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Selective hydrogenation of benzyl cyanide to 2-phenylethylamine over a Pd/Al₂O₃ catalyst promoted by synergistic effects of CO₂ and water

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(Abstract)

The selective hydrogenation of benzyl cyanide (BC) to the primary amine of 2-phenylethylamine (PEA) was investigated with a Pd/Al₂O₃ catalyst in different multiphase reaction media including n-hexane, water, and/or CO₂. In neat n-hexane, the hydrogenation of BC occurs at a large rate but no PEA was formed and the secondary amine of N,N-bis(2-phenylethyl)amine (BPEA) was produced as the main product. The pressurization of n-hexane with CO₂ decreased the rate of hydrogenation and the main product was BPEA. In this n-hexane – CO₂ medium, the catalyst lost its activity during the reaction. When a similar volume of water was added to n-hexane, the rate of hydrogenation did not change so much but a small amount of the primary amine was detected to form in addition to the main product of BPEA. In contrast to these reaction media, a high PEA selectivity of > 90% was obtained and no catalyst deactivation occurred in an n-hexane – water – CO₂ medium. The rate of hydrogenation was smaller than that in neat n-hexane but comparable to those in n-hexane – water and n-hexane – CO₂ media. Those results show that synergistic effects appears on the selective hydrogenation of BC to PEA when both water and CO₂ are included in the reaction medium. Possible roles and actions of water and CO₂ have been discussed on the basis of the results of hydrogenation runs under different conditions and in situ ambient and high pressure Fourier transform infrared spectroscopy measurements that give light to molecular interactions of CO₂ with reacting species.

Introduction

Water and carbon dioxide (CO₂) are environmentally benign fluids and can serve as interesting reaction solvents and promoters; that is, these are green components useable to design effective multiphase reaction media for organic synthetic reactions. The rate of reactions with molecular catalysts is promoted in the presence of water and the organic – aqueous interface is important for activating polar functional groups of organic substrates, as demonstrated by several examples in the literature.¹ Supercritical CO₂ is also an interesting solvent/promoter, which enhances the reaction rate and controls the product distribution of catalytic and non-catalytic reactions.² Carbon dioxide shows promotional effects even at pressures below its critical pressure (7.4 MPa).³ For an organic liquid substrate or solvent phase pressurized by CO₂, the dissolution of
CO₂ may affect the result of an organic reaction in the liquid phase. Interesting results using such CO₂-dissolved expanded liquid phases have been reported for oxidation, hydroformylation, hydrogenation, Heck coupling, Diels-Alder reaction, and so on.\(^3\)

It was previously indicated that when a liquid phase of nitrobenzene including a supported nickel catalyst was pressurized by CO₂ at pressures of 7 – 10 MPa, the rate of nitrobenzene hydrogenation was enhanced and the selectivity to aniline was almost 100% at any conversion level.\(^4\) These promotional effects of CO₂ pressurization result from an increase in the dissolution of a gaseous reactant of H₂ and molecular interactions of CO₂ with reacting species in the liquid phase. The dissolution of CO₂ causes the liquid phase to take a CO₂-philic nature, increasing the dissolution of H₂. The interactions of CO₂ molecules decrease the reactivity of the nitro group of the substrate and this retards the first step of the change to the corresponding imine. In contrast, the molecular interactions of CO₂ accelerate the subsequent reaction steps toward the final desired product of aniline. As a result, aniline can be selectively obtained at a high rate of hydrogenation. It should be noted, furthermore, that the same promotional effect of CO₂ can appear at a lower pressure of around 1 MPa when another foreign phase of water is added.\(^5\) The effectiveness of multiphase reaction media including water and CO₂ was shown for hydrogenation reactions by Hiyoshi et al. for acetophenone with a Pd/C catalyst\(^6\) and by Lin et al. for benzyl alcohol and its derivatives with supported Ru catalysts.\(^7\) These results allow ones to expect interesting synergistic effects of water and CO₂ for organic synthetic reactions.

The present work has been undertaken to examine the effects of additional components of water and CO₂ for selective hydrogenation of benzyl cyanide with a Pd/Al₂O₃ catalyst in an organic solvent of n-hexane. The features of the n-hexane – water – CO₂ medium have been compared with those of n-hexane, n-hexane – water and n-hexane – CO₂ media with respect to the rate of hydrogenation, the product selectivity and the catalyst deactivation. For hydrogenation reactions by H₂ over supported metal catalysts in the presence of CO₂, the catalysts often lose their activity due to the formation and adsorption of CO produced through reverse water gas shift reaction (CO₂ + H₂ → CO + H₂O).\(^3d,8\) In addition to the hydrogenation runs in different reaction media, molecular interactions of CO₂ with the substrate have been examined by in situ Fourier transform infrared spectroscopy (FTIR) with attenuated total reflection (ATR) mode at ambient and high pressures\(^9\) to discuss possible roles and actions of CO₂ and water in the selective hydrogenation of benzyl cyanide in n-hexane.

