

Boron nitride supported PtFe catalysts for selective hydrogenation of crotonaldehyde

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Abstract

The selective hydrogenation of crotonaldehyde was studied using boron nitride (BN) supported PtFe catalyst. A higher selectivity of crotyl alcohol than butyraldehyde was obtained, although butyraldehyde is thermodynamic favorable in the hydrogenation. The catalyst, PtFe/BN, was prepared by co-incipient wetness method. The metal loadings were 1.1 wt.% Pt and Fe ranging 0.1–0.6 wt.%. Commercial catalyst supports, graphite and γ -Al₂O₃, were also used to compare with BN. The higher iron content, the higher the crotyl alcohol selectivity was, while the activity was depressed. PtFe/ γ -Al₂O₃ gave the lowest selectivity of crotyl alcohol. PtFe/graphite had the product selectivities similar to PtFe/BN, but its activity was lower than that of PtFe/BN. A maximum yield of crotyl alcohol was found at 0.2 wt.% Fe (molar ratio Fe/Pt = 0.64) on PtFe/BN catalysts at 100 °C. XRD revealed that PtFe alloy was formed on PtFe/BN during H₂ reduction at 300 °C. The improvement of selectivity toward crotyl alcohol was attributed to the easier formation of PtFe alloy particle on BN surface than on γ -Al₂O₃. The Fe²⁺ on PtFe alloy polarizes the C=O bond of crotonaldehyde and the nearby Pt⁰ supplies the absorbed hydrogen to conduct the hydrogenation of the C=O bond, instead of the C=C bond. Therefore, both activity and the selectivity toward crotyl alcohol were enhanced appreciably.

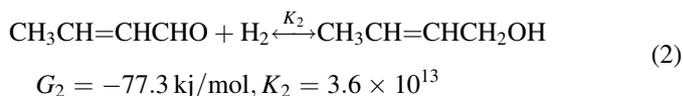
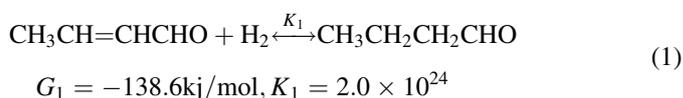
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Keywords: PtFe catalyst; Boron nitride; Selective hydrogenation; Crotonaldehyde

1. Introduction

The selective hydrogenation of an α , β -unsaturated aldehyde into an unsaturated alcohol is an important process in the pharmaceutical, fine chemicals, and fragrance industries [1]. However, the hydrogenation of the C=C bond is thermodynamically favorable over the C=O bond, which leads to the undesirable product, saturated aldehydes. Based on Gibbs free energy calculation, butyraldehyde is favorable product of crotonaldehyde hydrogenation. Eqs. (1) and (2) show the Gibbs free energies and equilibrium constants of butyraldehyde and crotyl alcohol from crotonaldehyde hydrogenation at 298 K, respectively [2]. The equilibrium constant of butyraldehyde is eleven order of magnitudes higher than that of crotyl alcohol. Improved selectivity for unsaturated alcohols was achieved by using reducible supports or additive promoter [3–6]. Supported bimetallic PtFe catalyst was also suggested to be an effective catalyst for the selective hydrogenation of α , β -unsaturated

aldehyde into an unsaturated alcohol, such as crotonaldehyde to crotyl alcohol [7,8].



Materials traditionally used as supports are insulating oxides such as SiO₂, γ -Al₂O₃, silica-alumina, and various zeolites. These oxides possess large surface area, numerous acidic/basic sites, and metal-support interaction that offer particular catalytic activity for many reactions. Metal oxides have also been thoroughly studied and employed in the chemical industry for decades. On the other hand, non-oxide materials hold many unique properties unlike metal oxides, such as high thermal conductivity, acid-base resistance and possibly negligible metal-support interaction. Such catalytic properties are worth to explore. Boron nitride (BN) has been used as catalyst support

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recently [9,10]. The graphite-like hexagonal BN is the most stable BN isomer under ambient conditions [11]. In general, BN is inert material for catalytic reaction. In a supported metal system such as Pt/BN, BN has been shown to have a negligible interaction with Pt in the catalytic oxidation [9]. The easy migration of Pt particles occurred on the crystalline face of BN due to the weaker bonding between the crystalline face and Pt [9,10]. Such effect may promote the metal sintering and lead to the formation of bimetallic alloy, a favorable active site for the selective hydrogenation of α , β -unsaturated aldehyde into unsaturated alcohol [7,8]. We therefore chose crotonaldehyde hydrogenation to investigate the unique catalytic property provided by a novel BN support. Our previous study indicated that PtSn alloy on BN support significantly enhanced the selectivity toward crotyl alcohol in crotonaldehyde hydrogenation [12]. In this study, the Fe addition on the surface characteristics and properties of Pt were explored in relation to the activity/selectivity of crotonaldehyde hydrogenation in vapor phase. The influence of different supports and the ratio of H_2 /crotonaldehyde on product selectivity were also studied.

