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**A multiphase reaction medium including pressurized carbon dioxide
and water for selective hydrogenation of benzonitrile with a Pd/Al₂O₃
catalyst**

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Abstract

The hydrogenation of benzonitrile was studied with a Pd/Al₂O₃ catalyst in the presence of pressurized CO₂ and water. This multiphase reaction system was effective for the selective production of the desired primary amine of benzylamine with no deactivation of the catalyst. The enhanced selectivity to the primary amine resulted from its transfer into water phase, which prevented the primary amine from reacting with an intermediate of imine into the secondary amine in the organic phase (benzonitrile). In addition, interactions of CO₂ molecules with the primary amine could also increase its selectivity. In the absence of water, the catalyst was deactivated by the accumulation of a carbamate salt on the surface of catalyst. But this deactivation was avoided by the addition of water because the salt was soluble in water and it did not deposit on the catalyst existing at interfacial layer between the water and organic phases.

Keywords: Benzonitrile, Selective hydrogenation, Carbon dioxide, Water, Multiphase reaction

1. Introduction

Multiphase reaction mixtures including pressurized CO₂ and/or water are an interesting medium for organic synthetic reaction and separation processes [1-3]. When an organic liquid phase (substrate, solvent) is pressurized by CO₂, a large amount of CO₂ is dissolved in the liquid. This causes its volume to expand and such a liquid is referred to as CO₂-dissolved expanded liquid phase [4, 5]. The dissolution of CO₂ may facilitate the dissolution of other coexisting gases such as H₂, O₂, and CO and promote the chemical reactions involving these gaseous reactants, as mentioned in recent reviews [6-8]. In addition to this physical effect, CO₂ molecules may have a chemical impact on reacting species and change the product selectivity as well as the overall reaction rate. For example, the complete selective hydrogenation of nitrobenzene to aniline can be achieved in a whole range of conversion up to 100 % with supported Ni catalysts in the presence of pressurized CO₂ [9]. *In situ* high-pressure Fourier transform infrared (FTIR) measurements indicate molecular interactions of CO₂ with the substrate of nitrobenzene and the intermediates of nitrosobenzene and *N*-phenylhydroxylamine; the interactions of CO₂ with the nitro group of the substrate decrease its reactivity to hydrogenation but increase the reactivity of these intermediates. As a result, the desired aniline can be produced at any conversion level. The pressurization with CO₂ can also promote the rate of nitrobenzene hydrogenation and the extent of promotion depends on its pressure used. Xie et al. studied hydrogenation of nitrile and imine in CO₂-dissolved expanded organic solvent phases [10]. In heterogeneous hydrogenation of benzonitrile (BN) and phenylacetonitrile with NiCl₂/NaBH₄ in CO₂-expanded ethanol, the yield of the primary amines was improved. The authors mentioned that the primary amines were protected by CO₂ and so their further hydrogenation to the secondary amines was effectively suppressed. Note, in addition, that the pressurization with CO₂ is also effective for

promoting the rate of Heck coupling reactions and modifying the yield and/or the selectivity in Diels-Alder reactions in which no gaseous reactants are involved [11-13].

Recently the authors found out that the addition of water caused the promotion effect of CO₂ pressurization to appear at a lower pressure of about 1 MPa for the hydrogenation of nitrobenzene [14]. Hiyoshi et al. communicated that the coexistence of CO₂ and water enhanced the hydrogenation of acetophenone with a Pd/C catalyst [15]. They discussed possible reasons for the rate enhancement observed and pointed out the importance of pH value in the aqueous phase, which was decreased by the dissolution of CO₂. Those results show that an interesting and effective multiphase reaction medium may be designed using green components of pressurized CO₂ and water. In the present work, the features of such a reaction system have been studied in detail for the selective hydrogenation of BN to the primary amine of benzylamine (BA) with a Pd/Al₂O₃ catalyst. The hydrogenation runs were conducted under different conditions and molecular interactions among the substrate, CO₂, water, and the catalyst were measured by *in situ* high-pressure FTIR methods [16, 17] in order to elucidate the roles of CO₂ and water. The medium of gas (H₂, CO₂) – liquid (water) – liquid (BN) – solid (catalyst) has been confirmed to be effective for the selective production of BA by BN hydrogenation with no catalyst deactivation. It is important to avoid the deactivation of supported noble metal catalysts in the presence of both H₂ and CO₂ at high pressures. For the hydrogenation with supported metal catalysts in CO₂-dissolved expanded liquids, the deactivation of catalysts occurs in some cases due to the formation and adsorption of CO from H₂ + CO₂ on the surface of metal catalysts [18, 19]. For example, in hydrogenation of phenol with Rh catalysts supported on C and Al₂O₃, the Rh/C does not lose its activity during the reaction but the Rh/Al₂O₃ is easily deactivated at an early stage of reaction [17]. This difference is caused by weak and strong adsorption of CO

(originating from CO₂) on the former and latter catalysts, respectively, as proved by *in situ* FTIR measurements.

The selective hydrogenation of nitriles to primary amines is one of industrially important chemical reactions [20-22]. The primary amines can find various applications as dyes, pharmaceuticals, explosives, agrochemicals, and others. The hydrogenation of nitrile compounds was previously studied by several authors using homogeneous [21] and heterogeneous [22] metal catalysts. For homogeneous catalysts, the selectivity to the primary amine is high > 95 % but the difficulty of catalyst separation after reactions is a main problem. Therefore, the use of heterogeneous catalysts is desirable but the low selectivity to primary amines due to the formation of secondary amines should be improved. Application of NH₃ with heterogeneous catalysts can improve the selectivity to primary amines [23], but the amount of NH₃ required is large. Another way is the addition of acids such as HCl and acetic acid over Pd/C and RANEY Ni catalysts [24-26]. A biphasic medium including acidic water (NaH₂PO₄) and dichloromethane is effective for a high selectivity of 95% to BA in hydrogenation of BN with supported Pd catalysts [27]. From an environmental point of view, however, it is desirable to avoid the use of those harmful base and acid additives. Recently, Bakker et al. reported an extensive work on heterogeneous hydrogenation of BN [28]. They compare the performance of various supported metal catalysts reported so far in the literature. It is reported that a high selectivity of 95% to the primary amine can be achieved by supported Pd catalysts at a H₂ pressure of 1 MPa [28]. The use of dense phase CO₂ in hydrogenation of nitriles was recently investigated by Chatterjee et al. [29]. They show that the selectivity to the primary and secondary amines can be tuned by CO₂ pressure and BA is produced with a Pd/MCM-41 catalyst in a high selectivity of about 90% at a CO₂ pressure of about 10 MPa. Those previous results and interesting impacts of dense

phase CO₂ and water have set the present authors to work on a multiphase medium including those two green components in the selective hydrogenation of nitriles, using BA as a model substrate.