Hydrogenation of nitriles to primary amines, which are important intermediates in chemical and pharmaceutical industries, is one of practically important reactions.\(^10\) Several authors investigated the selective hydrogenation of nitriles in the presence of CO₂ and/or water. Very recently, Chen et al.\(^11\) and Yoshida et al.\(^12\) investigated the hydrogenation of benzonitrile in different multiphase media using a Ni/Al₂O₃ catalyst and a Pd/Al₂O₃ one, respectively. These authors indicated the effectiveness of dense phase CO₂ on the selective production of the desired primary amine of benzylamine in the absence of water. However, the former group showed that a medium including both CO₂ and water was not effective while the latter group observed that the coexistence of CO₂ and water was more beneficial in improving the selectivity to the primary amine. One of important reasons for the high selectivity to benzylamine is the formation of water-soluble carbamate from benzylamine and CO₂ and its transfer from organic phase to water, which inhibits undesired further chemical changes of benzylamine to the secondary amine and others in the organic phase. Hégedűs et al. studied the hydrogenation of benzyl cyanide using a Pd/C catalyst in a mixture of water and dichloromethane and in the presence of an acidic additive of NaH₂PO₄.\(^13\) They reported a small selectivity to the primary amine at a complete conversion.
Previously, Xie et al. indicated that CO\textsubscript{2} would act as a protecting agent for primary and secondary amines during the hydrogenation of nitriles.\textsuperscript{14} Chatterjee et al. reported the selective hydrogenation of benzyl cyanide and others with a Pd/MCM-41 catalyst in the presence of CO\textsubscript{2} at a high pressure of 10 MPa.\textsuperscript{15} They did not mention the possibility of catalyst deactivation in the hydrogenation of benzyl cyanide.

**Experimental**

**Hydrogenation**

A commercially available 5 wt.-\% Pd/Al\textsubscript{2}O\textsubscript{3} (Wako) was used as a catalyst for hydrogenation of benzyl cyanide (Aldrich) in the presence of \textit{n}-hexane and/or distilled water (Wako). The hydrogenation reactions were carried out in a 100 cm\textsuperscript{3} Teflon-lined autoclave. The reactor was charged with 1.0 mmol (0.117 g) benzyl cyanide, 5 cm\textsuperscript{3} \textit{n}-hexane, 5 cm\textsuperscript{3} water and 58.5 mg Pd/Al\textsubscript{2}O\textsubscript{3} catalyst and it was flushed with H\textsubscript{2} for three times to remove the air. The reactor was heated in a heating mantle up to the desired temperature. After the reaction temperature was attained, 2 MPa H\textsubscript{2} (99.99\%) was introduced, followed by the introduction of liquid CO\textsubscript{2} (99.99\%) to the desired total pressure with a high pressure liquid pump (JASCO SCF-Get). The reactions were carried out at 323 K while stirring the reaction mixture with a magnetic stirrer. After the reaction, the reactor was cooled in an ice water bath and depressurized carefully to atmospheric pressure. The reaction mixture was analyzed by gas chromatograph (GL Sciences GC-390B) using a capillary column (TC 1701) and flame ionization detector. The total conversion was determined from the initial and final amounts of benzyl cyanide. The product and by-products were identified by GC-MS (Shimadzu 17A). Under the present reaction conditions, 2-phenylethylamine (PEA), \textit{N},\textit{N}-bis(2-phenylethyl)amine (BPEA), and bis-(2-phenylethyl) diazene (BPEDA) were observed to form. BPEDA is supposed to be formed from PEA and the reactant benzyl cyanide. Scheme 1 shows the possible reaction pathways of hydrogenation of benzyl cyanide.\textsuperscript{16}

