A novel BN supported bi-metal catalyst for selective hydrogenation of crotonaldehyde

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Abstract

A series of boron nitride (BN) supported Pt-Sn catalysts was prepared with a co-incipient wetness method employing hexachloroplatinic acid and tin(II) chloride. Pt loading was fixed at 1.1 wt%; Sn loading varied from 0.25 to 0.75 wt% on BN support. Selective hydrogenation of gas-phase crotonaldehyde was conducted in a steady-state flow reactor with temperatures ranging from 40 to 100 °C. The selectivity of crotyl alcohol reached over 80%. An optimum yield of crotyl alcohol reached 38% at 60% conversion of crotonaldehyde at 80 °C using Pt-Sn(0.75)/BN catalyst, while Pt-Sn(0.75)/γ-Al2O3 yielded less crotyl alcohol and a lower rate of crotonaldehyde conversion. The maximum yield rate of crotyl alcohol was 2.4 mmol/(g-cat. h) at 80 °C. Negligible deactivation was found during reaction for 4–6 h. The crystalline phases of PtSn and SnPt3 alloys were observed from the XRD spectra of Pt-Sn/BN catalysts with various Sn loadings. The selectivity of crotyl alcohol increased with Sn loadings but the activity values of the catalysts went through a maximum. The H2 reduction at 300 °C gave an optimum Pt–Sn alloy particle size so that the selectivity of crotyl alcohol increased without losing catalyst activity. The C=O bond of crotonaldehyde was preferentially hydrogenated and the hydrogenation of C=C bond was suppressed, resulting in the increase of crotyl alcohol selectivity.

Keywords: Pt-Sn/BN catalyst; Non-oxide support; 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. Improved selectivity for unsaturated alcohols was achieved by using reducible supports or additive promoter [2–5]. Supported bimetallic Pt-Sn 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 [6,7].

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.

The graphite-like hexagonal boron nitride (BN) is the most stable BN isomer under ambient conditions [8]. Boron nitride has large thermal conductivity, superior temperature stability and acid–base resistance. 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 and support in the catalytic oxidation. Boron nitride allows a possibility to reduce the Pt or Sn-support interaction. 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 Pt-Sn sintering and lead to the formation of PtSn alloy, a favorable phase for the selective hydrogenation of α, β-unsaturated aldehyde into unsatu-
rated alcohol [6]. We therefore choose crotonaldehyde hydrogenation as a probing reaction to investigate the unique catalytic property provided by a novel BN support. The effects of the Sn addition on the activity/selectivity of the catalysts for the hydrogenation of the C=O and C=C bonds in the vapor phase hydrogenation of crotonaldehyde. The effects of Sn loadings and H2 reduction temperatures were also examined.

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-Al2O3), a commonly used oxide support, was obtained from Merck (USA) and used for comparison. Precursor salt, H2PtCl6·6H2O, with approximately 40 wt% platinum, and pure SnCl2 were purchased from Alfa Aesar (USA). Methanol was chosen as the diluting solvent for improved soaking of the hydrophobic BN support. The supported Pt-Sn 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 Sn 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. All Pt loading was fixed at 1.1 wt%, Sn loadings varied from 0.25 to 0.75 wt%. The detailed incipient wetness procedure is described in the literature [11].

2.2. Characterization

The specific surface area of the support was measured by N2 adsorption in Micromeritics ASAP 2010. The particle sizes and distributions of BN and Al2O3 were measured by laser-light scattering. Al2O3 was suspended and dispersed ultrasonically in water for 3 min. BN was dispersed in ethanol due to its hydrophobicity. Coulter LS 230 was used to measure the scattering of incidental light at the 90° positions, and then the particle size was calculated using the Fraunhofer equation. Fresh catalyst was reduced in H2 flow at 300 °C for 2 h before chemisorption. The H2 chemisorption procedures were similar to those described by Yang and Goodwin [12]. The amount of irreversible H2 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 Pt-Sn particles dispersed on the support. Pt-Sn/Al2O3 or Pt-Sn/BN was dispersed ultrasonically in ethanol for 30 min, and then a small portion was taken from the top of the catalyst-suspended solution and dropped on a copper mesh. The particles adhered on the copper wire in the mesh after drying, and then the mesh was transported to the TEM chamber for analysis. The crystalline phases of Pt-Sn/BN 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. The reduction of fresh Pt-Sn catalyst was studied using the temperature programmed reduction (TPR). The gas used in TPR was a mixture of 5 vol% H2 in Ar. A fresh catalyst was loaded into a quartz tube and purged with N2. The gas was then switched to the H2/Ar mixture at room temperature. The TPR was performed in the H2/Ar mixture from 50 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 16 mm i.d. The catalyst was reduced for 2 h at 200, 300 or 450 °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 H2/crotonaldehyde mixture was maintained at 59 and passed through the reactor at 50 ml/min under atmospheric pressure. The reaction temperature was increased from 40 to 100 °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 Pt-Sn 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, 80 and 100 °C to investigate the variations of conversion and product selectivity. Normally an entire reaction took 4–6 h to evaluate a fresh catalyst without noticeable deactivation. The same hydrogenation reaction conducted on Sn/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. (1) and (2). The yield of crotyl
alcohol was calculated by multiplying the conversion by its selectivity and dividing by 100%.

