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Short Communication

Total hydrogenation of furan derivatives over silica-supported Ni-Pd alloy catalyst

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ABSTRACT

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1. Introduction

Hydrogenation is one of the most basic chemical transformations of organic substances. The importance of hydrogenation is even growing, since biomass-derived materials with high content of oxygen have been expected to play substitutes for petroleum as the sources of chemical products [1–4]. In this context, hydrogenations of unsaturated aldehyde such as furfural have been extensively studied in recent years [5-8]. The conversion processes from the hydrogenated products such as tetrahydrofurfuryl alcohol to more valuable compounds such as α, ω -diols have been also studied [9–11]. 5-Hydroxymethyl-2-furaldehyde (HMF) can be synthesized by the dehvdration of hexoses or even cellulose and is one of the most promising intermediates in the transformation of biomass into valuable products [12-21]. The hydrogenation of HMF has been tested by several groups using conventional catalysts such as Raney Ni, copper chromite, and carbon-supported noble metals (typically Pd) [22-24]. The products depend on the catalysts and reaction conditions, and are typically 2,5-bis(hydroxymethyl)furan (BHF), 2,5-bis(hydroxymethyl)tetrahydrofuran (BHTF), 2,5-dimethylfuran [23], and ring-opened products [22] (Scheme 1). The production of BHTF is important because BHTF is a key intermediate to convert renewable resources to 1,6-hexanediol, which is currently produced from petroleum and massively utilized in the manufacture of polymer plastics [25]. High yields of BHTF in the hydrogenation of HMF require harsh conditions (e.g. 433 K [22]) or large amount of catalysts [24], and the development of a more active catalyst may be

The Ni–Pd bimetallic catalysts supported on silica were prepared by co-impregnation method. The catalyst with Ni/Pd = 7 showed the best catalytic performance for the hydrogenation of 5-hydroxymethyl-2-furaldehyde (HMF). The catalyst was more active than commercial Raney Ni and more selective than Pd/C. The yield of 2,5-bis (hydroxymethyl)tetrahydrofuran reached 96%. Hydrogenation of other furanic compounds, cyclohexanone, phenol, and alkenols also proceeded. Characterizations by TEM and XRD revealed that Ni–Pd alloy particles were formed on Ni–Pd/SiO₂ (Ni/Pd = 7).

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necessary. Moss et al. have reported that Ni–Pd alloy catalysts with large Pd content (Ni/Pd \leq 3) are more active than monometallic Ni or Pd catalysts in hydrogenation of ethylene, and the best composition is 70% Pd [26]. Recently, Bertolini et al. have reported that Pd layers on the surface of Ni or Ni-rich Ni–Pd alloy show much higher TOFs in butadiene hydrogenation than the surface of bulk Pd [27–30]. However, attempts to prepare supported Ni-rich Ni–Pd bimetallic catalysts with higher performance than Pd have met with little success [31–34]. In this paper, we report that SiO₂-supported Ni–Pd alloy catalyst with Ni/Pd ratio of 7 catalyzes total hydrogenation of furanic compounds including HMF at low temperature (313 K) with high activity and selectivity.

2. Experimental

2.1. Preparation of catalyst

The catalysts were prepared by impregnating SiO₂ (G-6, Fuji Silysia Chemical Ltd., BET surface area 535 m²/g, granular size <100 mesh) with mixed aqueous solutions of Ni(NO₃)₂·6H₂O (WAKO Pure Chemical Industries, Ltd.) and PdCl₂ (Soekawa Chemical Co., Ltd.). After evaporating, they were dried at 383 K overnight and calcined in air at 773 K for 3 h. The reduction was conducted in H₂ flow from room temperature to 773 K (hold 0.5 h) at a heating rate of 10 K min⁻¹. After cooling, the reduced catalyst was passivated with 2% O₂/He flow for 2 h. Loading of Pd was 2 wt.%. The ratio of Ni to Pd was optimized to maximize the conversion of HMF and yield of the total hydrogenation product in hydrogenation catalysis, and was determined to be Ni/ Pd = 7 (molar basis). X-ray diffraction (XRD) patterns were recorded by a Philips X'pert diffractometer. TEM images were taken with a HITACHI HD-2700 microscope. Average particle size was calculated by

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Scheme 1. Hydrogenation of HMF.

