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Highly selective liquid-phase hydrogenation of furfural over N-doped carbon supported metallic nickel catalyst under mild conditions

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ABSTRACT

In this work, N-doped activated carbon supported metallic nickel (Ni/NAC) catalysts were fabricated by two-step calcination method in N_2 atmosphere for liquid-phase hydrogenation of furfural (FAL). It was found that the pyrolysis temperature and amount of melamine as N doping source have important influence on N doping content and type in activated carbon (AC) support, resulting in the subsequently formed Ni nanoparticles on N-doped AC with different sizes and thus affording different catalytic hydrogenation activities. The results demonstrated that using N-doped AC with 1.0 g melamine at 1073 K in N_2 atmosphere as support, the obtained Ni/NAC at 873 K in N_2 atmosphere with Ni nanoparticle sizes of ~13.1 nm (denoted as Ni/NAC-1-1073) exhibits a N doping content of 3.65 at.% and a surface area of 561.2 $m^2\,g^{-1}$ with a microporous structure. As catalyst for FAL hydrogenation, Ni/NAC-1-1073 demonstrated the best catalytic performance among all investigated catalysts, achieving almost 100% selectivity of tetrahydrofurfuryl alcohol (THFOL) with a complete FAL conversion at 353 K after 3 h reaction, while only 76.7% selectivity of THFOL with a FAL conversion of 86.4% was obtained using Ni/AC catalyst without N doping under the identical experimental conditions. Furthermore, it was found that almost 100% conversion of FAL to furfural alcohol (FOL) can be reached by transfer hydrogenation pathway in 2-proponal solvent using Ni/NAC-1-1073 at 413 K after 5 h reaction, whereas Ni/AC without N doping can only afford 30.2% conversion of FAL to FOL under the same conditions. The superior catalytic performance of Ni/NAC-1-1073 could be ascribed to a synergistic effect of nanosized Ni providing catalytic active sites, suitable N doping content and type in AC to promote catalytic performance, and advantageous structure characteristics of high surface area and porous structure favourable for the exposure of catalytic active sites and mass transport.

1. Introduction

Owing to the worldwide fossil fuel crisis and related environmental impact, fabrication of high value-added platform chemicals from renewable biomass and biomass-derivatives by thermal catalysis reaction has aroused great research attention [1–5]. Furfural (FAL) with C═C (furan ring) and C═O (branched chain) bonds has been widely investigated and regarded as one of the key platform molecules in biomass conversion to synthesize important non-petroleum-derived fuels and chemicals [6], such as furfuryl alcohol (FOL) [7], tetrahydrofurfuryl alcohol (THFOL) [8], 2-methylfuran (2-MF) [9] through catalytic hydrogenation or hydrodeoxygenation. Among FAL catalytically converted products, FOL and THFOL have been extensively used in industrial processes as green solvents or intermediates for fine chemical synthesis, such as resins, lubricants, adhesives, fibers and wetting agents [10,11]. The selective hydrogenation of FAL to FOL or THFOL is generally performed under liquid-phase and vapor-phase conditions, but the latter is frequently associated with easier catalyst deactivation and poorer selectivity in comparison with the former [6,12]. To date, varieties of chromium-free catalysts, including noble metals (Pt, Pd, Ru and

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Rh) and non-noble metals (Co, Ni and Cu) catalysts, have been developed to investigate the catalytic performance of liquid-phase selective hydrogenation of FAL [8,12–14]. Among them, noble-metal catalysts have demonstrated high catalytic activities in FAL hydrogenation reactions, but their poor selectivity accompanying with some undesirable side reactions and high cost/source scarcity have limited their practical applications [15,16]. Therefore, development of non-noble metal catalysts with high catalytic activity and selectivity is still highly demanded for catalytic hydrogenation of FAL to target products.

Many studies have demonstrated that Cu-based catalysts have been the most promising candidates to replace noble-metal catalysts for the selective conversion of FAL to FOL [17], exhibiting superior catalytic performance due to the prior adsorption of η^1 (O)-aldehyde group of FAL on Cu. However, such adsorption approach of FAL on Cu results in the poor selectivity of THFOL. Therefore, it is of great importance to explore more non-noble metal catalysts for highly efficient selective conversion of FAL to THFOL [11]. Thanks to easy hydrogenation properties and relatively low cost, nickel-based catalysts have been recently investigated for FAL hydrogenation or hydrogenolysis process [18–21]. Different with the Cu-based catalysts, the adsorption of FAL on Ni mainly occurs through both η^1 (O)-aldehyde and η^2 (C,O)-aldehyde modes, leading to superior catalytic activity of selective hydrogenation of FAL to THFOL [20]. In this respect, Nakagawa et al. reported that total hydrogenation of FAL to THFOL in vapor-phase reaction environment can be achieved with a selectivity of 94.3% over a highly dispersed Ni/SiO_2 catalyst, and they thought that the total hydrogenation process of FAL to THFOL experiences two separate steps, namely, FAL to FOL and FOL to THFOL [20]. Generally, harsh reaction conditions (*e.g.*, high temperature of 413 K, high H_2 pressure of 4.6 MPa, long reaction time of 5 h) are required to obtain high selectivity of THFOL with almost complete conversion of FAL over metallic nickel catalysts [6], which is undoubtedly high energy consumption. Some studies have revealed that high selectivity of FAL to THFOL in relatively mild reaction conditions can be obtained using modified metallic nickel catalysts [17]. For example, Nakagawa et al. reported that THFOL with 96% selectivity by FAL hydrogenation can be achieved at 313 K under 8 MPa after 2 h reaction using Ni–Pd alloy catalyst [22]. Even so, the introduction of noble metal Pd inevitably enhances the cost of catalysts, limiting their scale-up production applications.