\[
\text{conversion (\%)} = \frac{C_{\text{crotonaldehyde, Input}} - C_{\text{crotonaldehyde, Output}}}{C_{\text{crotonaldehyde, Input}}} \times 100\% 
\]

\[
\text{selectivity (\%)} = \frac{C_{\text{product}}}{C_{\text{crotonaldehyde, Input}} - C_{\text{crotonaldehyde, Output}}} \times 100\% 
\]

3. Results and discussion

The specific surface area of BN and γ-Al2O3 were 47.5 and 116 m²/g, respectively. The particle sizes of BN were in the range 0.4 and 90 μm and that of γ-Al2O3 was 6–190 μm. The mean particle size of BN and γ-Al2O3 were calculated to be 2.8 and 66.4 μm, respectively. Table 1 summarizes the results of H2 chemisorption on Pt/BN and Pt-Sn/BN series catalysts. The small amount of H2 chemisorption on Pt/BN was due to poor Pt dispersion as a result of sintering. The various amounts of H2 chemisorption on three Pt-Sn/BN catalysts might be just due to the different Pt dispersions among these catalysts during the preparation. In addition, the amounts of hydrogen chemisorption of Pt-Sn(0.5)/BN and Pt-Sn(0.75) were suppressed due to the Sn dilution of the surface Pt.

Fig. 1 shows the XRD spectra of Pt-Sn/BN catalysts, which were H2 reduced at 300 °C. The spectrum of Sn/BN was the same as that of pure BN. No characteristic peak of Sn was found; this absence indicated that either individual Sn particles did not exist or were very small in size. The major characteristic peaks of Pt are clearly shown at 39.8° and 46.2°. The crystalline phases of PtSn and SnPt3 alloys were also observed with various Sn loading catalysts. The characteristic peaks of SnPt3 were at 38.9° and 45.0° on all Pt-Sn/BN series catalysts. In addition to SnPt3, Pt-Sn(0.75)/BN also contained the PtSn crystalline at peaks of 30.1° and 62.5° [13]. The rest of the characteristic peaks of SnPt3 or PtSn were not marked because they were overlapped with those of Pt or BN. A small portion of Pt particles can be found on Pt-Sn(0.25)/BN, as shown in its XRD spectrum.

With a higher Sn loading, such as Pt-Sn(0.5)/BN and Pt-Sn(0.75)/BN, the characteristic peaks of Pt were diminished, indicating that no individual Pt particles were present. Therefore, the PtSn and/or SnPt3 alloy were formed during the H2 reduction. The SnPt3 particles of Pt-Sn(0.5)/BN were approximately 8.9 nm, as calculated by the Scherrer equation.

The XRD spectra (not shown) of Pt/γ-Al2O3 and Pt-Sn/γ-Al2O3 series catalysts reduced at 300 °C were the same as the background spectra of γ-Al2O3. The metal particles were

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Pt (wt%)</th>
<th>Sn (wt%)</th>
<th>Hydrogen atom (μmol/g-cat.)</th>
<th>H/Pt</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt/BN</td>
<td>1.1</td>
<td>0.00</td>
<td>3.2</td>
<td>0.058</td>
</tr>
<tr>
<td>Pt-Sn(0.25)/BN</td>
<td>1.1</td>
<td>0.25</td>
<td>6.2</td>
<td>0.110</td>
</tr>
<tr>
<td>Pt-Sn(0.50)/BN</td>
<td>1.1</td>
<td>0.50</td>
<td>1.2</td>
<td>0.021</td>
</tr>
<tr>
<td>Pt-Sn(0.75)/BN</td>
<td>1.1</td>
<td>0.75</td>
<td>4.0</td>
<td>0.071</td>
</tr>
</tbody>
</table>