**Phase behavior observation**

When a liquid solvent or substrate phase is pressurized by CO\textsubscript{2}, it expands by dissolution of CO\textsubscript{2}. This will facilitate the dissolution of other co-existing gases such as O\textsubscript{2}, H\textsubscript{2}, and CO and this may accelerate the reactions involved with these gaseous reactant.\textsuperscript{3d,17} To examine the chemical reactions in the presence of CO\textsubscript{2}, the phase behavior study is important to check whether the reaction is occurring in a single phase homogeneously or heterogeneously in two or more phases.\textsuperscript{18} A 10 cm\textsuperscript{3} high pressure sapphire window view cell was used for phase behavior study. The observation was made with a similar volumetric ratio of solvent \textit{n}-hexane to the reactor as used in the hydrogenation reactions. A certain amount of \textit{n}-hexane was added into the cell and it was purged with H\textsubscript{2} three times. The cell was heated up to 323 K (reaction temperature) by circulation of preheated water outside the cell, followed by the introduction of 2 MPa H\textsubscript{2}. Then CO\textsubscript{2} was slowly introduced into the cell to the desired pressure while stirring the mixture by a magnetic stirrer. The phase behavior was visually examined by naked eyes at different CO\textsubscript{2} pressures.
**In situ FTIR measurement**

Interactions between substrate and CO$_2$ molecules were examined by in situ high-pressure FTIR measurements using a JASCO FTIR-620 spectrometer with a triglycine sulfate detector at a wavenumber resolution of 2 cm$^{-1}$ and at 323 K (reaction temperature). The FTIR-ATR spectra were collected in an in situ high-pressure ATR cell (1.18 cm$^3$) attached with a ZnSe crystal rod. The temperature of the cell was controlled by a temperature controller and a heating jacket containing rod heaters. The FTIR spectra were collected for a mixture of CO$_2$ dissolved in liquid benzyl cyanide at different pressures.

**Results and discussion**

**Hydrogenation in different media**

The hydrogenation of benzyl cyanide (BC) was studied with a 5wt. % Pd/Al$_2$O$_3$ catalyst in different reaction media at 323 K. Under the reaction conditions employed, phenylethylamine (PEA), $N,N$-bis(2-phenylethyl)amine (BPEA), and bis(2-phenylethyl)diazene (BPEDA) were observed to form. Possible reaction pathways for these products are shown in Scheme 1. The primary amine of PEA is produced through the formation of an intermediate of phenylethylimine (PEI), which can further react with the product of PEA and be converted to the secondary amine of BPEA. The BC conversion and the product distribution were significantly changed depending on the reaction media used, as explained in the following.

Scheme 1 Possible reaction pathways in hydrogenation of benzyl cyanide. BC: benzyl cyanide, PEI: phenylethylimine, PEA: 2-phenylamine, BPEA, $N,N$-bis(2-phenylethyl)amine, BPEDA bis(2-phenylethyl)diazene.
Table 1 shows the reaction results obtained using four different types of reaction media. In the absence of CO_2 and water (medium a), the reaction took place very fast as compared to the others examined and almost all BC was consumed in 1 h. However, the main product was the undesired secondary amine of BPEA and no formation of the objective product of PEA was detected. In the presence of 3 MPa CO_2 (medium b), the conversion in 1 h decreased to 61% and no PEA was produced with the formation of BPEA as the main byproduct, similar to the medium (a). When water was added in the same volume as of n-hexane (medium c), the primary amine of PEA was formed, although its selectivity was still not high (24%). A BC conversion of 73% was slightly larger than that (61%) obtained in the medium (b). In contrast to those media, in the presence of both water and CO_2 (medium d), the selectivity to PEA was significantly enhanced to 93% along with a decrease in the conversion to 56%. Namely, the coexistence of water and CO_2 is indispensable for the highly selective hydrogenation of BC to PEA. Influence of CO_2 and water on the BC conversion and the PEA selectivity will be discussed later.

Table 1 Results of benzyl cyanide hydrogenation with Pd/Al_2O_3 catalyst in the presence and absence of CO_2 and/or water.

<table>
<thead>
<tr>
<th>Medium</th>
<th>Time (min)</th>
<th>Conversion (%)</th>
<th>Selectivity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>PEA</td>
</tr>
<tr>
<td>(a) Hexane</td>
<td>5</td>
<td>63</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>99</td>
<td>0</td>
</tr>
<tr>
<td>(b) Hexane - CO_2</td>
<td>60</td>
<td>61</td>
<td>0</td>
</tr>
<tr>
<td>(c) Hexane - H_2O</td>
<td>60</td>
<td>73</td>
<td>24</td>
</tr>
<tr>
<td>(d) Hexane - CO_2 - H_2O</td>
<td>60</td>
<td>56</td>
<td>93</td>
</tr>
</tbody>
</table>

Reaction conditions: Benzyl cyanide 1 mmol, catalyst 58.5 mg, n-hexane 10 cm^3 (for a, b) and 5 cm^3 (for c, d), H_2O 5 cm^3 (for c, d), temperature 323 K, H_2 2 MPa, CO_2 3 MPa