2. Experimental

2.1. Catalyst preparation

Hexagonal-BN was obtained from High Performance Materials Inc. (Taiwan). It was crystallized at roughly 800 °C during synthesis, a temperature lower than the typical 1000 °C. Gamma alumina (γ - Al_2O_3) from Merck (USA) and graphite (G) from Hon-Ming Tech (Taiwan) were used as supports for comparison. Precursor salt, $H_2PtCl_6 \cdot 6H_2O$ (Alfa Aesar), contains approximately 40 wt.% platinum. Reagent grade $Fe(NO_3)_3 \cdot 9H_2O$ were purchased from Riedel-de Haen. Methanol (Fluka) was chosen as the diluting solvent for improved soaking of the hydrophobic BN and graphite supports. The supported PtFe catalysts were prepared utilizing a co-incipient wetness method. The quantity of methanol required to completely fill the support's pore volume was predetermined. Calculated amounts of Pt and Fe precursor salts were dissolved together in methanol to obtain the desired metal loadings. After the co-incipient wetness process was applied, catalysts were air-dried at room temperature for 24 h; these are referred to as fresh catalysts. The detailed incipient wetness procedure can be found in the literature [13]. Pt loading was fixed at 1.1 wt.%; Fe loadings varied from 0.1 to 0.6 wt.%. The X.X wt.% of Fe loading was assigned as Pt1.1FeX.X/BN (or G, γ - Al_2O_3). In addition, monometallic 1.1 wt.% Pt and 0.8 wt.% Fe catalysts were also prepared for comparison. In some catalysts, both Pt and Fe loadings proportionally increased four times in order to obtain enough signal strength in characterization. The catalytic hydrogenation was also tested on these catalysts. The product selectivities were found to be the same as those with normal metal loadings.

2.2. Characterization

The specific surface area of the support was measured by N_2 adsorption in Micromeritics ASAP 2010. The particle sizes and

distributions of BN, graphite and Al_2O_3 were measured by laser-light scattering. Al_2O_3 was suspended and dispersed ultrasonically in water for 3 min. BN or graphite was dispersed in ethanol due to its hydrophobicity. Coulter LS 230 was used to measure the scattering of incidental light at the 90° position, then the particle size was calculated using the Fraunhofer equation. Fresh catalyst was reduced in H_2 flow at 300 °C for 2 h before chemisorption. The H_2 chemisorption procedures were similar to those described by Yang and Goodwin [14]. The amount of irreversible H_2 chemisorption was taken to determine the Pt dispersion. A transmission electron microscope (TEM, Hitachi H-7100) was employed to observe the shape of BN and the appearance of PtFe particles dispersed on the support. The crystalline phases of catalysts were identified by X-ray diffraction (XRD). The XRD equipment, type M03XHF22 from the Material Analysis and Characterization Company, was operated at 40 kV, with a 1.54056 Å X-ray wavelength from a Cu target, and a scanning speed of 0.5°/min. X-ray photoelectron spectroscopy (XPS) was conducted on a spectrometer of VG Microtech MT500. The measured binding energy was referenced to carbon (1s) at 285.6 eV. The reduction of fresh PtFe catalyst was studied using the temperature programmed reduction (TPR). The gas used in TPR was a mixture of 5 vol.% H_2 in Ar. A fresh catalyst was loaded into a quartz tube and purged with N_2 . The gas was then switched to the H_2 /Ar mixture at room temperature. The TPR was performed in the H_2 /Ar mixture from 30 to 600 °C at a constant heating rate of 10 °C/min.

2.3. Catalytic reaction

Fresh catalyst (0.3 g) was charged in the middle of a straight-tube quartz reactor with a 10-mm I.D. The catalyst was reduced for 2 h at 300 °C, using pure hydrogen (99.999%) in the reactor and then cooled to 40 °C before switching to the reactant mixture. The reactant mixture was composed by flowing pure hydrogen into a saturator filled with liquid crotonaldehyde. Crotonaldehyde (98%) was purchased from Fluka. The concentration of crotonaldehyde in the reactant mixture was adjusted by tuning the saturator temperature, and the concentration was further confirmed by an on-line GC before reaction. The molar ratio of H_2 /crotonaldehyde mixture varied from 30 to 90 and passed through the reactor at 50 ml/min under atmospheric pressure. The reaction temperature was increased from 40 to 120 °C in a tubular furnace. A thermocouple was placed in the center of the catalyst bed to record the reaction temperature and to control the furnace. All gas lines were wrapped in heating tape and kept warm to prevent condensation. The products of crotonaldehyde hydrogenation were measured by an on-line GC (HP GC6890) equipped with a 30 m HP-Innowax capillary column using a flame ionization detector. The activities of PtFe catalyst were measured after achieving steady-state at 40 °C. It took about 30 min to obtain steady-state conversion. The reaction temperature was then raised to 60 °C, 80 °C, 100 °C and 120 °C to investigate the variations of conversion and product selectivity. The same hydrogenation reaction conducted on Fe/