Catalysts H2 reduced at 300 °C for 2 h before chemisorption.
too small to be observed in the XRD, revealing highly dispersed Pt and/or Pt-Sn particles on the $\gamma$-Al$_2$O$_3$ support. The effect of the H$_2$ reduction temperature on Pt-Sn(0.75)/BN is shown in Fig. 2. The PtSn and SnPt$_3$ alloys were formed, as their respective characteristic peaks of XRD can be easily found. A portion of pure Pt crystalline phase was formed at a reduction temperature of 200 °C, but diminished at higher reduction temperatures. Pt and Sn were sintered to Pt–Sn alloy with increasing reduction temperatures due to metal migration on BN surface. Fig. 3 shows the TEM micrograph of Pt-Sn(0.75)/BN. Some of the metal particles with sizes 8–15 nm can be observed in the TEM micrograph, which indicates that most of the Pt-Sn particles were located on the edges of BN particles.

Fig. 4 depicts the reaction paths of $\alpha$, $\beta$ hydrogenation on crotonaldehyde. The products are crotyl alcohol or butyraldehyde via C=O or C=C hydrogenation, respectively. Butyraldehyde is thermodynamically favorable in crotonaldehyde hydrogenation based on Gibbs free energy calculation. The end product is butanol with further hydrogenation. Fig. 5 shows the conversions of crotonaldehyde hydrogenation and the selectivities of crotyl alcohol using Pt/BN and Pt/$\gamma$-Al$_2$O$_3$ catalysts, respectively. While the selectivities of crotyl alcohol were within the same range (10–20%), the Pt/BN gave much lower conversion (2–15%) values compared to those of Pt/$\gamma$-Al$_2$O$_3$. The low activity of Pt/BN was obviously due to its poor Pt dispersion (Table 1). The crotonaldehyde conversion and the selectivity of crotyl alcohol were substantially increased on Pt-Sn(0.75)/BN under the same reaction conditions as shown in Fig. 6.

![TEM micrograph of Pt-Sn(0.75)/BN catalyst.](image)

![Conversion of crotonaldehyde and selectivity of crotyl alcohol on Pt/BN and Pt/$\gamma$-Al$_2$O$_3$.](image)

![Conversion of crotonaldehyde and selectivity of crotyl alcohol on Pt-Sn(0.75)/BN and Pt-Sn(0.75)/$\gamma$-Al$_2$O$_3$.](image)
selectivity of crotyl alcohol was improved to over 80% at 40 °C. The optimum yield of crotyl alcohol achieved was 38% with a conversion of 60% at 80 °C. However, for Pt-Sn(0.75)/γ-Al₂O₃, the conversion was significantly reduced to 0.3–4.7% with the selectivity of crotyl alcohol ranging from 50 to 30% under the same reaction conditions (Fig. 6). The production rates of crotyl alcohol based on the unit weight of catalyst are shown in Fig. 7. The apparent activation energy is near 20 kJ/mol, calculated by using the Arrhenius equation. The maximum rate of crotyl alcohol was near 2.4 mmol/(g-cat. h) on Pt-Sn(0.75)/BN at 80 °C. To our knowledge, this is the highest rate of supported bi-metallic Pt-Sn catalysts currently reported in the literature [6,14–16].

The conversion and selectivity trends of the Pt-Sn/BN series catalysts at temperatures ranging from 40 to 100 °C were similar to those shown in Fig. 6. For simplicity, Table 2 summarizes the effect of Sn loadings on the product selectivities at a reaction temperature of 80 °C. The conversion of crotonaldehyde increased as Sn loadings increased. Surprisingly, the selectivity of crotyl alcohol also increased resulting in its high yield. On the other hand, the selectivity of butyraldehyde decreased significantly as Sn loadings increased, while that of butanol remained within a narrow range. Thus, that the activity and the selectivity of crotyl alcohol increased simultaneously implies that not only is the rate of crotonaldehyde enhanced but also the hydrogenation of C=C is significantly suppressed.

The influence of H₂ reduction temperature on Pt-Sn(0.75)/BN was further studied and the results at a reaction temperature of 80 °C are summarized in Table 3. The selectivities of crotyl alcohol increased as reduction temperatures increased. The Pt-Sn(0.75)/BN reduced at 300 °C gave the highest rate of conversion at 60.1%. Conversion then fell with a higher reduction temperature of 450 °C. Although the highest selectivity of crotyl alcohol occurred when Pt-Sn(0.75)/BN was reduced at 450 °C, its decreased yield was due to its declining activity.