2. Experimental

2.1. Hydrogenation

A commercially available 5 wt% Pd/Al₂O₃ (Wako) was used as a catalyst for the hydrogenation of BN. Prior to the reaction, the catalyst sample was reduced in a glass tube with a pure H₂ (99.99 %) stream of 60 cm³ min⁻¹ at room temperature for 30 min and then heated at 5 K min⁻¹ to 473 K, at which it was further reduced for 1 h. The reduced sample had an average Pd particle size of 3.6 nm measured by transmission electron microscopy (JEOL JEM-2000ES) and it had a BET surface area of 98.0 m² g⁻¹ and an average pore diameter of 9.1 nm measured by nitrogen adsorption at 77 K (Quantachrome NOVA 1000). The hydrogenation of BN (Aldrich) was conducted in a 50 cm³ stainless steel autoclave. The reactor was charged with 9.7 mmol (1.0 g) BN, 5 cm³ water (Wako), and 20 mg Pd/Al₂O₃, flushed with H₂ for three times to remove the air, and heated to a reaction temperature of 323 K in a water bath. After the introduction of 2 MPa H₂, liquid CO₂ (99.99 %) was introduced into the reactor to the desired pressure with a high pressure liquid pump (JASCO SCF-Get). The reaction was conducted while stirring the reaction mixture with a magnetic stirrer. After the reaction, the reactor was cooled in an ice-water bath and depressurized carefully. The reaction mixture was analyzed by a gas chromatograph (GL Sciences GC-4000) using a capillary column (Phenomenex ZB-5) and a flame ionization detector. The total conversion was determined from the initial and final amounts of BN. Under the conditions used, BA, dibenzylamine (DBA), and toluene were detected to form and the product selectivity

was determined by the following equation: $\alpha \times (\text{moles of a product}) / (\text{moles of BA} + 2 \times \text{moles of DBA} + \text{moles of toluene})$, in which $\alpha = 1$ for BA and toluene and $\alpha = 2$ for DBA. For the present reaction runs, the stirring speed was set in a range where it little affected the overall rate of reaction, which was confirmed by a few preliminary runs conducted at different stirring speeds. Note, generally speaking, that the use of magnetic stirring was unable to completely take off its influence on the rate of chemical reactions in liquid phases in the presence of solid catalysts and/or gaseous reactants.

2.2. *In situ* high-pressure FTIR measurement

Molecular interactions of pressurized CO₂ with reacting species are important for determining the rate of reaction and the product selectivity [30]. *In situ* high-pressure FTIR was used to examine the interactions between CO₂ and BN molecules in the absence and presence of water using a JASCO FTIR-620 spectrometer with a triglycine sulfate detector at a frequency resolution of 2 cm⁻¹. The FTIR measurements were made with a home-designed high pressure cell of 1.18 cm³ attached with a ZnSe rod in attenuated total reflection (ATR) mode [31]. A certain volume of BN was introduced into the cell and it was purged with CO₂ several times. After heating to 323 K by resistivity heating with coils embedded in the cell, compressed CO₂ was introduced into the cell to the desired pressure while stirring the mixture. The FTIR spectra were collected for a mixture of CO₂ dissolved in liquid BN at different pressures. Similar measurements were also made for a mixture of bulk water dissolving CO₂ and BN.

In situ high-pressure FTIR was also used to examine the formation and adsorption of CO from compressed H₂ and CO₂ over Pd/Al₂O₃ using a 1.5 cm³ high pressure cell. The Pd/Al₂O₃ sample was ground in a mortar and the powder was

pressurized at 50 MPa for 1 h to prepare a sample pellet. The pelletized sample was placed into the cell and it was purged with H₂ three times. The cell was heated to 343 K and then H₂ was introduced to 4 MPa to reduce the catalyst sample for 1 h. Then, the cell was purged with N₂, cooled to 323 K, and the spectrum was collected. The cell was loaded with 2 MPa H₂ followed by the introduction of CO₂ to the desired pressures. The FTIR spectra were measured at different CO₂ pressures in the absence of BN and water vapor. When BN co-existed, as mentioned later, a certain carbamate species was produced from CO₂ and BA, the product of BN hydrogenation, which accumulated on and covered the surface of catalyst. So, it was impossible to examine the formation and adsorption of CO from H₂ and CO₂ in the presence of BN. The influence of BN and/or water on the adsorption of CO was examined using CO instead of CO₂ and H₂ using the same FTIR cell. The pelletized sample was treated in the same manner as described above and a certain amount of water and/or BN was introduced into the cell with a syringe through a small hole where N₂ was flowing out. Then CO (1 % in He) was introduced into the cell at ambient pressure for 15 min, and the FTIR spectra were collected. The FTIR spectra were further measured after purging with N₂ to remove water and/or BN vapor from the atmosphere.

2.3. Phase behavior observation

There are a few different phases in the present reaction medium and so it is important to examine the phase behavior under high pressure reaction conditions. A 10 cm³ sapphire-windowed view cell was used for this purpose [32]. The observation was made with a similar volumetric ratio of BN to the reactor as used in the hydrogenation reactions. A certain amount of BN was added into the cell and it was purged with H₂ 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 H₂. Then CO₂ 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 CO₂ pressures. The mixture was observed to change from three-phase state (gas – liquid – solid) to two-phase state (gas – solid) at a certain pressure. In addition, the dispersion of granules of Pd/Al₂O₃ catalyst in the present multiphase reaction medium was examined at atmospheric pressure.