The formation of BPEDA is unclear at present. When PEA alone (1 mmol) or a PEA – BC mixture (1 mmol each) was treated in n-hexane in the presence of atmospheric N_2 and Pd/Al_2O_3 at 323 K for 1 h, the formation of BPEDA was not detected. These observations suggest that, for the formation of BPEDA, the coupling of two PEA molecules and that of BC and PEA are not responsible and the presence of intermediate PEI is indispensable. BPEDA might be formed via the reaction of PEI with the reactant BC or the product PEA. As shown in Table 1, the selectivity to BPEDA was very low in the n-hexane – water – CO_2 medium, in which PEA formed was suggested, as discussed later, to move to the aqueous phase, resulting in decrease in the chance for PEA to react with PEI. If BPEDA is produced from PEI and BC, the selectivity to BPEDA would be high even in this medium because both PEI and BC exist in the same n-hexane phase. However, this was not the case; hence, BPEDA should be produced via the reaction between PEI and PEA.

For the reaction in the n-hexane medium, the selectivity to BPEDA was found to be about 25% at BC conversion of 60% - 90% but it tended to decrease slightly with the conversion, which
was about 15% close at the complete conversion. It is then possible that a part of BPEDA is reversely decomposed to PEI and PEA and those species formed are recombined to 1-amino-
N,N-bis(2-phenylethyl)amine, which then transforms to the secondary amine of BPEA. However, the decrease in the BPEDA selectivity observed is not so large that the contribution of BPEDA to the formation of BPEA should be less significant.

It was previously indicated for hydrogenation reactions in the presence of dense phase CO2 that supported metal catalysts often lost their activity during the reactions. One important reason is the formation of CO through reverse water gas shift reaction (CO2 + H2 → CO + H2O) and its adsorption on the surface of supported metal particles. To examine the possibility of such a catalyst deactivation in our cases, time – conversion profiles were measured for the above-mentioned four reaction media. The results obtained are given in Fig. 1, indicating that the Pd/Al2O3 catalyst became deactivated for the medium (b) but not for the others. It is noteworthy that the deactivation of Pd/Al2O3 catalyst can be hindered by the addition of water even in the presence of CO2. Possible reasons for the influence of water will be discussed later. Previously, Chatterjee et al. studied the hydrogenation of nitriles with a Pd/MCM-41 catalyst in supercritical CO2. They reported its good performance for the selective hydrogenation of BC to PEA at 343 K and at a higher CO2 pressure of 10 MPa (H2 2 MPa), under which a high PEA selectivity of 98% was obtained at a conversion of 82% in 4 h. No time – conversion profile was presented in their work and so they did not mention the catalyst deactivation. They noted from the results of recycling test with another substrate of benzonitrile (BN) that the Pd/MCM-41 catalyst was stable although comparison was made at relatively high conversion levels ≈ 90%. It is difficult at present to explain why the Pd/Al2O3 catalyst deactivated in our case with BC at a low CO2 pressure of 3 MPa but the Pd/MCM-41 catalyst did not in their case with BN (not BC) at a higher CO2 pressure of 10 MPa. The reaction mixture includes three phases of gas (H2, CO2), liquid (organic), and solid (catalyst) in our case while two phases of gas and solid in their case. The phase behavior of our reaction mixture under ambient and CO2 pressurized conditions are displayed in Fig. 2. The phase behavior of reaction mixture was examined at a reaction temperature of 323 K and at different CO2 pressures. It was observed that the volume of liquid phase expanded when it was pressurized by CO2 and the two-phase state (gas-liquid phase) changed to one-phase state (gas phase) at a certain pressure.
Fig. 1 Time profiles of total conversion in hydrogenation of BC in the four different multiphase media given in Table 1 such as (a) n-hexane, (b) n-hexane-CO₂, (c) n-hexane-H₂O and (d) n-hexane-CO₂-H₂O.

