



Factors influencing the activity of SiO₂ supported bimetal Pd-Ni catalyst for hydrogenation of α -angelica lactone: Oxidation state, particle size, and solvents



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ABSTRACT

We have previously reported the superior catalytic activity of Pd-NiO/SiO₂ to Pd-Ni/SiO₂ in hydrogenation of α -angelica lactone (α -AL) to gamma-valerolactone (GVL) in a batch reactor. To gain deeper insight into the structure-activity relationship of Pd-Ni bimetal catalyst, a series of NiO/SiO₂ with different NiO particle sizes (about 3, 9, and 20 nm in average) were prepared by impregnation method in the presence or absence of ethylene glycol. These materials were used as the support of Pd catalysts for the liquid-phase hydrogenation of α -AL in a fixed bed reactor. The corresponding reduced catalysts, namely Pd-Ni(3, 9, 20)/SiO₂ with different Ni particle sizes were obtained by in situ reduction before reaction and then their catalytic activities were investigated. By comparing the catalytic performances of Pd-NiO/SiO₂ and Pd-Ni/SiO₂ in water or tetrahydrofuran (THF), the effects of oxidation state and particle size of nickel species on the hydrogenation of α -AL in terms of activity and stability were systematically studied. The bimetal catalysts were characterized by BET, XRD, TEM and in situ XAS. The catalytic tests suggested that there was no clear correlation between the initial activity and the particle size of NiO or Ni species, whereas the catalyst durability was particle size dependent and solvent dependent as well. The deactivation mechanism is likely associated with a strong adsorption of organic species on the catalyst surface according to FTIR study on the adsorption behavior of α -AL and GVL on various materials, as well as the C1s XPS spectra of the spent catalysts. The beneficial effect of water in hydrogenation is thereby explained by the less coke tendency due to the relative stronger interaction between water and catalyst surface than that between THF and surface.

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1. Introduction

Bimetallic catalysts have been extensively studied recently because they outperform either of their parent metals in many important reactions [1–3]. Bimetallic catalysts often showed enhanced activity as well as good selectivity to the preferred products. Lee et al. [4] have demonstrated that the activity of bimetallic catalysts for hydrogenation of a carbonyl group can be 110 times higher than monometallic catalysts. It is generally accepted that the synergistic and cooperative catalytic performances between the bimetal components are attributed to the electronic and/or geometric effect between two metals, which will affect the adsorp-

tion energy of reactants and intermediates on the catalyst surface [5,6]. Among bimetallic catalysts, the combination of minute amount of noble metal and another transition metal is a very promising strategy which allows for the preparation of cheap yet active catalyst [7]. Pd-Ni bimetallic catalyst is such an interesting combination that has found wide applications in several reactions including, but not limited to, C–C coupling, aqueous-phase reforming, hydrogenation and oxidation [8–12]. The formation of Pd-Ni ensembles with various atomic ratios and the resulting electronic interaction are proposed to be responsible for their unique catalytic performance. It is believed that the presence of the Ni atoms in the surface provides the ensemble effect for the catalysis. Rai et al. [8] found that Ni-Pd bimetallic nanoparticle catalysts with high Ni to Pd atomic ratios (99:1) showed unprecedented high activity in C–C coupling reactions under moderate reaction conditions. Theoretical calculations suggested that a substantial Ni to Pd

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charge transfer occurred, resulting in a highly negatively charged Pd center which accounts for facile oxidative addition of aryl halides. Lu et al. [9] demonstrated the metal composition dependent activities of the Pd-Ni bimetallic nanocluster. The alloy containing an atomic ratio of Ni:Pd = 2:3 exhibited 3.5 times greater activity than that of a typical colloidal palladium catalyst. In another study, Budroni and coworkers [10] deposited Pd selectively onto pre-reduced nickel hydride surface by a redox reaction at different pH values of 1 and 3, forming a strong alloy and a weaker segregated nickel-palladium catalyst, respectively. The catalytic tests suggested that the strong alloy was more active for hydrogenation of crotonaldehyde, reinforcing the promotion effect on the hydrogenation reaction by ensembles of Pd atoms electronically modified by neighboring Ni atoms. The ensemble effect of neighboring Ni atoms is even more pronounced for catalyst prepared by photo-assisted deposition (PAD) method in nitrobenzene hydrogenation [11]. A volcano effect is observed in terms of hydrogenation activity and the Ni/Pd ratio, with 1.5 mol% Ni/Pd ratio being the best one. The authors proposed that the surface Pd and Ni atoms account for the activation of hydrogen and adsorption of benzene ring, respectively. Nakagawa and co-workers [12] also found that Ni-Pd bimetallic catalyst with atomic ratio of Ni: Pd = 7:1 supported on silica was more active than commercial Raney Ni and more selective than Pd/C for the hydrogenation of 5-hydroxymethyl-2-furaldehyde. These studies emphasize the vital role of Pd-Ni ensemble effect in catalysis. In general, a bimetallic particle with specific composition of Ni/Pd is preferred.