Table 1
Hydrogen chemisorption of BN supported metal catalysts

Catalyst	Fe (wt.%)	Fe/Pt(at)	H ₂ (μmol/g-cat)	H/Pt
Pt1.1/BN	0	0.00	7.93	0.28
Pt1.1Fe0.1/BN	0.1	0.32	6.15	0.22
Pt1.1Fe0.2/BN	0.2	0.64	5.53	0.20
Pt1.1Fe0.4/BN	0.4	1.27	4.13	0.15
Pt1.1Fe0.6/BN	0.6	1.91	0.60	0.02
Pt1.1/G ^a	0	0.00	15.04	0.53
Pt1.1Fe0.2/G	0.2	0.64	11.82	0.42
Pt1.1Fe0.4/G	0.4	1.27	6.76	0.24
Pt1.1Fe0.6/G	0.6	1.91	4.04	0.14
Pt1.1/γ-Al ₂ O ₃	0	0.00	36.06	1.28
Pt1.1Fe0.2/γ-Al ₂ O ₃	0.2	0.64	6.01	0.21
Pt1.1Fe0.4/γ-Al ₂ O ₃	0.4	1.27	4.84	0.17
Pt1.1Fe0.6/γ-Al ₂ O ₃	0.6	1.91	4.29	0.15

Catalysts H₂ reduced at 300 °C for 2 h before chemisorption.

^a G: graphite.

BN catalyst and BN support found no activity up to 100 °C. The conversion of crotonaldehyde and the selectivity of product were calculated using Eqs. (3) and (4). The yield of crotyl alcohol was calculated by multiplying the conversion by its selectivity.

Conversion (%)

$$= \frac{C_{\text{crotonaldehyde Input}} - C_{\text{crotonaldehyde Output}}}{C_{\text{crotonaldehyde Input}}} \times 100\% \quad (3)$$

$$\text{Selectivity} = \frac{C_{\text{product}}}{C_{\text{crotonaldehyde Input}} - C_{\text{crotonaldehyde Output}}} \quad (4)$$

3. Results

The specific surface areas of BN, graphite and γ-Al₂O₃ are 46.3, 7.8 and 114.9 m²/g, respectively. The mean particle size of BN, graphite and γ-Al₂O₃ are calculated to be 2.8, 11 and 66.4 μm, respectively, from the results of the laser-light scattering. Table 1 summarizes the results of H₂ chemisorption on all catalysts. Various H₂ chemisorptions of monometallic Pt on BN, graphite and γ-Al₂O₃ indicate the different Pt dispersions, which are due to the nature of supports. The

lowest Pt dispersion on BN is because the easy migration of Pt creates large particle on BN surface during H₂ reduction. For all catalysts, the higher the Fe loading, the lesser the H₂ chemisorption. The amounts of H₂ chemisorption on PtFe catalysts decrease due to the Fe dilution or coverage of the surface Pt in these catalysts. The support, γ-Al₂O₃, shows the ratio of H/Pt > 1 may be caused by H₂ spillover.

3.1. Hydrogenation of crotonaldehyde

Fig. 1 depicts the reaction paths of α, β hydrogenation on crotonaldehyde. The product is either crotyl alcohol or butyraldehyde via C=O or C=C hydrogenation. Butyraldehyde is thermodynamically favorable in crotonaldehyde hydrogenation based on Gibbs free energy calculation. The final product is butanol with further hydrogenation of either crotyl alcohol or butyraldehyde.

Fig. 2 shows the effect of Fe loadings on the selectivity of crotyl alcohol and the yields of products on BN supported catalysts at 100 °C. The yields of crotyl alcohol, butanol and butyraldehyde increase because the conversions increase with Fe adding on the catalysts. When Fe loadings increase from 0.1 to 0.6 wt.%, the yields of butyraldehyde and butanol decrease significantly. The selectivity of crotyl alcohol consistently increases with Fe loading is due to the suppression of butyraldehyde and butanol. Such trends are similar in other temperatures (i.e. 40, 60, 80 and 120 °C). A 0.2 wt.% Fe loading (i.e. Pt1.1Fe0.2/BN) shows an optimum combination of crotyl alcohol selectivity and conversion resulting in the highest yield.

Fig. 3 shows the conversions of crotonaldehyde hydrogenation and the selectivities of crotyl alcohol, butanol and butyraldehyde on Pt1.1Fe0.2/BN catalyst in the reaction temperature ranging 40–120 °C. By and large, the selectivities of three products change within a narrow range from 40 to 120 °C. The selectivity of crotyl alcohol increases slightly with increasing temperature up to 100 °C. The conversion and the selectivity of crotyl alcohol increased simultaneously implies that not only the rate of crotonaldehyde hydrogenation is increased but also the hydrogenation of C=C is significantly suppressed. On the other hand, the selectivity of butanol decreases to 100 °C then slightly increases at 120 °C because high temperature (>100 °C) accelerates the hydrogenation thus increases the final product, butanol.