Fig. 2 Phase behavior of the present reaction mixtures: (a) n-hexane – water – catalyst under ambient conditions. (b) n-hexane – CO₂ mixture at different CO₂ pressures given.
Hydrogenation in the presence of water and CO$_2$

The above-mentioned results demonstrate that the multiphase reaction medium (d), including n-hexane, water, and CO$_2$, is effective for the selective hydrogenation of BC to the primary amine PEA. Further reaction experiments were carried out to examine the effects of CO$_2$ and H$_2$ pressures and pH of the aqueous phase for this medium. Fig. 3a shows that the rate of BC hydrogenation obtained in the medium (d) at CO$_2$ and H$_2$ pressures of 1 MPa and 2 MPa, respectively, is smaller than that in neat n-hexane, medium (a), at a H$_2$ pressure of 4 MPa. When the CO$_2$ pressure is raised to 3 MPa, the rate of BC hydrogenation decreases but not so significantly. The PEA selectivity does not change with H$_2$ and CO$_2$ pressures so much (Fig. 3b). A low CO$_2$ pressure of 1 MPa is sufficient for the effectiveness of medium (d) to appear in the selective hydrogenation of BC to PEA.

![Graph](image_url)

Fig. 3 Total conversion against reaction time (A) and PEA selectivity against total conversion (B) in hydrogenation of BC in the presence of water and CO$_2$ (medium (d)). H$_2$ pressure (in MPa): 4 (a), 2 (b, c); CO$_2$ pressure (in MPa): 1 (a, b), 3 (c).

The pH of water phase decreases on CO$_2$ pressurization and this would affect the rate of reaction and the product distribution.$^{20-22}$ When the water is pressurized by CO$_2$ at pressures of 1–8 MPa, the pH value decreases to about 3.$^{20}$ So, an acetic acid solution of about pH 3 was used instead of pure water for the BC hydrogenation. Table 2 indicates that the acidic medium is more effective for the total conversion and the PEA selectivity (entry 2), as compared to the reaction with pure water alone (entry 1). Although the PEA selectivity levels were very similar between the reactions in the acidic media (entries 2, 3), the conversion obtained in the presence of 3 MPa CO$_2$ was smaller than that in the acetic acid. The dissolution of CO$_2$ into the aqueous and organic phases causes a dilution of reacting species (negative effect). The solubility of H$_2$ (in mole fraction) is $1.35 \times 10^{-5}$ in pure water$^{23}$ while it increases to $1.75 \times 10^{-4}$ in acetic acid$^{24}$ (positive effect). These may be responsible for the larger conversion in the presence of acetic acid instead of pure water (entries 1, 2). Furthermore, the primary amine PEA is a strong base with a pK$_b$ = 4.17 (pK$_a$ = 9.83)$^{25}$ and it is more stabilized in an acidic environment. This may contribute to the high PEA selectivity in the presence of either acetic acid or CO$_2$ (entries 2, 3).
In addition, the reactions were conducted in a protic solvent of ethanol. The rates of BC conversion obtained in n-hexane and ethanol were similar but the primary amine PEA was formed in the latter although the main product was still the secondary amine BPEA (entry 4). The protic nature of solvent might somewhat be beneficial for the rate of BC hydrogenation. When the ethanol was pressurized by CO₂ (entry 5), the PEA selectivity increased to 38% but less significantly compared to the medium including water and CO₂ (entry 3). The reaction mixture with ethanol includes three phases (gas, liquid, solid), similar to the above-mentioned mixture with n-hexane.

<table>
<thead>
<tr>
<th>Entry</th>
<th>CO₂ (MPa)</th>
<th>Aqueous Media</th>
<th>Conversion (%)</th>
<th>Selectivity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>PEA</td>
</tr>
<tr>
<td>1</td>
<td>0</td>
<td>Water</td>
<td>73</td>
<td>24</td>
</tr>
<tr>
<td>2</td>
<td>0</td>
<td>Acetic acid a</td>
<td>93</td>
<td>90</td>
</tr>
<tr>
<td>3</td>
<td>3</td>
<td>Water</td>
<td>56</td>
<td>93</td>
</tr>
<tr>
<td>4</td>
<td>0</td>
<td>Ethanol</td>
<td>&gt;99</td>
<td>26</td>
</tr>
<tr>
<td>5</td>
<td>3</td>
<td>Ethanol</td>
<td>63</td>
<td>38</td>
</tr>
</tbody>
</table>

Reaction conditions: Benzyl cyanide 1 mmol, catalyst 58.5 mg, n-hexane 5 cm³, aqueous phase 5 cm³, temperature 323 K, H₂ 2 MPa, CO₂ 3 MPa, reaction time 1h.

a 0.1 mole-% acetic acid solution (pH 2.79)

Previously, Hiyoshi et al. studied the hydrogenation of acetophenone with a Pd/C catalyst in a few different solvents in the absence and presence of CO₂. The rate of hydrogenation was larger in an order of water > methanol > ethanol > heptane and the presence of dense phase CO₂ was effective to enhance the rate of hydrogenation in the former three solvents. They note that the increase in the conversion of acetophenone in water with the addition of CO₂ coincides with the decrease in pH of the aqueous phase, suggesting that the hydrogenation is enhanced by the protons derived from carbonic acid formed by CO₂ pressurization. Lin et al. investigated the ring hydrogenation of aromatic compounds such as benzyl alcohol and its derivatives in different multiphase reaction media including CO₂ and/or water. The presence of water resulted in a high yield of the desired product of cyclohexanemethanol of > 96% and the pressurization of CO₂ further promoted the rate of hydrogenation with no effect on the selectivity. These authors also believe that the carbonic acid should act as a promoter.