Activity and selectivity enhancement are attributed to the formation of PtSn and/or SnPt₃ particles on BN support (Fig. 1). Only SnPt₃ was found at Sn loadings below 0.5 wt%. At higher Sn loadings, both PtSn and SnPt₃ were found (Fig. 1). Consequently, the production rate of crotyl alcohol should be further enhanced due to PtSn alloy. The enhanced hydrogenation of the C=O bond was due to the promoting effect of the oxidized Sn species [6]. The active sites might be in the boundary zone between Pt and tin oxide on the PtSn alloy. The high portion of PtSn alloy and surface Sn⁰ with moderate levels of metal dispersion in Pt-Sn(0.75)/BN gave the best results for the selective hydrogenation of the C=O bond in crotonaldehyde.

The H₂ reduction of fresh Pt-Sn/BN catalysts were studied by employing TPR as shown in Fig. 8. The H₂ consumption of all Pt-Sn/BN series catalysts were in the range of 120 to ~180 °C, while that of all Pt-Sn/γ-Al₂O₃ series catalysts were in a higher temperature range of 180 to ~280 °C (not shown). The decomposition and/or reduction of Pt and Sn precursors at lower temperature indicate less metal-support interaction on BN than on γ-Al₂O₃. The tendency to form Pt-Sn particles was also much easier on BN than on γ-Al₂O₃. The high portion of PtSn alloy and surface Sn⁰ with moderate levels of metal dispersion in Pt-Sn(0.75)/BN gave the best results for the selective hydrogenation of the C=O bond in crotonaldehyde.

Boron nitride provides an inert and slippery surface that facilitates the formation of Pt–Sn 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 Sn during H₂ reduction due to the metal-support affinity, thus preventing the formation of Pt–Sn alloy particles. The size of Pt–Sn alloy particles is also an important factor to be considered because crotonaldehyde hydrogenation is struc-

![Fig. 7. Activities of Pt/BN and Pt-Sn/BN series catalysts.](image)

<table>
<thead>
<tr>
<th>Reduction Temperature (°C)</th>
<th>Conversion (%)</th>
<th>Selectivity (%)</th>
<th>Yield (%)</th>
<th>*crotyl alcohol</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Crotaldehyde</td>
<td>Butyraldehyde</td>
<td>Butanol</td>
</tr>
<tr>
<td>200</td>
<td>30.6</td>
<td>45.9</td>
<td>29.6</td>
<td>24.5</td>
</tr>
<tr>
<td>300</td>
<td>60.1</td>
<td>62.7</td>
<td>9.1</td>
<td>28.1</td>
</tr>
<tr>
<td>450</td>
<td>42.9</td>
<td>72.8</td>
<td>10.8</td>
<td>16.4</td>
</tr>
</tbody>
</table>

* Yield = conversion × selectivity/100.

Table 3: The Effect of H₂ reduction on selective hydrogenation using Pt-Sn(0.75)/BN at reaction temperature 80 °C
structure-sensitive [17]. The Pt–Sn alloy particles may exist on Pt-Sn/γ-Al₂O₃ but are too small to either enhance C=O hydrogenation or inhibit C=C hydrogenation. However, the formation of large Pt–Sn alloy particles also reduces the dispersion of Pt, so that the activity of hydrogenation decreases. Therefore, a higher H₂ reduction temperature gave higher crotyl alcohol selectivity but resulted in a low conversion of crotonaldehyde hydrogenation (Table 3).

The improved selectivity of crotyl alcohol in crotonaldehyde hydrogenation is proposed schematically in Fig. 9, which displays a PtSn/SnPt₃ particle with surface Sn⁺⁺ on BN support. The surface Sn⁺⁺ behaves as a Lewis acid site attracting the C=O group of a crotonaldehyde molecule. The nearby Pt 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 PtSn/SnPt₃ particle can easily maintain the reduced state of the surface Pt, thus causing weaker adsorbed hydrogen. Such highly active hydrogen facilitates the process of hydrogenation. The partial coverage of Sn⁺⁺ on PtSn/SnPt₃ particles also inhibits the hydrogenation of the C=C bond.

4. Conclusions

This study has presented favorable findings for the selective hydrogenation of α, β-unsaturated aldehyde into unsaturated alcohol by employing BN supported Pt-Sn catalysts. Although butyraldehyde and butanol in crotonaldehyde hydrogenation are favorable based on thermodynamic equilibrium, the product selectivity can be shifted to crotyl alcohol by controlling the reaction kinetics on the Pt-Sn/BN catalyst. The yield of crotyl alcohol achieved as high as 38% on Pt-Sn(0.75)/BN at 80 °C. Moreover, crotyl alcohol selectivity reached 80% at a conversion of 10% near 40 °C. Boron nitride exhibits superior properties, including chemical inertness, thermal stability and minimum metal-support interaction. Therefore, boron nitride is a promising support for selective hydrogenation catalyst.

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References