalytic process, thus greatly enhance the catalytic activity for benzene hydrogenation even without pretreatment by H_2. The as-prepared catalysts are characterized by different techniques, including TEM, XRD, XPS, Raman, low temperature nitrogen adsorption and H_2-TPR. The promotion mechanism of CNTs in presence of EG for benzene hydrogenation has been discussed in detail.

2. Experimental

2.1. Catalyst preparation

Raw multi-walled CNTs were supplied by Chengdu Organic Chemicals Co. Ltd. of the Chinese Academy of Science (China). To remove impurities, they were firstly treated with concentrated nitric acid. Typically, 3 g of raw CNTs were refluxed in 150 mL concentrated HNO_3 (68 wt%) at 120 °C for 5 h. After being cooled to room temperature, the mixture was filtrated and washed with distilled water until pH reached around 7, then dried at 60 °C for 12 h. Afterwards, 0.5 g of the above purified CNTs was immerged into 20 mL aqueous solution containing 2.5, 5, 7.5 and 10 mL of EG, respectively, and ultrasonicated for 20 min at room temperature. Subsequently, a certain amount of nickel salt ($Ni(NO_3)_2 \cdot 6H_2O$) dissolved in distilled water was transferred into above solution. The mixture was vigorously stirred at room temperature for 2 h, after dried at 80 °C for 12 h, further dried at 120 °C for 12 h. Finally the dried product was calcined at 400 °C in Ar atmosphere for 3 h with a heating rate of 5 °C min^{-1}. The resulted catalyst sample was designated as Ni/CNTs-E. The catalysts with different Ni loadings (5, 7.5 10, 15 and 17.5 wt%) were also obtained at fixed amount of 5 mL EG using the same preparation method. For comparison, Ni/CNTs-N sample was prepared without EG by the same as above procedures and Ni/CNTs-H was prepared by reducing Ni/CNTs-N sample with H_2 at 400 °C for 3 h. Furthermore, Ni/AC-N and Ni/AC-E were also prepared with the same method using active carbon as support. Before use, active carbon was treated in diluted HNO_3 solution with a concentration of 27.2 wt% at 80 °C for 3 h. Then it was washed with distilled water until pH reached around 7 and dried at 60 °C for 12 h. The nominal Ni-content of each catalyst was 10.0 wt%.

2.2. Catalyst characterization

Transmission electron microscope (TEM) images were measured using a JEOL-JEM-2010 transmission electron microscope at the accelerating voltage of 200 kV. Powder X-ray diffraction (XRD) measurements were performed on Philips X'pert Pro X-ray diffractometer with Cu Kα radiation at 40 kV/40 mA, a step size of 0.02°, a scanning rate of 4° min^{-1}, and a 2 theta range of 10–80°. Nitrogen adsorption measurements were determined by Micromeritics ASAP 2020 at −196 °C. The BET method was utilized to calculate the specific surface area. The pore volume and pore size distribution were derived from the desorption branches of the isotherms using the BJH method. Raman spectra were recorded at ambient temperature on a Horiba Jobin Yvon LabRam Aramis Raman spectrometer with a laser excitation wavelength of 532 nm. X-ray photoelectron spectroscopy (XPS) was made with a PHI5000 VersaProbe electron spectrometer. All the binding energies were referenced to C_{1s} at 284.6 eV. The reducibility of sample was studied by temperature programmed reduction (TPR) in a mixture flow of 5 vol% H_2 in Ar. The temperature was increased from room temperature to 780 °C at a rate of 10 °C min^{-1}.

2.3. Catalytic reaction test

The benzene hydrogenation in gas phase was performed in a microreactor under atmospheric pressure and hydrogen was employed as carrier gas. For each run, 30 mg of catalysts in 0.4–0.8 mm particle size were put into U-type quartz tube and the reaction temperature was maintained at 160 °C. The benzene vapor saturated at 30 °C was fed into the microreactor by H_2 at a flow rate of 12 mL min^{-1} ($H_2/C_6H_6 = 4.8$). The resulting products were analyzed on a gas chromatography (GC-5890) equipped with a flame ionization detector (FID) using a 3 mm × 3 m stainless steel column packed with Silicon SE-30 at 100 °C, and with nitrogen as carrier gas. For all prepared samples, the catalytic selectivity for benzene hydrogenation reaction was 100%.

3. Results and discussion

3.1. Catalysts characterization

3.1.1. TEM

The TEM images of Ni/CNTs-E, Ni/CNTs-N and Ni/CNTs-H are shown in Fig. 1. For the sample Ni/CNTs-E it can be seen clearly that lots of dark nanoparticles are supported on the external surface of CNTs and uniformly dispersed as displayed in Fig. 1a. The