**In situ FTIR**

The molecular interactions of BC with the solvents and CO₂ were investigated by in situ FTIR-
ATR measurements. Fig. 4 shows the FTIR spectra of BC in different solvents under ambient conditions in the range of vibration of the nitrile group. The absorption band is centered at 2251 cm\(^{-1}\) for neat BC and also for BC in either water or acetic acid but it is a little blue-shifted to 2253 cm\(^{-1}\). It is thus assumed that the reactivity of the nitrile group does not change with interactions with neutral water and acidic water.

![FTIR spectra](image)

Fig. 4 In situ high pressure FTIR-ATR spectra collected at 323 K for (a) neat BC (b) BC in acetic acid (c) BC in water (d) BC in ethanol at ambient conditions.

Further, in situ FTIR-ATR spectra were collected in the presence of CO\(_2\) at different pressures. Fig. 5 displays the spectra of neat BC and BC in either water or ethanol. The CO\(_2\) pressurization weakened the absorption band of the nitrile group and changed the absorption band in a higher frequency region. When the liquid phase (neat BC, water, or ethanol) was pressurized by CO\(_2\) in FTIR-ATR measurements, the concentration of BC was lowered. This is responsible for the decrease in the intensity of the absorption band of the nitrile group with CO\(_2\) pressure. Careful examination of those spectra shows that the absorption band of the nitrile group is blue-shifted with increasing CO\(_2\) pressure for the BC in water; the extent of the blue-shift was 4.8 cm\(^{-1}\) at 6 MPa, indicating that the CN bond was likely to become stronger and its reactivity became lowered. In contrast, the blue-shift was marginal for the neat BC and the BC in ethanol, which was 1.5 cm\(^{-1}\) for the former at 10 MPa and 1.4 cm\(^{-1}\) for the latter at 6 MPa. The chemical impact of CO\(_2\) molecules on the CN bond is stronger in the presence of water compared to that for the neat BC and BC in ethanol. A low CO\(_2\) pressure of 3 MPa was used in the present hydrogenation of BC but a similar impact of CO\(_2\) should also appear. In addition, because of the stronger interactions of CO\(_2\) with the nitrile group in the presence of water, for the BC-water-CO\(_2\) mixture, the absorption band of hydroxyl group in the frequency of 3950 – 2800 cm\(^{-1}\) was examined but, unfortunately, the absorption band did not significantly vary with CO\(_2\) pressure, due probably to low concentration of BC and CO\(_2\) in water and broad absorption band.
Fig. 5 *In situ* high pressure FTIR-ATR spectra collected at 323 K for (a) neat BC (b) BC in water (c) BC in ethanol under compressed CO$_2$ at pressures given.

**Possible roles/functions of water and CO$_2$**

The present results demonstrate that the multiphase medium including both water and CO$_2$ is promising for the selective hydrogenation of BC to the primary amine PEA. A CO$_2$ pressure of 3 MPa or lower is sufficient and no such a high pressure as the critical pressure of CO$_2$ (7.4 MPa) is needed. Note, furthermore, that the catalyst deactivation can be suppressed in this medium, which often occurs in the presence of CO$_2$ alone. That is, synergistic effects will appear when water and CO$_2$ coexist in the reaction medium. In the following, possible explanations for the effects of water and CO$_2$ will be considered.