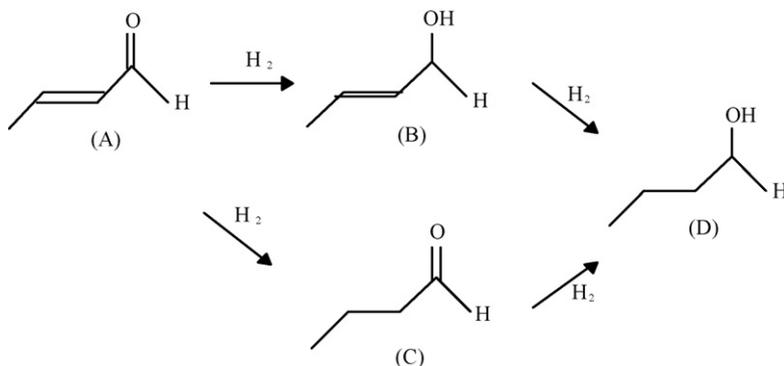


Fig. 1. The hydrogenation path of crotonaldehyde: (A) crotonaldehyde, (B) crotyl alcohol, (C) butyraldehyde, (D) butanol.

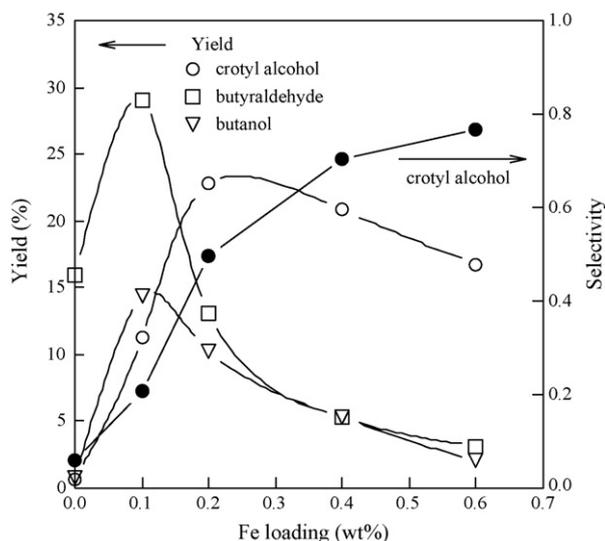


Fig. 2. The effect of Fe loadings on the conversions and selectivities on PtFe/BN catalysts at 100 °C, feed 50 ml/min, H_2 /crotonaldehyde = 59.

The influence of H_2 partial pressure is shown in Fig. 4. The conversions increase with H_2 /crotonaldehyde ratio because of increasing reaction rate by higher H_2 pressure. The selectivity of crotyl alcohol only decrease slightly with increasing H_2 pressure. Butanol is the final product from further hydrogenation (Fig. 1). Therefore, butanol is favorable under higher H_2 pressure and its selectivity increases.

The conversions and product selectivities varied substantially on different catalysts. However, temperature is found to be a weak effect on the product selectivity under our experimental conditions. For a certain catalyst, its product selectivities only slightly change in the temperature range of 40–120 °C. For conciseness, a reaction temperature 100 °C is selected to represent the performance of all catalysts. Table 2 summarizes the activity, conversion, the crotyl alcohol

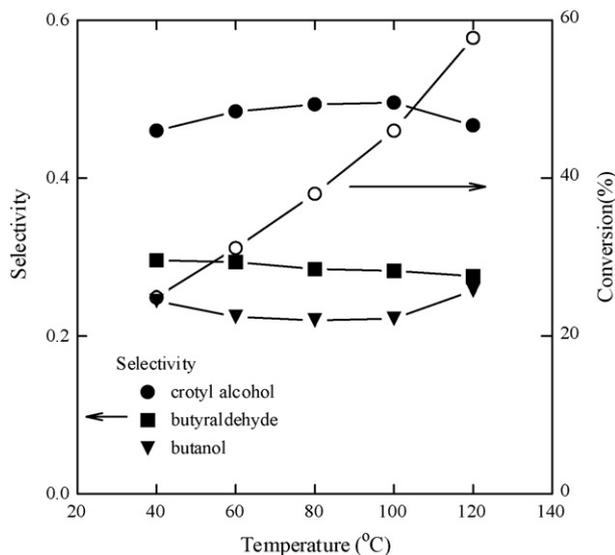


Fig. 3. Conversion of crotonaldehyde and selectivity of products on Pt1.1Fe0.2/BN, feed 50 ml/min, H_2 /crotonaldehyde = 59.