3. Results and discussion

3.1. Hydrogenation in different media

The hydrogenation of BN was examined with a Pd/Al₂O₃ catalyst in different multiphase reaction media at 323 K and a H₂ pressure of 2 MPa. Generally, several products may be formed, including BA, DBA, and toluene, as depicted in Scheme 1 [20-22, 27, 28]; benzylideneimine is an intermediate and its condensation with BA results in the formation of DBA. The tertiary amine may also be formed in a similar way from DBA and benzylideneimine. In the present hydrogenation of BN, the products of BA, DBA, and toluene were detected to form without any other ones. The product distribution was observed to depend on the reaction media and conditions employed.

Table 1 shows the results obtained in different reaction media in the absence and presence of CO₂ and/or H₂O. In neat BN (entry 1), a conversion of 44 % was obtained with a BA selectivity of 85 %. The addition of either CO₂ (9 MPa) or H₂O decreased the total conversion but did not change the selectivity so much (entries 2, 3). When both CO₂ and H₂O were added, the conversion was also lowered to 13 % but, interestingly, the BA selectivity was significantly enhanced to 96 % (entry 4). This high BA selectivity remained unchanged during the reaction up to an almost complete

conversion (in a longer reaction time) (entry 5). These results show that the co-existence of pressurized CO₂ and H₂O is indispensable for the selective hydrogenation of BN to the primary amine of BA. To understand the features of this multiphase reaction medium, the influence of CO₂ pressure was further examined.

3.2. Hydrogenation in the presence of CO₂ and water

Fig. 1a gives the changes of total conversion and product selectivity with CO₂ pressure in the absence of H₂O. The conversion slightly decreased but the selectivity did not change with CO₂ pressure < 10 MPa. At higher pressures, however, the conversion and the BA selectivity significantly decreased while the DBA selectivity increased. The phase behavior observations of the reaction mixture indicated that the volume of liquid BN simply decreased due to its dissolution into the CO₂ phase with increasing pressure and disappeared at about 10.6 MPa. The significant decreases in the total conversion and the BA selectivity occurred in the homogeneous CO₂ phase. Hence, in the absence of H₂O, pressurized CO₂ has no positive impact on the selective hydrogenation of BN to BA under both gas – liquid (BN) – solid (catalyst) and gas – solid conditions. The results obtained in the presence of H₂O are given in Fig. 1b, indicating quite different impacts of pressurized CO₂. The presence of 1 MPa CO₂ increased the total conversion and the BA selectivity up to > 95% but decreased the DBA selectivity. When CO₂ pressure was further raised up to 14 MPa, the conversion and the selectivity did not change so much. The phase behavior of the reaction mixture was gas – liquid (BN) – liquid (H₂O) – solid (catalyst) at CO₂ pressures < 11 MPa and gas – liquid (H₂O) – solid at higher pressures. Thus, the reaction medium including both pressurized CO₂ and H₂O is effective for the selective hydrogenation of BN to BA irrespective of the phase behavior.

The influence of reaction time was then examined for BN hydrogenation in the presence of CO₂ and/or H₂O. Fig. 2a shows that the reaction went smoothly in the absence of CO₂ and was almost completed in < 15 h under the conditions used. In the presence of 1 MPa CO₂, the rate of reaction became lowered and leveled off with time and the reaction stopped in 12 h. Similar but larger negative effects of CO₂ were observed at 14 MPa. The catalyst (Pd/Al₂O₃) was deactivated by pressurized CO₂ in the absence of H₂O. The reason for this catalyst deactivation will be discussed in detail later. When H₂O co-existed, in contrast, the reaction went smoothly up to 100 % BN conversion even in the presence of pressurized CO₂; that is, no catalyst deactivation occurred in this multiphase reaction medium. The selectivity to BA is plotted against total BN conversion in Fig. 2b. The addition of H₂O alone is effective for enhancing the selectivity but more significant enhancement is caused by the presence of both CO₂ and H₂O, giving a BA selectivity > 95 % during the whole course of reaction up to 100 % BN conversion.

The state of the multiphase reaction mixture was visually examined. The catalyst granules were observed to exist at the interface between the organic (BN) and aqueous phases (Fig. S1 in SI). The authors attempted to modify the surface properties of the catalyst and examine its activity after the surface modification. The catalyst was treated by immersing in either hot water or 1-heptanol at 353 K for 6 h and dried under ambient conditions. The hot water and 1-heptanol treatments were expected to make the catalyst more hydrophilic and more hydrophobic, respectively. This was confirmed by FTIR measurements that the broad absorption band due to surface hydroxyl groups at 3700 – 3000 cm⁻¹ became larger by the hot water treatment, while the new absorption bands due to the surface C₇H₁₃O- group appeared by the 1-heptanol treatment (Fig. S2 in SI). Table 2 shows the results of BN hydrogenation with these surface modified

Pd/Al₂O₃ catalysts. The product distribution was little affected by the surface treatments but the total conversion was lowered and improved by the treatments with hot water and 1-heptanol, respectively. The hydrophobic nature is better for the catalyst to give a larger total conversion in this multiphase reaction medium. It was indicated by X-ray photoelectron spectroscopy that the surface properties of supported Pd particles were not different between the hot water and 1-heptanol treated samples (Fig. S3 in SI).

It is known that the pH of H₂O phase decreases on CO₂ pressurization [33] and this pH change could affect the rate of reaction and the product distribution in the present BN hydrogenation. When H₂O phase is pressurized by CO₂ at pressures of 1 – 8 MPa, the pH value decreases to about 3 according to the literature [34]. So, an acetic acid solution of pH 3 was used instead of pure H₂O for the reaction. Table 3 indicates that acidic medium may be slightly better for the total conversion and the BA selectivity (entry 2), as compared to the reaction with pure H₂O alone (entry 1). Although the conversion levels were very similar between the reaction with pressurized CO₂ and H₂O (entry 3) and that in the acetic acid solution, the BA selectivity was larger in the former medium than in the latter.