The rates of BC hydrogenation observed in the media including water and/or CO$_2$ are smaller than that in neat $n$-hexane (Table 1). When the organic phase including $n$-hexane, BC, and Pd/Al$_2$O$_3$ catalyst is pressurized by CO$_2$, the concentration of the reacting species is lowered by the dissolution of CO$_2$ molecules and this should result in the decrease in the conversion of
BC hydrogenation. In addition, some BC molecules may be dissolved in the dense phase CO₂ gas phase and this would also reduce its concentration in the organic phase. However, the CO₂ pressure applied is not high (3 MPa) and so the dissolution of BC into the CO₂ gas phase would be less significant, as suggested by the results of phase behavior observation for n-hexane (Fig. 2b) and others.²⁶ For the n-hexane – water medium, the catalyst is dispersed mainly in the aqueous phase (Fig. 2a) and the reaction should occur at the organic – aqueous interface. The chance of contacting of the catalyst with the organic substrate should be more difficult in the n-hexane – water medium than in the homogeneous organic phase. The rate of BC hydrogenation at the interface is therefore assumed to be smaller than that in the homogeneous organic phase of n-hexane (excluding the solid catalyst). When this n-hexane – water medium is pressurized by CO₂, the above-mentioned negative dilution effect by the CO₂ dissolution also appears on one hand. The dissolution of CO₂ into the organic phase may assist the dissolution of H₂ on the other hand but not so significantly in the present case, judging from the phase behavior observations (Fig. 2b). The water phase becomes acidic by the dissolution of CO₂ but the solubility of BC in water does not change with the pH value so much.²⁷ Furthermore, another negative effect is induced through interactions of BC with CO₂ in the aqueous phase, which decrease the reactivity of its nitrile group (Fig. 5). The interactions of CO₂ molecules with the BC substrate should be significant at the organic – aqueous interface than those in either n-hexane or ethanol, in which CO₂ and BC exist in the same phase, as indicated by FTIR results (Fig. 5). It is speculated that the interactions of the polar nitrile group of BC with CO₂ molecules are promoted at the organic – aqueous interface with some assistance of water. Importance of the organic – aqueous interface is noted for organic synthetic reactions assisted by water.¹

The most important feature of the n-hexane – water – CO₂ medium is the highly selective hydrogenation of BC to the primary amine of PEA in a selectivity > 90%. For the n-hexane – water medium, the selectivity to PEA is small (< 25%) but it does form. It is a water-soluble organic compound; a part of PEA formed, probably near the organic – aqueous interface, is dissolved in the water phase and so it becomes unlikely to further react with an intermediate of 2-phenylethylimine (PEI) yielding the secondary amine in the organic phase.³ Such a further hydrogenation to the secondary amine BPEA cannot be avoided in the neat n-hexane and n-hexane – CO₂ media. Also PEA molecules produced are likely to react with CO₂ and move as carbamate salt from organic to aqueous phase. This may reduce the chance for PEA to react with PEI yielding the secondary amine. The carbamate salt is insoluble in BC organic phase, resulting in high selectivity to PEA. The formation of the carbamate salt from benzylamine and CO₂ was reported by Chatterjee et al.¹⁵ and Yoshida et al.¹² The formation of carbamate salt in hydrogenation of BN using NiCl₂/NaBH₄ in CO₂ expanded ethanol at 303K was shown by Xie et al. and they also observed an enhanced benzylamine selectivity.¹⁴ For the high PEA selectivity obtained in the presence of water and CO₂ (Table 1), the acidic character of aqueous phase is also an important factor; the basic PEA molecules may be more stabilized compared to neutral water.

When the hydrogenation of BC in n-hexane pressurized by CO₂, the Pd/Al₂O₃ catalyst loses its activity during the reaction (Fig. 1). In the presence of H₂ and CO₂, CO is formed through reverse water gas shift reaction and adsorbed on the surface of supported metal particles.⁸b,⁹ On the Pd catalyst, bridged type CO is adsorbed and should cause its deactivation. The presence of water influences the adsorption of CO as evidenced by in situ high pressure FTIR measurements with Al₂O₃-supported Pd and other noble metal catalysts.⁹ The CO molecules adsorbed on the rough surface (high Miller index planes) of supported Pd particles are removed by water
molecules. These water molecules would be replaced by the substrate BC molecules or assist the contacting of the BC molecules to the Pd surface, and so the rough Pd surface should serve as active sites for the BC hydrogenation. Hence, the catalyst deactivation can be avoided but some CO molecules exist on and cover a certain partial area of Pd particles, resulting in the reduction of the overall rate of BC hydrogenation as compared to the reactions in the absence of CO₂.

**Catalyst recyclability in the water – CO₂ multiphase medium**

Finally, the catalyst recyclability was tested in the multiphase medium including both water and CO₂. The catalyst was separated by simple filtration and washed by distilled water and ethanol for 4-5 times. The reactor was loaded with the recovered catalyst, BC, n-hexane, and water and the next reaction was conducted in the same manners as used in the first run. The reaction was repeated four times (three recycling tests) with the same catalyst sample. The results obtained are presented in Table 3, including the weight of catalyst that was separated and recovered by the above-mentioned procedures, which caused some loss in the catalyst weight. The conversion was found to decrease on the recycling and the extent of decrease in the conversion was larger than expected from the decrease in the weight of catalyst recovered and used for the repeated runs. Namely, catalyst deactivation occurred to some extent on the recycling.