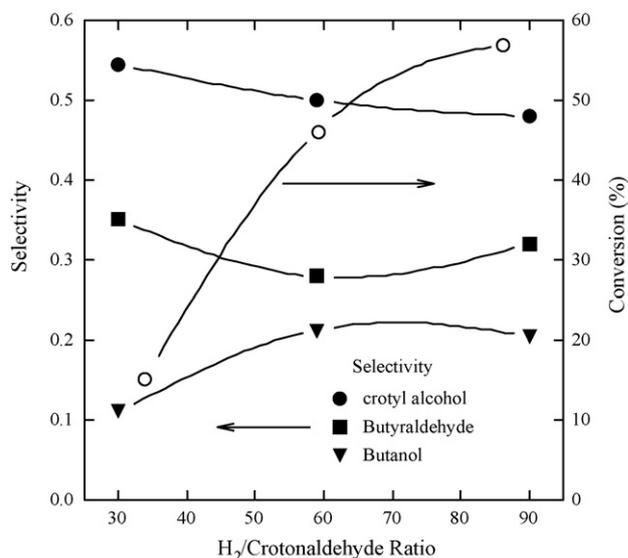


Fig. 4. Effect of H_2 /crotonaldehyde ratio on conversion and selectivities in Pt1.1Fe0.2/BN at reaction temperature 100 °C, feed 50 ml/min.

selectivity and yield for all catalysts at 100 °C. Among the monometallic Pt catalysts, the Pt1.1/BN has the lowest conversion, 17.1%, compared with those of Pt1.1/G and Pt1.1/ γ - Al_2O_3 . The low activity of Pt/BN is obviously due to its poor Pt dispersion (Table 1). All monometallic catalysts give very low crotyl alcohol selectivity.

Surface Pt is the major role in the hydrogenation because of its capability of H_2 dissociation. Fe addition suppresses the activity of hydrogenation due to the Fe coverage yet increases the crotyl alcohol selectivity. Although the exposure Pt can be expressed by H_2 chemisorption (Table 1), the active site may be underestimated due to the influence of Fe on PtFe catalysts. In stead of turnover frequency (TOF), the activity is reported based on the Pt loading to show the efficiency of Pt contribution.

The selectivity of crotyl alcohol increases substantially on bimetallic PtFe catalysts under the same reaction conditions.

Table 2
Summary of the crotonaldehyde hydrogenation on all catalysts at 100 °C

Catalyst	Conversion (%)	Selectivity	Yield (%) ^a	Activity (mmol/g-Pts)
Pt1.1/BN	17.1	0.04	17.1	1.93
Pt1.1Fe0.1/BN	57.9	0.21	12.2	6.14
Pt1.1Fe0.2/BN	46.1	0.50	23.1	5.20
Pt1.1Fe0.4/BN	29.5	0.71	20.9	3.33
Pt1.1Fe0.6/BN	21.8	0.77	16.8	2.46
Pt1.1/G ^b	59.7	0.16	9.5	6.73
Pt1.1Fe0.2/G	24.5	0.66	16.2	2.77
Pt1.1Fe0.4/G	15.3	0.81	12.4	1.73
Pt1.1Fe0.6/G	9.9	0.82	8.1	1.11
Pt1.1/ γ - Al_2O_3	66.6	0.09	6.0	4.80
Pt1.1Fe0.2/ γ - Al_2O_3	67.9	0.08	5.4	6.41
Pt1.1Fe0.4/ γ - Al_2O_3	52.5	0.14	7.4	4.17
Pt1.1Fe0.6/ γ - Al_2O_3	32.2	0.20	6.4	2.54

Catalysts H_2 reduced at 300 °C for 2 h, total flow rate is 50 ml/min.

^a Yield = $\frac{\text{conversion} \times \text{selectivity}}{100}$.

^b G: graphite.

Surprisingly, compared with Pt1.1/BN, both conversion (or activity) and selectivity increase simultaneously on PtFe/BN series catalysts resulting in the significant crotyl alcohol yield increase. The selectivity of crotyl alcohol increases while the conversion decreases with increasing Fe loadings on PtFe/BN series catalysts. The selectivity of crotyl alcohol is improved to 0.77 with 0.6 wt.% of Fe. The optimum yield of crotyl alcohol achieved 23.1% with a conversion 46.1% on Pt1.1Fe0.2/BN.

For graphite-supported catalysts, compared with Pt1.1/G, the conversions of PtFe/G series catalysts decrease dramatically while selectivities of crotyl alcohol are greatly enhanced with increasing Fe loadings. For γ -Al₂O₃ supported catalysts, the Fe addition somewhat decreases the conversion and slightly improves the crotyl alcohol selectivity compared with Pt1.1/ γ -Al₂O₃. Overall, the yields of crotyl alcohol in PtFe/BN series catalysts are much higher than those of PtFe/G and PtFe/ γ -Al₂O₃.