3.3. *In situ* high-pressure FTIR measurements

(a) *Molecular interactions of CO₂ with BN*

Carbon dioxide molecules are dissolved in organic liquids at high pressures and may interact with chemical species in these phases [9, 30, 31, 35]. For example, CO₂ molecules interact with carbonyl group of cinnamaldehyde [35] and nitro group of nitrobenzene [9], as evidenced by *in situ* high-pressure FTIR measurements for the organic compounds dissolved in pressurized CO₂. The interactions with CO₂ increase the reactivity of the carbonyl group and decrease that of the nitro group, which results in

the improved selectivity to cinnamyl alcohol and to aniline in hydrogenation of cinnamaldehyde and nitrobenzene, respectively, in the presence of compressed CO₂. Similar FTIR measurements were made for liquid BN dissolving CO₂ at high pressures by ATR mode [31]. Fig. 3a presents the FTIR-ATR spectra obtained in the range of 2260 – 2200 cm⁻¹ at different CO₂ pressures. The absorption band appeared at around 2228 cm⁻¹, assignable to the stretching vibration of C-N bond of BN. The peak position was blue-shifted with increasing CO₂ pressure, indicating that the CN bond became stronger and pressurized CO₂ should decrease its reactivity. Similar FTIR spectra were collected for BN dissolved in H₂O compressed by CO₂ in the same ATR mode. Fig. 3b shows the spectra collected, indicating that the absorption band of C-N bond became weaker with increasing pressure due to the transfer of BN from H₂O to CO₂ phase. It was seen, however, that the peak position of $\nu(\text{CN})$ absorption band was blue-shifted with increasing CO₂ pressure and the extent of the blue-shift was the same irrespective of the absence and presence of H₂O. So, the interactions between BN and CO₂ molecules are unlikely to change by the presence of H₂O. In other words, a BN molecule should be preferentially surrounded by CO₂ molecules. Note again, thus, that the reactivity of C-N bond of BN is lowered by the presence of CO₂ and this does not depend on the presence of H₂O.

(b) Formation and adsorption of CO

There is a possibility of the formation and adsorption of CO through reverse water gas shift reaction ($\text{CO}_2 + \text{H}_2 \rightarrow \text{CO} + \text{H}_2\text{O}$) or other pathways when hydrogenation reactions are conducted with supported metal catalysts in the presence of pressurized H₂ and CO₂. A few authors investigated this phenomenon using *in situ* high-pressure FTIR techniques and stated that the formation of CO was responsible for

the catalyst deactivation observed in several hydrogenation reactions [18, 19]. The present authors also observed the formation and adsorption of CO on pelletized Pd/Al₂O₃ catalyst in the presence of H₂ and CO₂ at 323 K using *in situ* high-pressure FTIR technique (Fig. S4 in SI). The adsorbed CO species still remained under ambient conditions. To examine the competitive adsorption of CO and BN, CO was adsorbed on the catalyst in the presence of H₂O and/or BN vapor. Fig. 4 shows that the absorption bands assignable to bridged CO species are located at about 1970 and 1910 cm⁻¹ [36] and a weak absorption band of linear CO species at 2080 cm⁻¹ [37, 38] in the absence of both H₂O and BN. When H₂O co-exists, the absorption band of linear CO disappears while those of bridged CO still remain [39]. In the presence of BN, in contrast, the absorption bands of the bridged and linear CO species appear at 1920 and 2010 cm⁻¹, respectively. The spectrum obtained in the presence of both H₂O and BN is similar to that with BN alone. The adsorbed CO species can exist in the presence of H₂O and some CO species may be replaced by BN molecules. In addition to those FTIR measurements, a reaction run was conducted with a catalyst sample on which CO was pre-adsorbed by exposure to 1 % CO gas at 0.1 MPa for 10 min. The reaction was observed to occur with this catalyst. The pre-adsorption of CO on the catalyst does not cause its deactivation because the adsorbed CO species may easily be replaced with the substrate BN. Those results imply that CO is also formed and adsorbed on the surface of Pd/Al₂O₃ catalyst in the presence of pressurized H₂ and CO₂. However, this is not responsible for the catalyst deactivation observed in the presence of pressurized CO₂ alone (without H₂O). We should consider other possible reasons for the catalyst deactivation, which will be discussed later.

3.4. Features of the reaction medium including both CO₂ and water

From those results obtained, the authors will discuss the possible roles of pressurized CO₂ and H₂O in hydrogenation of BN with respect to the total conversion, the BA selectivity, and the catalyst life in the following. The multiphase reaction media studied are categorized as illustrated in Fig. 5. The media (b) and (d) were examined at a H₂ pressure of 2 MPa, similar to those (a) and (c), and at different CO₂ pressures. The media of (a) and (c) initially included two (gas – organic liquid) and three (gas – organic liquid – water) phases, respectively, except for the solid catalyst. The phases existing in the initial mixtures of (b) and (d) were different depending on CO₂ pressure used. The organic liquid phase of BN decreased in its volume with increasing CO₂ pressure and disappeared at 10.6 MPa, as illustrated in SI (Figs. S4, S5), while the volume of water did not change so much at CO₂ pressures examined. When the reaction proceeds, BN transforms mainly into BA, a water-soluble compound. The solubility of H₂O into the gas phase (H₂ and/or CO₂) is negligible under the conditions used. The phase behavior changes during the reaction in different manners: for the systems of (a) and (b) of Fig. 5 including no H₂O, no change but the component of the liquid phase changes from BN to BA; for the systems of (c) and (d) including H₂O, the liquid phase (BN) decreases and disappears due to the dissolution of the product of BA into H₂O.

Medium (a)

In the absence of CO₂ and H₂O, the hydrogenation of BN goes smoothly to 100 % conversion; however, the BA selectivity is about 80 % at an initial stage of reaction and tends to decrease with conversion to about 60 % at a conversion of 60 % (Fig. 2). No catalyst deactivation occurs in this reaction medium. The selective hydrogenation of BN to BA can be achieved with an alumina-supported Pd catalyst under ordinary conditions; Bakket et al. reported a high BA selectivity of about 95% in

a solvent of 2-propanol at a H_2 pressure of 1 MPa and at 353 K [28].