<table>
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<th>Run No.</th>
<th>Catalyst weight (mg)</th>
<th>Conversion (%)</th>
<th>Selectivity (%)</th>
<th>PE A</th>
<th>BPE A</th>
<th>BPE DA</th>
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<tr>
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**Table 3 Recycling test of Pd/Al₂O₃ catalyst for hydrogenation of BC in CO₂-H₂O medium**

Reaction conditions: Benzyl cyanide 1 mmol, catalyst- 58.5 mg, n-hexane 5 cm³, aqueous phase 5 cm³, temperature 323 K, H₂ 2 MPa, CO₂ 3 MPa, reaction time 2 h.

The surface of supported Pd particles on Al₂O₃ was examined by means of X-ray photoelectron spectroscopy (XPS on JEOL JPS-9200). Fig. 6 displays Pd 3d XPS spectra for the fresh and recycled (three runs) catalyst samples, indicating no difference in the BE between the two samples. The surface of Pd particles was unlikely to change during the reaction, separation, and recovery procedures. The atom concentration of Pd/Al/O in % was found to be 5.3/36/59 for the fresh catalyst but 3.7/39/57 for the recycled one; the Pd/Al (Pd/O) ratio decreased from 0.15 (0.090) to 0.095 (0.065) after the three repeated runs. That is, the number of exposed Pd atoms on the Pd/Al₂O₃ catalyst was reduced by the recycling. A possible reason for this reduction is the leaching of Pd species from the solid catalyst into an acidic water caused by the dissolution of CO₂. Yoshida et al. previously pointed out the possibility of metal leaching from a Pd/Al₂O₃ catalyst for hydrogenation of phenol in the water – CO₂ medium. Another possibility is the dissolution and re-deposition of Al species on the surface of Pd particles. The aqueous phase is acidic and so the leaching of Al species, as well as Pd, from the catalyst could happen during the
reaction and the subsequent re-deposition on the Pd particles during the post-separation (filtration, washing, drying). Further work is in progress to study the catalyst deactivation in the water – CO$_2$ medium and to find effective ways to avoid the deactivation by using other support materials different in the solubility in acidic water and interactions with Pd compared to Al$_2$O$_3$.

Fig. 6 XPS Pd 3d spectra for fresh and recycle (three times) Pd/Al$_2$O$_3$ catalyst samples. Charge-up corrections of binding energy (BE) was made by reference to Al 2p BE at 74.7 eV for γ-Al$_2$O$_3$.29

Conclusions

The multiphase medium including both water and CO$_2$ in addition to an organic solvent of $n$-hexane is effective for the selective hydrogenation of BC to the primary amine of PEA over a Pd/Al$_2$O$_3$ catalyst. The rate of BC hydrogenation in this multiphase medium is smaller than that obtained in a homogeneous phase of neat $n$-hexane but comparable to those obtained in $n$-hexane added with either water or CO$_2$. In neat $n$-hexane and $n$-hexane – CO$_2$ media, PEA is not obtained and the secondary amine is mainly produced. In the latter medium, the catalyst loses its activity during reaction due to the formation and adsorption of CO via reverse water gas shift reaction. In contrast to these three media, the desired product of PEA is obtained in a selectivity > 90% and no catalyst deactivation occurs in the $n$-hexane – water – CO$_2$ medium. The water-soluble PEA molecules produced are likely to react with CO$_2$ and move as a carbamate salt from organic phase to water. This may reduce the chance for PEA to react with the intermediate of PEI yielding the secondary amine in the organic phase, resulting in the highly selective production of PEA. The aqueous phase takes acidic nature by the dissolution of CO$_2$, which is also important for the high selectivity to PEA. It is likely that CO is also formed and adsorbed on the surface of supported Pd particles in this medium. However, some adsorbed CO molecules may be removed by water molecules, which allows some Pd sites to serve as active ones for the hydrogenation and then causes no perfect catalyst deactivation. The use of green components of water and CO$_2$ can significantly contribute to the design of effective media for organic synthetic reactions. The
separation of water and CO$_2$ from organic phases is easy and this is also advantageous for practical application. In the water – CO$_2$ medium, however, the catalyst deactivation occurs to some extent on the repeated runs, for which an acidic nature of water caused by the dissolution of CO$_2$ should be responsible.

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