3.2. Characterization of catalysts

Fig. 5 shows the XRD spectra of BN supported series catalysts with 4 times metal loadings. These catalysts were prepared using the same procedure as those of normal metal loadings, and were H₂ reduced at 300 °C. The spectrum of Fe3.2/BN is the same as that of BN support. No characteristic peak of Fe can be found. This absence indicates that either individual Fe particles do not exist or are very small in size. The major characteristic peaks of Pt are clearly shown at 39.8° and 46.2° in Pt4.4/BN (i.e. Pt1.1/BN) and Pt4.4Fe0.8/BN (i.e. Pt1.1Fe0.2/BN). The characteristic peaks of PtFe alloy are at 40.4° and 47.0° and are observed in Pt4.4Fe0.8/BN (i.e. Pt1.1Fe0.2/BN), Pt4.4Fe1.6/BN (i.e. Pt1.1Fe0.2/BN) and Pt4.4Fe2.4/BN (i.e. Pt1.1Fe0.2/BN) [15]. The rest of the characteristic peaks of PtFe alloy are not marked because they

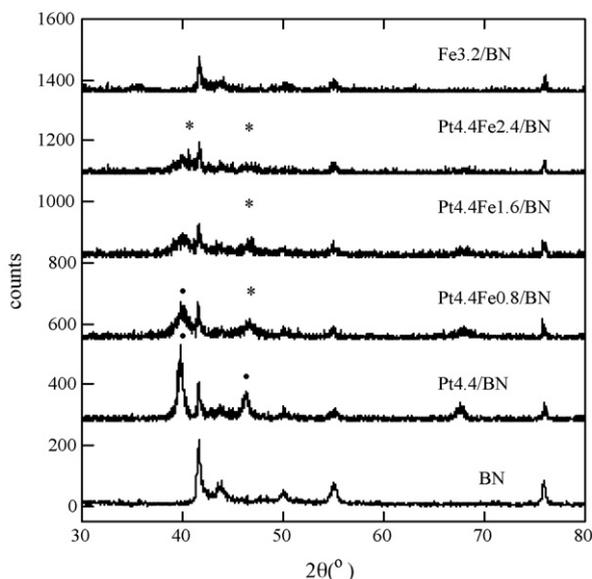


Fig. 5. XRD spectra of PtFe/BN catalysts H₂ reduced at 300 °C, (●) Pt, (*) PtFe.



Fig. 6. TEM micrograph of Pt1.1Fe0.2/BN catalyst.

are overlapped with those of Pt or BN. A small portion of Pt particles can be found in Pt4.4Fe0.8/BN (i.e. Pt1.1Fe0.2/BN), as shown in its XRD spectrum. With a higher Fe loading, such as Pt4.4Fe1.6/BN and Pt4.4Fe2.4/BN, the characteristic peaks of Pt are diminished, indicating that no individual Pt particles are present. Therefore, the PtFe alloy is formed during the H₂ reduction in PtFe/BN series catalysts. The XRD spectra (not shown) of Pt/ γ -Al₂O₃ and PtFe/ γ -Al₂O₃ series catalysts reduced at 300 °C are the same as the background spectra of γ -Al₂O₃. The metal particles are too small to be observed in the XRD, revealing highly dispersed Pt and/or PtFe particles on the γ -Al₂O₃ support. For graphite supported Pt and PtFe catalysts, no characteristic peaks can be identified. Thus, the size of metal particles may be similar to those on the γ -Al₂O₃ support.

Fig. 6 displays the TEM micrograph of Pt1.1Fe0.2/BN. BN support appears flaky and has an irregular shape. Most of metal particles with sizes less than 10 nm can be observed in the TEM micrograph. Furthermore it can be observed that most of the Pt or PtFe particles are located on the edges of BN support.

Fig. 7 shows the XPS of the fresh and H₂ reduced of Pt4.4Fe0.8/BN (i.e. Pt1.1Fe0.2/BN) catalysts, respectively. The chemical status is identified to be Fe²⁺ as indicated by its binding energy of Fe 2p_{3/2} at 709.3 eV [16]. The Fe²⁺ is retained even after H₂ reduction at 300 °C.

The Pt chemical status of Pt4.4Fe0.8/BN (i.e. Pt1.1Fe0.2/BN) and Pt4.4BN (i.e. Pt1.1/BN) is disclosed in Fig. 8. The binding energy of Pt 4f_{7/2} in Pt4.4/BN is detected at 71.5 eV indicating the metal Pt⁰ after H₂ reduction for 2 h at 300 °C. The Pt 4f_{7/2} of the fresh Pt4.4Fe0.8/BN is located at 75.7 eV indicating the Pt⁴⁺ state [16]. Compared with reduced Pt4.4/BN, the binding energy of Pt in the H₂ reduced Pt4.4Fe0.8/BN