Medium (b)

When 1 MPa CO_2 is added to medium (a), the conversion is slightly lowered. It does not change with increasing CO_2 pressure up to about 10 MPa but decreases at higher pressures (Fig. 1a). The large decrease in the conversion at pressures > 10 MPa may be ascribed to the dilution effect; the reacting species, except for the solid catalyst, are completely soluble in the CO_2 gas phase at 10.6 MPa and become more diluted with increasing pressure. A few possible factors would be related to the influence of pressurized CO_2 at pressures < 10 MPa, in which the reaction mixture includes gas (CO_2 , H_2), liquid (BN), and solid (catalyst). The molecular interactions with CO_2 decrease the reactivity of C-N bond of the substrate, decreasing the rate of BN hydrogenation. The conversion levels are almost the same at different CO_2 pressures in the range of 1 – 10 MPa. So, the decreased reactivity of BN could be offset by an increase in the concentration of H_2 , which is assisted by the dissolution of CO_2 . In medium (b), the rate of hydrogenation stopped after a certain period of time; namely, the catalyst deactivation occurs (Fig. 2). The *in situ* FTIR measurements show that CO is formed from H_2 and CO_2 at high pressures and adsorbed on the catalyst (Fig. S6 in SI) but this is not responsible for the catalyst deactivation. When CO_2 was introduced to liquid BA, we shortly observed the formation of a white solid material. It should be a carbamate salt [10, 29], as depicted in Scheme 2. It is likely to accumulate on and cover the surface of catalyst during the reaction, resulting in the catalyst deactivation.

Fig. 1a also shows that the BA selectivity decreases with CO_2 pressure in a similar way as does the total conversion. The homogeneous CO_2 gas phase (except for the solid catalyst) facilitates the formation of the secondary amine DBA, which is

produced via condensation between the primary amine of BA and the intermediate of benzylideneimine (Scheme 1). The imine intermediate might be concentrated on the catalyst in the CO₂ gas phase at high pressures due to dilution of H₂ and/or interactions with CO₂ molecules. As mentioned above, when CO₂ was added to liquid BA, a white solid material was shortly produced; so, unfortunately, the authors failed to examine the interactions between the BA and CO₂ molecules by the *in situ* high-pressure FTIR method.

The hydrogenation of BN to BA in the presence of pressurized CO₂ was recently studied by Chatterjee et al. using Pd catalysts on MCM-41 and C supports at a H₂ pressure of 2 MPa and at 323 K [29]. The total conversion and the BA selectivity were reported to increase with CO₂ pressure up to 10 MPa, which are different from the CO₂ pressure effects observed in the present work (Fig. 1a). With the Pd/MCM-41 catalyst, the BA selectivity was maximal (about 90%) at a conversion of 90% at a CO₂ pressure of around 10 MPa, at which the reaction mixture was in a single phase (except for the solid catalyst). It is noted that the formation of carbamate from BA and CO₂, which may depend on the phase behavior, is an important factor for the high selectivity to BA.

Medium (c)

When H₂O is added to medium (a), the BA selectivity is enhanced (Fig. 2). This may be explained by the nature of BA, which is soluble in H₂O phase and so it becomes unlikely to react with the imine intermediate producing the secondary amine in the organic BN phase. The initial BA selectivity is about 90 % but, unfortunately, the BA selectivity decreases with conversion, similar to the case of medium (a). Some quantity of BA is likely to be soluble in the organic BN phase and react with the imine

intermediate. A larger amount of BA is formed at a larger conversion and so the change of BA to the secondary amine should be more significant in a later stage of reaction. The total conversion is lowered by the addition of H₂O (Table 1). The catalyst granules may be dispersed in organic BN phase in medium (a) but these exist at the H₂O – BN interface in medium (c). The contact between the catalyst and BN phase in the latter should be smaller than that in the former, which would be a reason for the smaller conversion in medium (c). The importance of the catalyst – BN contact is supported by the differences in the activity among untreated and surface-treated, hydrophilic and hydrophobic Pd/Al₂O₃ catalysts in the hydrogenation of BN in the presence of H₂O (Table 2)

Medium (d)

The BA selectivity is more significantly enhanced by the presence of both CO₂ and H₂O. A high BA selectivity of > 95% can be obtained at a low CO₂ pressure of 1 MPa (Fig. 1b), which is even lower compared to 10 MPa needed for the high BA selectivity with Pd/MCM-41 in the presence of CO₂ alone [29]. Fig.2b indicates that this high BA selectivity can remain unchanged during the whole course of reaction, being different from the case of medium (c). The BA molecules produced are likely to react with CO₂ and move as the carbamate salt from the organic phase to the aqueous phase. This may reduce the chance for BA to react with the intermediate of benzylideneimine yielding the secondary amine. The carbamate salt is insoluble in the BN organic phase, resulting in that the high BA selectivity can remain unchanged even at larger conversion levels. A similar effect was previously reported by Xie et al., who investigated the hydrogenation of BN using NiCl₂/NaBH₄ in CO₂-expanded ethanol at 303 K [10]. They indicated the formation of carbamate salt in the ethanol phase and

observed an enhanced BA selectivity of 98 %. The formation of carbamate salt from BA and CO₂ was also reported by Chatterjee et al., who noted its importance for the high BA selectivity [29]. The carbamate salt is unstable and so the corresponding primary amine can easily be obtained by heating [40]. Compared to medium (a), this medium (d) gives a smaller conversion (Table 1). This may also be explained by a difference in the catalyst – BN contact between the media (a) and (d).

The multiphase reaction medium (d) including both CO₂ and H₂O is significant for not only the selective production of BA but also no catalyst deactivation in hydrogenation of BN with Pd/Al₂O₃. Carbon monoxide is formed even in the presence of H₂O but does not cause the catalyst deactivation. As mentioned above, the carbamate salt is formed from BA and CO₂ and it is soluble in H₂O. So, the salt does not cover the surface of Pd/Al₂O₃ catalyst and it cannot cause the deactivation during the reaction.