 $\Sigma n_i d_i^3 / \Sigma n_i d_i^2$ (d_i : particle size, n_i : number of particle with d_i). Activated Raney Ni was supplied from Sigma-Aldrich Co., Ltd. Pd/C (5 wt.% Pd) was purchased from N. E. Chemcat. 5-Hydroxymethyl-2-furaldehyde (TCI) was purified by column chromatography (Silica gel 60 (Merck), methanol/ether = 2/98), which procedure was essential for reproducible results. Furfural (WAKO) was purified by distillation. Cyclohexanone (WAKO), phenol (WAKO), 3-buten-1-ol (TCI) and crotyl alcohol (TCI) were used as received. 2,5-Bis(hydroxymethyl) furan (BHF) was synthesized by hydrogenation of 5-hydroxymethyl-2-furaldehyde with sodium borohydride and checked by NMR and MS. 2,5-Bis(hydroxymethyl)tetrahydrofuran (BHTF) was separated from the reaction mixture by column chromatography (silica gel 60, methanol/ether = 5/95) and checked by NMR and MS.

2.2. Activity test

Activity tests were performed in a 190-ml stainless steel autoclave with an inserted glass vessel. An aqueous solution of substrate (0.5 M) was put into the autoclave together with a spinner, catalyst and acetic acid. After sealing the reactors, their air content was purged by flushing with argon. Autoclaves were then heated to 313 K, and the gas phase was replaced with 8 MPa hydrogen. Stirring rate was 500 rpm. After an appropriate reaction time, the autoclave contents were transformed to vials and the catalysts were separated by filtration. The gas phase was also collected in a gas bag. The products were analyzed using a gas chromatograph equipped with FID. A TC-WAX or an InertCap 5 capillary column was used for the separation. Products were also identified using GC–MS (Shimadzu QP 5050).

3. Results and discussion

TEM image of Ni–Pd/SiO₂ (Ni/Pd = 7) after reduction and passivation treatments is shown in Fig. 1. Particles with an average size of 10.7 nm were formed on SiO₂ support. In the XRD pattern (Fig. 2), no signals assignable to pure Ni (2θ = 44.5 and 51.7°) or Pd (40.1, 46.7 and 68.1°) were observed. Instead, there were signals at 43.7 and 50.8°, which corresponded to the fcc structure with a bond length of 2.53 Å. This value agreed with the average of 7Ni (2.49 Å) + Pd (2.75 Å), suggesting the formation of an alloy. This forms a marked contrast to the reported difficulty in obtaining supported Ni–Pd alloy with



Fig. 1. (a) TEM image of Ni-Pd/SiO₂ (Ni/Pd=7) and (b) size distribution of particles.

homogeneous composition by simple co-exchange method [35]. The linewidth of the signal at 43.7° (1.6° at half maximum) was larger than that (0.8°) calculated for 10.7 nm crystal by Scherrer's equation. It has been reported that Pd tends to be concentrated into near-surface layers (up to four layers [36]) in Ni–Pd alloy to lower the surface energy [31-34,36], which might cause the broadening of the signals.

The results of the hydrogenation of HMF were summarized in Fig. 3. Raney Ni and Ni/SiO₂ catalysts showed little activity. The main product was BHF, showing that the aldehyde group of HMF was first hydrogenated. The Pd/SiO₂ catalyst showed a higher activity than Ni catalysts and the main product was also BHF. On the other hand, the bimetallic Ni–Pd/SiO₂ catalysts showed a much higher activity and that with Ni/Pd = 7 (molar ratio) showed the best performance. It



Fig. 2. XRD patterns of Ni/SiO₂, Pd/SiO₂ and Ni–Pd/SiO₂ (Ni/Pd = 7).