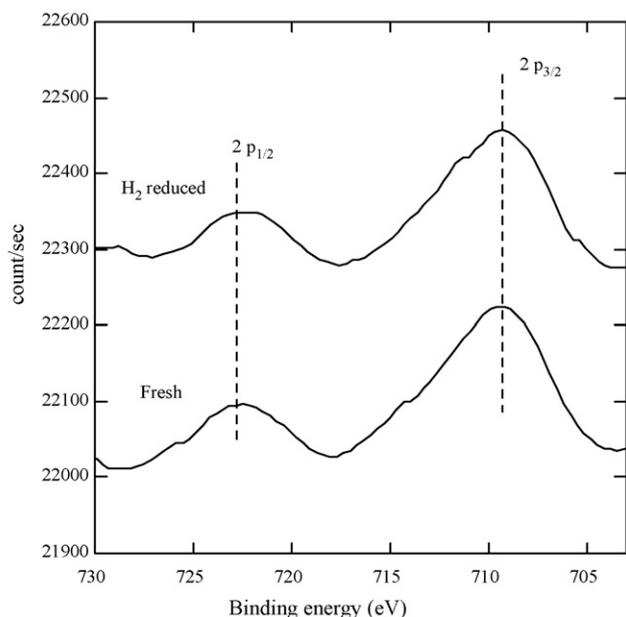


Fig. 7. XPS of Fe $2p_{3/2}$ and $2p_{1/2}$ on Pt_{4.4}Fe_{0.8}/BN, Fresh and H₂ reduced at 300 °C.

shows 0.4 eV positive shift to 71.9 revealing surface Pt may be positively charged due to the surrounding Fe²⁺ on PtFe alloy [17]. After H₂ reduction, the surface Pt on Pt_{4.4}Fe_{0.8}/BN is mostly reduced but Fe is not reducible (Fig. 7).

The H₂ reduction of fresh PtFe/BN series catalysts is studied by employing TPR as shown in Fig. 9. The Pt_{1.1}/BN gives lowest reduction temperature at 155 °C. Table 3 summarizes the peaks of reduction temperatures on all catalysts on three supports. The reduction temperatures of Pt_{1.1}/G and Pt_{1.1}/ γ -Al₂O₃ are at 184 °C and 228 °C, respectively. The decomposition and/or reduction of Pt precursor at lower temperature

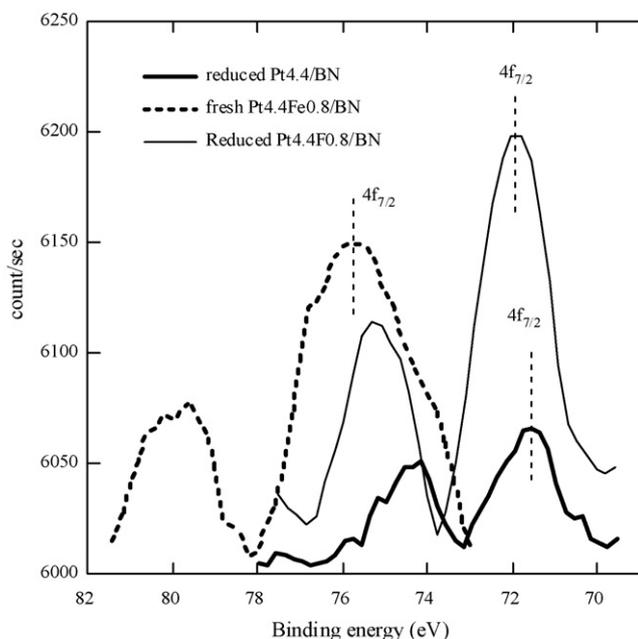


Fig. 8. XPS of Pt $4f_{7/2}$ and $4f_{5/2}$ on Pt/BN and Pt_{4.4}Fe_{0.8}/BN catalysts.

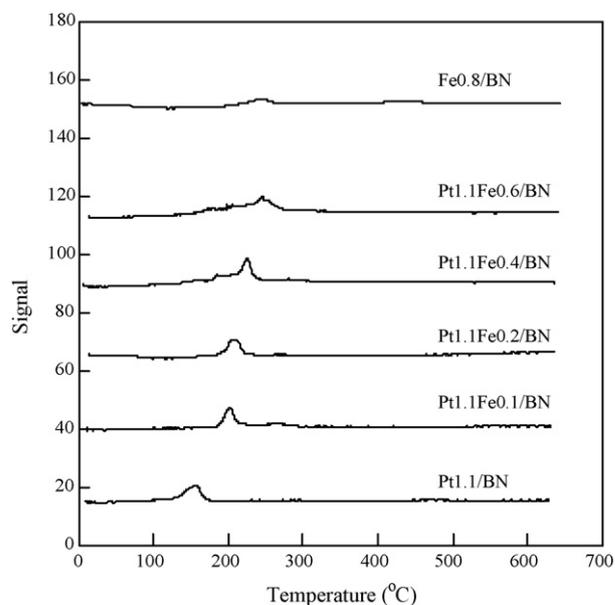


Fig. 9. Temperature programmed reduction of fresh PtFe/BN catalysts.