4. Conclusion

The multiphase reaction medium including both pressurized CO₂ and H₂O is promising for the selective hydrogenation of BN to the primary amine BA with a Pd/Al₂O₃ catalyst. The BA selectivity is > 95 % at any conversion level and the catalyst is not deactivated during the reaction even though CO is formed from H₂ and CO₂. The high BA selectivity results from a synergistic effect of CO₂ and H₂O. The hydrogenation product of BA reacts with CO₂ giving a carbamate salt and this water-soluble species moves into the aqueous phase, preventing the BA from reacting with the intermediate of benzylideneimine yielding the secondary amine. The carbamate species accumulates on the surface of catalyst and causes its deactivation in the absence of H₂O. When H₂O co-exists, however, the carbamate salt is soluble in the aqueous phase and the catalyst is unlikely to be covered and deactivated by this species. Carbon dioxide interacts with the

C-N group of the substrate and decreases its reactivity. When pressurized CO₂ is introduced into the reaction mixture including H₂O, however, the total conversion is enhanced. The CO₂ is soluble in the organic and aqueous phases and may change their solvent properties, which might influence the state of dispersion of catalyst granules at their interface, the rate of hydrogenation of BN, the concentration of H₂ in the organic liquid phase, and other factors.

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Captions for Figures, Tables, and Schemes

Fig. 1. Influence of CO₂ pressure on total conversion and product selectivity in hydrogenation of BN in the absence (a) and presence (b) of H₂O using Pd/Al₂O₃ at 323 K and at a H₂ pressure of 2 MPa for 4 h.

Fig. 2. (a) Time profiles of total conversion in hydrogenation of BN in the absence (○, ◇, □) and presence (●) of H₂O (5 cm³) and at CO₂ pressures given. (b) The relationship between BA selectivity and total conversion in the absence (◇) and presence (●, ●) of H₂O (5 cm³) and at CO₂ pressures given.

Fig. 3. *In situ* high-pressure FTIR – ATR spectra collected at 323 K for liquid BN (a) and for H₂O dissolving BN (b) compressed by CO₂ at pressures given

Fig. 4. *In situ* high-pressure FTIR spectra of CO adsorbed on Pd/Al₂O₃ after reduction (a), after exposure to atmospheric CO for 10 min (b), and after purging with N₂ (c) in the absence (1) and presence of H₂O (2), BN (3), and H₂O + BN (4).

Fig. 5. Illustration of features of BN hydrogenation reactions in four different multiphase media in the absence and presence of CO₂ and/or H₂O. The solid catalyst phase is not displayed herein.

Table 1 Results of hydrogenation of BN in the absence and presence of pressurized CO₂ and/or H₂O with Pd/Al₂O₃ catalyst ^a

Table 2 Influence of surface modification with either hot water or 1-heptanol on the activity of Pd/Al₂O₃ catalyst in BN hydrogenation ^a

Table 3

Results of BN hydrogenation in different aqueous media in the absence and presence of pressurized CO₂ and acetic acid ^a

Scheme 1 Possible reaction pathways in the hydrogenation of benzonitrile (BN)

Scheme 2 Formation of a carbamate salt from BA and CO₂

Table 1

Results of hydrogenation of BN in the absence and presence of pressurized CO₂ and/or H₂O with Pd/Al₂O₃ catalyst ^a

Entry	CO ₂ (MPa)	H ₂ O (cm ³)	Phases present ^b	Conv. (%)	Selectivity ^c (%)		
					BA	DBA	TOL
1	0	0	G-L ₁	43.6	84.6	14.8	0.6
2	9	0	G-L ₁	21.6	82.7	16.1	1.2
3	0	5	G-L ₁ -L ₂	10.7	83.0	12.1	4.9
4	7	5	G-L ₁ -L ₂	13.4	95.9	0.9	3.2
5	7	5	G-L ₁ -L ₂	99.6	98.4	1.3	0.3

^a Reaction conditions: BN 1.0 g (9.7 mmol), catalyst 20 mg, H₂ 2 MPa, Temperature 323 K, Reaction time 4 h (24 h for entry 5).

^b Phases present in the reaction mixture except for the solid catalyst. G: H₂ and/or CO₂, L₁: BN, L₂: water.

^c BA: benzylamine, DBA: dibenzylamine, TOL: toluene.

Table 2

Influence of surface modification with either hot water or 1-heptanol on the activity of Pd/Al₂O₃ catalyst in BN hydrogenation ^a

Entry	Modification	Conv. (%)	Selectivity ^b (%)		
			BA	DBA	TOL
1	—	13.4	95.9	0.9	3.2
2	H ₂ O	11.5	94.5	0.9	4.6
3	1-Heptanol	20.4	95.3	3.1	1.6

^a Reaction conditions: BN 1.0 g (9.7 mmol), catalyst 20 mg, H₂ 2 MPa, Temperature 323 K, Reaction time 4 h

^b BA: benzylamine, DBA: dibenzylamine, TOL: toluene

Table 3

Results of BN hydrogenation in different aqueous media in the absence and presence of pressurized CO₂ and acetic acid ^a

Entry	CO ₂ (MPa)	Aqueous media	Conv. (%)	Selectivity ^b (%)		
				BA	DBA	TOL
1	0	H ₂ O	10.7	83.0	12.1	4.9
2	0	Acetic acid ^c	13.2	89.7	5.9	4.4
3	7	H ₂ O	13.4	95.9	0.9	3.2

^a Reaction conditions: BN 1.0 g (9.7 mmol), catalyst 20 mg, Aqueous media 5 cm³, H₂ 2 MPa, Temperature 323 K, Reaction time 4 h