Fig. 3. Hydrogenation of HMF over various catalysts. Conditions: HMF (0.5 M aq., 10 ml), acetic acid (5.7 μ l; 0.1 mmol), catalyst (19 μ mol Pd), H₂ (8 MPa), 313 K, 0.5 h. ^aRaney Ni (100 mg; ca. 1.4 mmol Ni). ^bNi/SiO₂ (10 wt.%, 100 mg; 170 μ mol Ni).

Table 1 Hydrogenation of unsaturated compounds over Ni-Pd/SiO₂ $(Ni/Pd = 7)^{a}$.

Entry	Substrate	H ₂ [MPa]	Temp. [K]	Time [h]	Conv. [%]	Hydrogenation products (yield [%])
1	HMF	8	313	2	99	BHTF (96), BHF (<1),
						HMTF (1)
2 ^b	Furfural	8	313	2	99	Tetrahydrofurfuryl
						alcohol (96)
3 ^c	Furan	8	313	2	99	Tetrahydrofuran (98)
4	Cyclohexanone	1	313	2	99	Cyclohexanol (99)
5	Phenol	8	353	48	97	Cyclohexanol (97)
6 ^d	3-Buten-1-ol	0.2	313	4	99	1-Butanol (86)
7 ^d	Crotyl alcohol	0.2	313	4	99	1-Butanol (83)

 a Conditions: substrate (0.5 M aq.; 10 ml), acetic acid (5.7 $\mu l,$ 0.1 mmol), catalyst (100 mg, 19 μmol Pd), and H_2 (8 MPa), 313 K.

^b Acetic acid (0.02 mmol).

- ^c Furan (0.1 M aq., 50 mL).
- ^d Catalyst (50 mg), acetic acid (0.02 mmol). By-products were 1- and 2-butenes in both cases.

should be noted that the hydrogenation of furan ring as well as that of aldehyde group significantly proceeded on this catalyst. With longer reaction time $(0.5 \rightarrow 2 \text{ h})$, the yield of the total hydrogenation product BHTF reached 96% (Table 1, entry 1). On the other hand, physical mixture of Ni/SiO₂ and Pd/SiO₂ gave no enhancing effect on the conversion of HMF and the selectivity to tetrahydrofuran derivatives, showing the synergetic effects in Ni–Pd/SiO₂ catalyst. While commercial Pd/C catalyst showed high conversion, side reactions such as C–O dissociation proceeded significantly and the selectivity to BHTF was poor. Lower selectivity to BHTF in the Pd/C-catalyzed hydrogenation than those of Ni-based catalysts has been reported [24].

The Ni–Pd/SiO₂ (Ni/Pd = 7) catalyst was applied to the hydrogenations of various water-soluble substrates (Table 1). Furfural, which is also an important intermediate in the transformation of biomass, was hydrogenated to tetrahydrofurfuryl alcohol in a high yield of 94% (entry 2). Hydrogenation of unfunctionalized furan also proceeded (entry 3). Both cyclohexanone and phenol were highly selectively converted into cyclohexanol (entries 4 and 5). Hydrogenations of alkenols also proceeded (entries 6 and 7). Therefore, Ni–Pd/SiO₂ (Ni/Pd = 7) is a highly active and selective catalyst for the total hydrogenation of unsaturated compounds in water. In this system, reuse of the catalyst lowers the activity (the catalyst recovered by

centrifugation gave 39% conversion of HMF and 21% selectivity to BHTF in the same conditions in Fig. 3) probably because of the leaching of Ni during the activation of oxidized particle surface with an acid. Indeed, ICP-AES analysis showed that 16% of Ni was leached from Ni–Pd/SiO₂ during the reaction of entry 1 in Table 1 while no leaching of Pd was observed. Application of the catalyst to systems more immune to leaching, e.g. gas phase hydrogenations, is a future work.

4. Conclusions

Co-impregnation of Ni and Pd with a Ni/Pd molar ratio of 7 on silica and subsequent calcination–reduction procedure produced bimetallic particles. The supported particles catalyzed the total hydrogenation of unsaturated compounds including bio-derived HMF and furfural in water. The catalyst was easy to prepare and handle, and was more active than commercial Raney Ni and more selective than Pd/C.

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