indicates less metal-support interference on BN than on graphite or γ -Al₂O₃. The H₂ reduction of all PtFe/BN series catalysts are in the range of 202–245 °C. The reduction temperature increases with increasing Fe loadings. Similar trend of the reduction temperature (216–247 °C) is also observed on PtFe/G series catalysts, but not on PtFe/ γ -Al₂O₃ series catalysts. All reduction temperatures of PtFe/ γ -Al₂O₃ series catalysts are near that of Pt/ γ -Al₂O₃ at ~230 °C indicating that only Pt is reduced on PtFe/ γ -Al₂O₃. Such observable fact implies that γ -Al₂O₃ may constrain the mobility of Pt and Fe during H₂ reduction due to the metal-support affinity. It is suspected that no PtFe alloy is formed on γ -Al₂O₃ support under 300 °C. The tendency to form PtFe alloy may be the reason resulting in the increase reduction temperature. From the reduction temperatures indicate that the formation of PtFe alloy is much easier on BN than on γ -Al₂O₃, and graphite is in between.

Table 3

The H₂ reduction temperatures of Pt and PtFe on different supports

Catalyst	H ₂ reduction temperature (°C)
Pt _{1.1} /BN	155
Pt _{1.1} Fe _{0.1} /BN	202
Pt _{1.1} Fe _{0.2} /BN	210
Pt _{1.1} Fe _{0.4} /BN	226
Pt _{1.1} Fe _{0.6} /BN	245
Pt _{1.1} /G ^a	184
Pt _{1.1} Fe _{0.2} /G	216
Pt _{1.1} Fe _{0.4} /G	237
Pt _{1.1} Fe _{0.6} /G	247
Pt _{1.1} / γ -Al ₂ O ₃	228
Pt _{1.1} Fe _{0.2} / γ -Al ₂ O ₃	228
Pt _{1.1} Fe _{0.4} / γ -Al ₂ O ₃	227
Pt _{1.1} Fe _{0.6} / γ -Al ₂ O ₃	234

^a G: graphite.

4. Discussion

The activity boost of crotonaldehyde hydrogenation and the selectivity enhancement of crotyl alcohol are attributed to the formation of PtFe alloy particles on BN support. Both Pt and PtFe alloy are formed at low Fe wt.%, but only PtFe are found at a higher Fe loadings on BN support (Fig. 5). The enhanced hydrogenation of the C=O bond is due to the promoting effect of the oxidized Fe²⁺ species [7]. The active sites may be in the boundary zone between Pt and iron oxide on the PtFe alloy particle. Therefore, the high portion of PtFe alloy and surface Fe²⁺ with moderate levels of metal dispersion in Pt_{1.1}Fe_{0.2}/BN give the highest yield for the selective hydrogenation of the C=O bond in crotonaldehyde.

Boron nitride provides an inert and slippery surface that facilitates the formation of PtFe alloy during H₂ reduction due to the unrestrained migration of metal particles. On the other hand, γ -Al₂O₃ may constrain the mobility of Pt and Fe during H₂ reduction due to the metal-support affinity, thus preventing the formation of PtFe alloy particles. The size of PtFe alloy particles is also an important factor to be considered because crotonaldehyde hydrogenation is structure-sensitive [18]. Although graphite also provides a similar surface like BN thus the PtFe alloy particles are formed on PtFe/G, the PtFe particles may be too small to notably either enhance C=O hydrogenation. However, the formation of PtFe alloy particles also reduces the dispersion of Pt on BN and graphite, so that the activity of hydrogenation is depressed with increasing Fe loadings (Table 2).

A PtFe alloy particle with surface Pt⁰ and Fe²⁺ on BN support is proposed to be the origin to improve the selectivity of crotyl alcohol and the activity in crotonaldehyde hydrogenation. The surface Fe²⁺ behaves as a Lewis acid site attracting the C=O group of a crotonaldehyde molecule. The nearby Pt⁰ can supply the absorbed hydrogen to conduct the hydrogenation of the C=O bond, instead of the C=C bond. The negligible interaction of BN and the PtFe particle can easily maintain the reduced state of the surface Pt⁰, thus causing a weaker adsorbed hydrogen. Such highly active hydrogen facilitates the process of hydrogenation. The partial coverage of Fe²⁺ on PtFe particles also inhibits the hydrogenation of the C=C bond. In addition, partially Fe²⁺ covered PtFe alloy particle balances the activity and selectivity of crotyl alcohol thus gives the highest yield.

5. Conclusions

This study has presented favorable findings for the selective hydrogenation of α , β -unsaturated aldehyde into unsaturated alcohol by employing BN supported PtFe catalysts. Although butyraldehyde and butanol in crotonaldehyde hydrogenation are favorable based on thermodynamic equilibrium, the product selectivity is shifted to crotyl alcohol because C=O hydrogenation is preferential on the PtFe alloy particles in BN support. Boron nitride exhibits a unique property of minimum metal-support interference compared with traditional metal oxides. Therefore, boron nitride offers a promising support for selective hydrogenation catalyst.

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