^b BA: benzylamine, DBA: dibenzylamine, TOL: toluene

^c 0.1 mol% of acetic acid solution

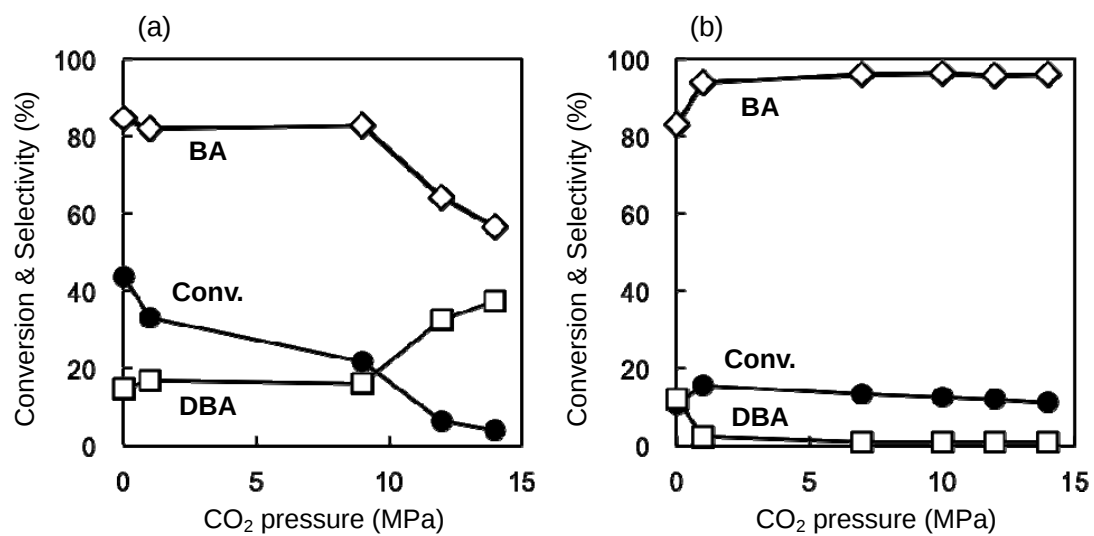


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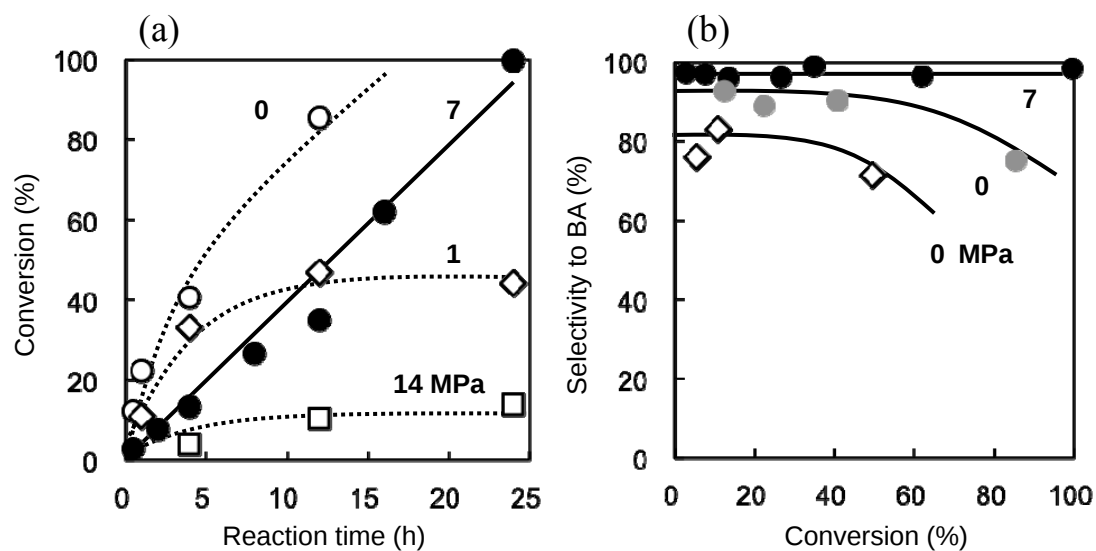


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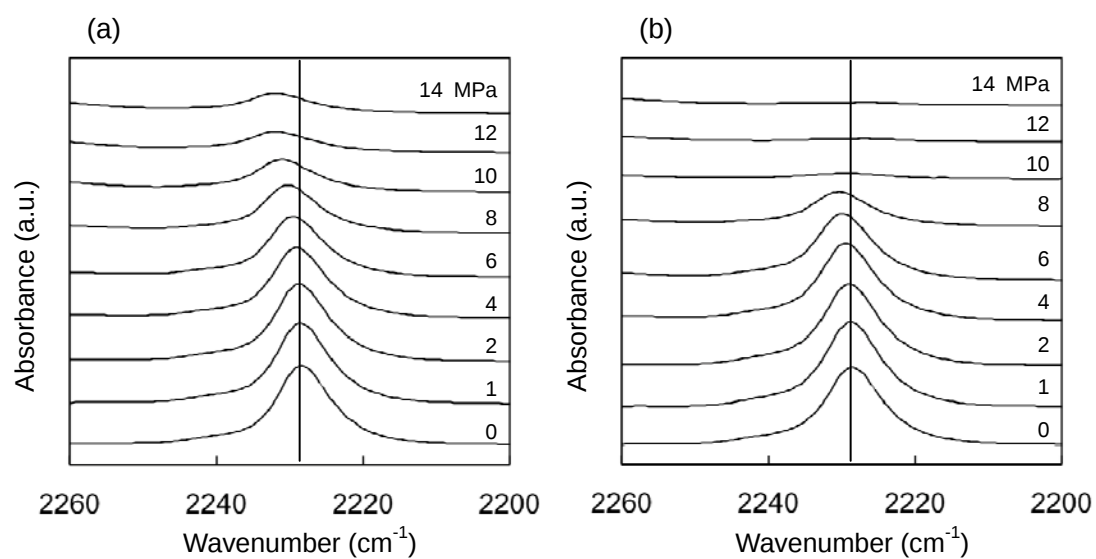


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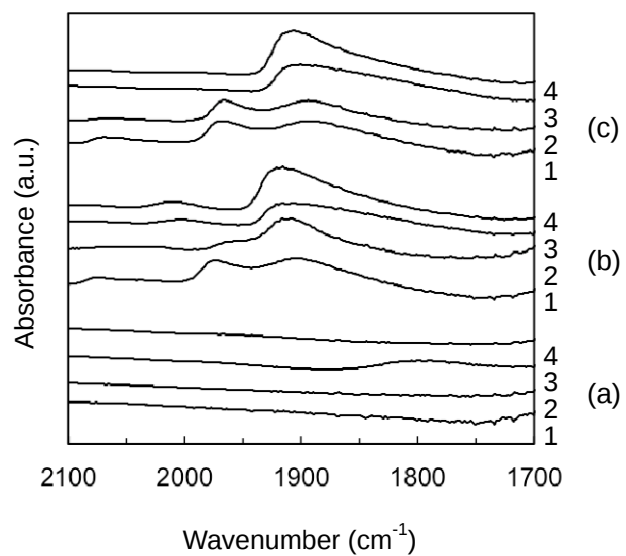