On the other hand, the catalytic activity or selectivity of noble metal nanoparticles can be greatly enhanced by putting an oxide additive adjacent to the active metal due to the so-called metal-support interaction [13–15]. Very recently, Kennedy and coworkers have clearly illustrated that the reducible metal oxides such as TiO₂ and Co₃O₄ as support most likely regulate the preferential adsorption mode of reactants therefore tuning the selectivity of products [14,15]. Similarly, nickel oxide (NiO) also significantly improves the catalytic performance of Pd nanoparticles in aforementioned reactions [16–22]. Nie et al. [16] reported that the intimate interaction between Ni₂O₃ nanoparticles and Pd clusters appears to be beneficial for activating the Pd surface for the Suzuki–Miyaura cross-coupling reactions. Zhou et al. [17,18] found that the presence of NiO next to Pd nanoparticles may favor the hydrogenation of p-chloronitrobenzene while achieving high selectivity to p-chloroaniline by minimizing the formation of dechlorinated by-products such as aniline and p-aminophenol. Shi and coworkers showed that the NiO supported Pd nanoparticles are highly active catalysts for selective hydrogenation of nitroaromatic compounds and substituted aromatic rings, as well as reductive amination of aldehydes and amine [19–21]. By comparing the activity of Pd supported on nickel-doped carbon aerogel and that on commercial NiO particles, a distinct NiO structure-dependent catalytic activity was noticed [19]. More interestingly, the interaction between Pd and NiO is also related to the exposed facets of Pd nanoparticles [22].

Based on the above results, it can be concluded that both metallic Ni and oxidic NiO can remarkably enhance the catalytic performance of Pd centers via distinct mechanisms depending on the catalyst preparation means and reaction conditions. We have recently demonstrated that a series of Pd-xNiO/SiO₂ with very low Pd loading (0.2 wt.%) can efficiently catalyze the hydrogenation of α -Angelica lactone (α -AL) to gamma-valerolactone (GVL) under mild conditions [23]. However, the catalytic activities of Pd-xNiO/SiO₂ (x > 5 wt.%) dramatically decreased when NiO was reduced to metallic Ni in the batch reactor, meaning that the structure change of Ni species significantly affects the overall hydrogenation activity. Herein we conducted a continuous study on the factors influencing the activity of bimetal Pd-Ni catalyst for

hydrogenation of α -AL in a high pressure fixed-bed reactor, such as oxidation state, particle size, and solvents.

2. Experimental section

2.1. Materials

Nickel(II) nitrate hexahydrate (Ni(NO₃)₂·6H₂O, AR), Ethylene glycol (AR), sodium hydroxide (AR), sodium borohydride (AR) were all purchased from Sinopharm chemical agent Co., Ltd. Palladium (II) chloride (99.9%) was provided by J&K Chemical. SiO₂ (AEROSIL-A200) from Degussa was used without further treatment.

2.2. Preparation of NiO/SiO₂ supports with different particle sizes

NiO/SiO₂ samples were prepared by incipient impregnation with Ni(NO₃)₂·6H₂O as precursor. Our previous study has shown that when NiO content was 10 wt.%, the Pd-NiO/SiO₂ reached the highest hydrogenation activity. Therefore, 10 wt.% was chosen for all supports in this study. The particle size of NiO was tuned by adopting literature method [24] using varying amount of ethylene glycol (EG) as modulator and denoted as NiO(\sim x)/SiO₂, wherein x (= 20, 9, and 3 nm) stands for the average particle size of NiO.

NiO(\sim 20)/SiO₂. The preparation of large NiO particles was performed as described in our previous study [23]. Desired amount of Ni(NO₃)₂·6H₂O was incipiently impregnated on SiO₂, dried and then calcined at 500 °C in air for 1 h with heating rate of 10 °C/min.

NiO(\sim 9)/SiO₂. To decrease the NiO particle size, EG was introduced during the impregnation step with EG/Ni²⁺ mole ratio of 0.2. The sample was dried at 110 °C overnight and then calcined at 400 °C for 2 h with heating rate of 2 °C/min.

NiO(\sim 3)/SiO₂. To further decrease the NiO particle size, more amount of EG was introduced with EG/Ni²⁺ mole ratio of 5. The sample was dried at 110 °C overnight and then calcined at 400 °C for 2 h with heating rate of 2 °C/min.

2.2.1. Preparation of Pd catalysts

Supported Pd catalysts (\sim 0.25 wt.% Pd) are prepared by a typical deposition-precipitation-reduction method. The support (0.5 g) was dispersed in H₂O (60 mL) with stirring. A desired amount of H₂-PdCl₄ aqueous solution (21.512 g_{Pd}/L) was added to the mixture and stirred for 3 h. The final pH value of the suspension was adjusted to 10 by adding NaOH solution (1 M). Then, NaBH₄ aqueous solution (NaBH₄/Pd = 20, molar ratio) was added into the suspension and the mixture was stirred for another 30 min allowing for the full reduction of Pd²⁺ species. Thus obtained catalyst was dried at 110 °C overnight. The sample was denoted as Pd-NiO(\sim x)/SiO₂ (x stands for the average particle size of NiO based on XRD).

Pd-Ni(\sim x)/SiO₂ catalysts were obtained by in situ reduction with flowing hydrogen (60 mL/min) prior to reaction. The catalyst was heated from r.t. to 460 °C with heating rate of 5 °C/min and kept for 10 min. Then the reduced catalyst was cooled to 30 °C in flowing H₂.

2.3. Characterization

The power X-ray diffraction (XRD) patterns were collected on a Rigaku Ultima IV X-ray diffractometer using Cu K α radiation (λ = 1.5405 Å) operated at 35 kV and 25 mA. Transmission electron microscopy (TEM) images were taken on a FEI Tecnai G² F30 microscope operating at 300 kV.

Nitrogen adsorption-desorption isotherms at –196 °C were obtained on a BELSORP-Max equipment. Prior to the measurement, the samples were first degassed at 150 °C under vacuum for 6 h. Specific surface areas (SSA) were calculated by the Brunauer-

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