Hydrogenation of aniline to cyclohexylamine in supercritical carbon dioxide: Significance of phase behaviour

M. Chatterjee*, M. Sato, H. Kawanami, T. Ishizaka, T. Yokoyama, T. Suzuki

Research Center for Compact Chemical System, AIST Tohoku, 4-2-1 Nigatake, Miyagino-ku, Sendai, 983-8551, Japan

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ABSTRACT

Hydrogenation of aniline to cyclohexylamine was carried out in supercritical carbon dioxide using a variety of noble metal (Pt, Pd and Rh) catalysts. At 80 °C and 8 MPa of CO_2 pressure, >95% of aniline conversion with 93% selectivity to cyclohexylamine was achieved on 5% Rh/Al_2O_3. A strong influence of phase behaviour related to the CO_2 pressure was found on the conversion and selectivity. Optimization of reaction parameters resulted in a higher overall activity in the biphase (liquid substrate + gaseous H_2 and CO_2) than in the single phase (liquid substrate–CO_2–H_2) condition. It has been found that the interaction of CO_2 with amine leads to the formation of solid carbamic acid, which enhanced the selectivity of cyclohexylamine, but reduced the conversion significantly. Furthermore, reaction temperature played a crucial role in preventing the formation of carbamic acid and also maintained a reasonably high reaction performance in terms of conversion and selectivity.

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1. Introduction

The development of an efficient method for production of amine is an interesting research area because amines are an important class of compounds. Among them, cyclohexylamine (CHA) is one of the most versatile intermediates from the commercial standpoint. It can be used in the synthesis of artificial sweeteners (sodium or calcium cyclamate), metal corrosion inhibitors, rubber vulcanizing additives, dyestuff, plasticizers and extracting agents for natural products [1]. Commercially, CHA may be produced via either of two processes (i) reductive amination of cyclohexanol or phenol or (ii) hydrogenation of aniline. However, the main disadvantages are formation of by-products and the use of a large excess of ammonia.
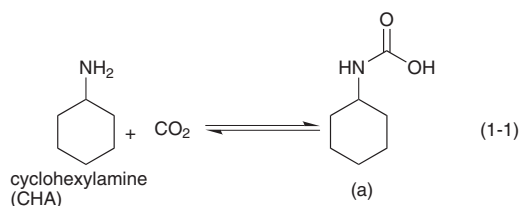
A variety of metals such as Ni, Co, Rh, Ru, Pd and Pt were used to study the hydrogenation of aniline in vapour phase as well as in the liquid phase condition. Different reaction parameters such as catalyst, reaction temperature, solvent used and whether the reaction was carried out in gas phase or in liquid phase strongly influenced the product distribution. For instance, in vapour phase hydrogenation, Moss and Kemball [2] described the formation of benzene and ammonia instead of CHA over Pt foil catalyst. On the contrary, dicyclohexylamine (DCHA) and CHA were formed at 200 °C, using

Rh/Al_2O_3, and the selectivity of CHA was low. Instead of noble metal catalysts, Narayanan and Unnikrishnan [3] compared the activity and selectivity of aniline hydrogenation over 50 wt% Ni/Al_2O_3 and Co/Al_2O_3 catalyst and in each case the obtained product was a mixture of CHA, DCHA and N-phenylCHA; maximum selectivity of CHA was ~70%. Aniline hydrogenation has also been reported in the liquid phase using batch or continuous mode, acidic and non-acidic medium. Several patents were issued describing specific catalyst formulations [4], many of which contain mixtures of Ru and Pd on Al_2O_3 supports. However, in most of the cases, objectionable quantities of DCHA or other by-products were formed. To prevent the formation of DCHA, the most used technique for heterogeneously catalyzed reaction is application of ammonia. However, the disadvantages of using ammonia are pressurized storage and excessive amount required which results in environmental and economical concerns. Again, when the reaction was conducted in acidic medium to improve the selectivity of CHA, an additive was necessary, whereas non-acidic medium required higher temperature (100–250 °C) and pressure up to 35 MPa. Such high pressure and temperatures are unfavorable from the safety viewpoint. Instead of organic solvent, Sokolskii et al. [5] studied the hydrogenation of aniline in water using Rh/Al_2O_3 catalysts; however, the selectivity of CHA was 64–79% with low conversion.