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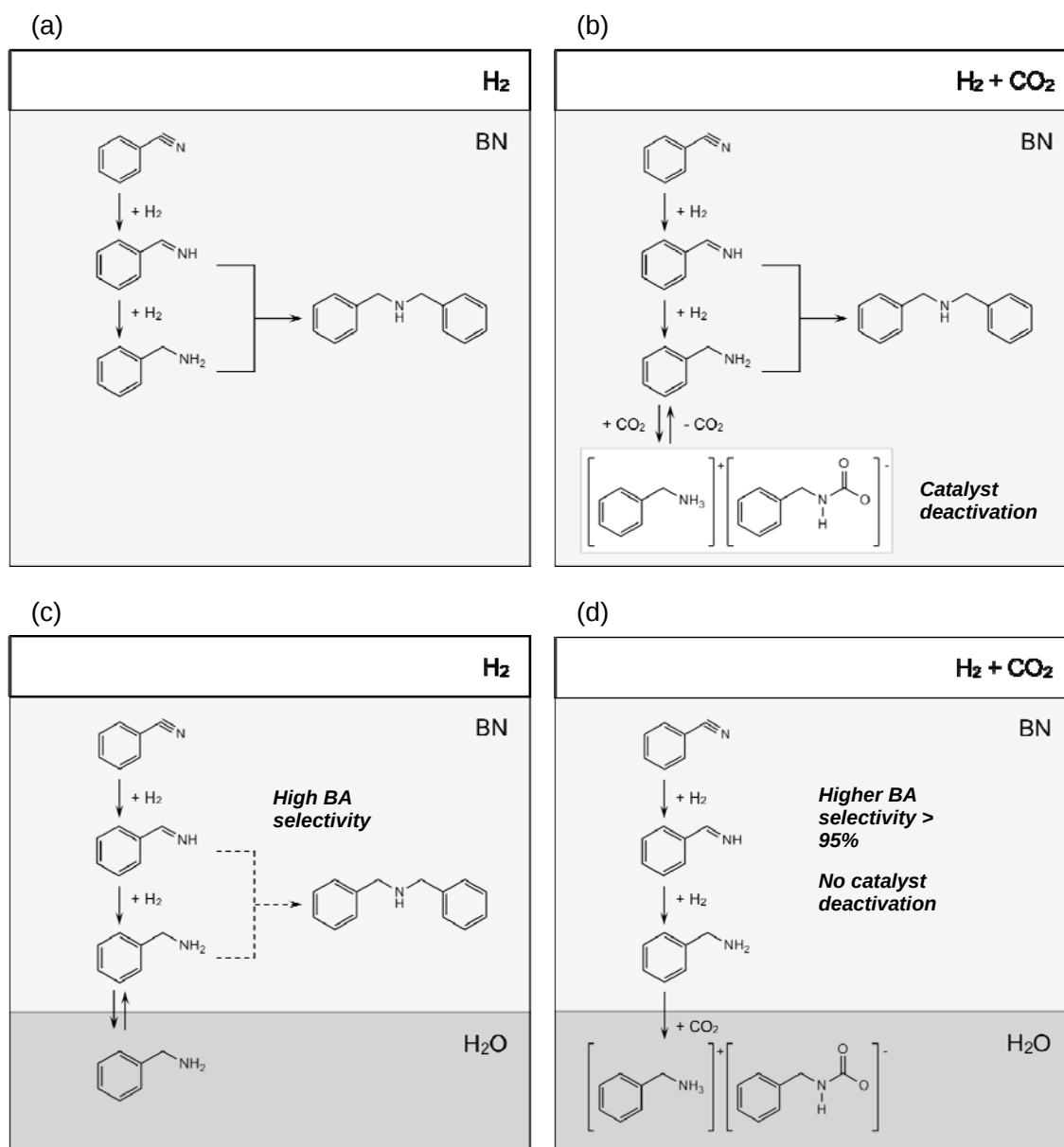
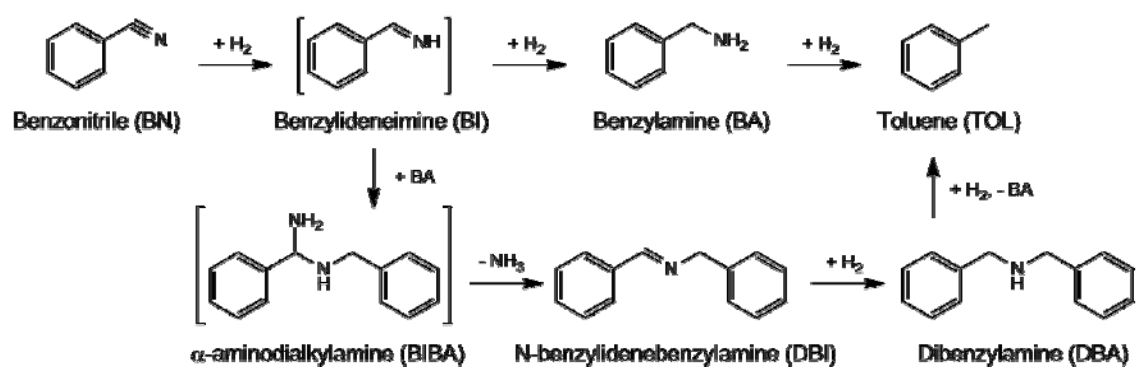
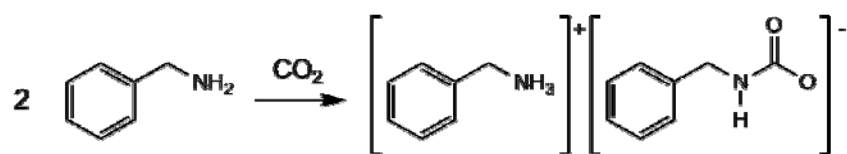


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