Recently, N-doped carbon supported metal catalysts have been widely investigated for catalytic hydrogenation reactions, demonstrating superior catalytic activity and selectivity owing to N doping effectively tuning the electronic structure and surface property of carbon supports to promote the catalytic performance [23,24]. The N atom possesses higher electronegativity than the C atom, doping with the electron-rich nitrogen atoms can modify the surface structure of carbon materials with enhanced π-binding ability and improved basicity [25,26]. These advantages resulted from N doping in carbon materials effectively promotes the catalytic hydrogenation performance of N-doped carbon supported metal catalysts. In this respect, Xu et al. synthesized N-doped carbon supported metal Pd catalyst ($Pd@CN_{0.132}$) for catalytic hydrogenation of vanillin in aqueous media under mild reaction conditions [27]. In their study, the high catalytic performance of $Pd@CN_{0.132}$ can be due to the electronic activation of metal Pd particles with high stability and uniform dispersibility in water and the effect of N doping in carbon support [27]. Recently, Cui and co-workers reported well-dispersed Ru nanoparticles supported on nitrogen-doped carbon material, exhibiting excellent catalytic activity and selectivity in the hydrogenation of aromatic ethers and phenols [28]. It has been generally accepted that N-doping in carbon structure can effectively regulate the surface electronic structure and physical/chemical property (*e.g.,* surface Lewis basicity resulted from pyridinic-N doping) of carbon material, demonstrating significantly improved electro-catalysis activity [29–31]. These benefits caused from N doping may be fully utilized to construct N-doped carbon supported non-noble metal (*e.g.*, metallic nickel) catalysts for improving catalytic hydrogenation performance under relatively mild reaction conditions.

Herein, N-doped activated carbon (AC) supported metallic nickel (Ni/NAC) catalysts were fabricated by two-step calcination method in N_2 atmosphere, and investigated for liquid-phase hydrogenation of FAL. It was found that N doping content and type in AC have important influence on the sizes of subsequent metallic nickel nanoparticles and catalytic hydrogenation activity of Ni/NAC. The results demonstrated that using N-doped AC with 1.0 g melamine at 1073 K in N_2 atmosphere as support, the obtained Ni/NAC at 873 K in N_2 atmosphere with Ni nanoparticle sizes of ~13.1 nm (denoted as Ni/NAC-1-1073) achieves a N doping content of 3.65 at.% and an atomic ratio of pyridinic-N to graphitic-N of 1.5, exhibiting almost 100% selectivity of THFOL with a complete FAL conversion at 353 K after 3 h reaction, obviously better than that of Ni/AC without N doping. Simultaneously, it was found that Ni/NAC-1-1073 can afford almost 100% conversion of FAL to FOL by transfer hydrogenation pathway in 2-proponal solvent at 413 K after 5 h reaction, while only 30.2% conversion of FAL to FOL can be obtained for Ni/AC without N doping under the identical experimental conditions. The performance enhancement mechanism has been discussed on the basis of the experimental results.

2. Experimental section

2.1. Preparation of Ni/NAC catalysts

Activated carbon (AC, Aladdin) was first washed by dilute acid and deionized water, followed by drying at 333 K for overnight. In a typical synthesis, 0.5 g AC and melamine with different amounts of 0.5, 1 and 2 g were dispersed into 10 mL of ethanol, and the resultant mixture was heated to 363 K to volatilize the solvent under stirring. The obtained solid mixture was dried at 333 K in air for 12 h, and then calcined at different pyrolysis temperatures (973, 1073 and 1173 K) for 2 h with a ramp rate of 2 K min^{-1} in N_2 atmosphere to obtain N-doped AC with different N doping contents and types. The prepared N-doped AC was denoted as NAC-x-y (x represents melamine mass and y represents pyrolysis temperature). For preparation of Ni/NAC-x-y, 0.5 g NAC-x-y was first dispersed into 0.5 mL of 3 mol L^{-1} nickel nitrate ($Ni(NO_3)_2·6H_2O$, AR, Sinopharm Reagents, China) to adequately adsorb Ni^{2+} for 30 min under ultrasonication. Subsequently, Ni^{2+}-adsorbed NAC-x-y was dried at 333 K for 12 h, and then calcined at 873 K for 2 h with a ramp rate of 5 K min^{-1} in N_2 atmosphere to obtain Ni/NAC-x-y catalysts. For comparison, Ni/AC without N doping was fabricated by the same procedure aforementioned except commercial AC instead of NAC-x-y as support.

2.2. Characterization

The morphologies of samples were obtained by transmission electron microscopy (TEM, JEOL-2010) operated at an acceleration voltage of 200 kV. Powder X-ray diffraction (XRD) patterns of the samples were recorded on a Philips X-Pert Pro X-ray diffractometer with using the Ni-filtered monochromatic Cu K_α radiation ($\lambda K_{\alpha 1} = 1.5418$ Å) at 40 keV and 40 mA. The surface area and porosity of samples were measured at 77 K by a Surface Area and Porosity Analyzer (Autosorb iQ Station 1). The composition of samples was analyzed on an ESCALAB 250 X-ray photoelectron spectrometer (Thermo, USA) equipped with Al $K_{\alpha 1,2}$ monochromatized radiation at 1486.6 eV X-ray source. Ni content in Ni/NAC-x-y composites was

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