Supercritical carbon dioxide ($scCO_2$) has gained considerable attention for different types of chemical reactions. Over the past few years, several heterogeneously catalyzed reactions have been successfully carried out in $scCO_2$ medium, often with higher reaction

* Corresponding author. Tel.: +81 22 237 5213; fax: +81 22 237 5388.
E-mail addresses: c-maya@aist.go.jp (M. Chatterjee), h-kawanami@aist.go.jp (H. Kawanami).

Scheme 1. Formation of cyclohexylcarbamic acid.

Scheme 2. Probable reaction path of aniline hydrogenation under the studied reaction condition.

rates and different product distributions, as well as high selectivity, in comparison with those available in conventional organic solvents [6–11]. In the CO_2 medium, enhanced reaction rate and high product selectivity are mainly tuned by the pressure and temperature. In practice, depending on pressure, the solubility of the reaction components in CO_2 is varied; this is called phase behaviour. It has considerable importance for the reaction in CO_2, since sometimes reaction outcomes can be dictated by the phase behaviour of the reaction components. Furthermore, CO_2 has a great potential to overcome difficulties associated with the conventional homogeneous and heterogeneous catalysts such as mass transfer limitation that frequently occur between the reactants in gas and liquid phase. In particular, $scCO_2$ can be regarded as an ideal medium for hydrogenation because, unlike organic solvents, H_2 is completely miscible in CO_2. At a given pressure of gas, the effective concentration of H_2 can be nearly an order of magnitude higher than in classical organic solvents, which will increase the H_2 concentration to the catalyst surface leading to the enhanced reaction rate. Also, $scCO_2$ is non-inflammable and non-toxic; these physically and toxicologically inert properties have made it a most promising solvent for organic synthesis.

In this work, we have attempted the hydrogenation of aniline in $scCO_2$ medium. No additives like ammonia or any acids were used to increase the selectivity of CHA. Our strategy was based on the fact that CO_2 has a tendency to interact with nucleophilic amine to form carbamic acid. However, less basic aniline ($pK_b = 9.40$) by itself does not react spontaneously with CO_2 to form carbamic acid/carbamate [12], whereas CHA ($pK_b = 3.34$) could easily form solid carbamic acid (Scheme 1), which might prohibit the formation of DCHA, but at the same time, there could be the possibility of reduced conversion because of the phase separation due to solid carbamic acid deposition. Therefore, it is necessary to identify the conditions under which the best performances in terms of selectivity of CHA and conversion of aniline could be achieved in $scCO_2$.
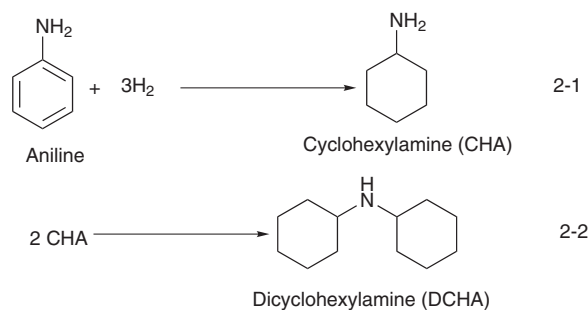
2. Experimental

2.1. Materials

Aniline, CHA and DCHA (Wako Pure Chemicals) were used as received. Pd/C, Pd/Al$_2$O$_3$, Pt/C, Pt/Al$_2$O$_3$ and Rh/C were from Aldrich. Rh/Al$_2$O$_3$ was purchased from Wako. Carbon dioxide (>99.99%) was supplied by Nippon Sanso Co. Ltd.

The catalyst used here is commercially available Rh/Al$_2$O$_3$. The particle size of Rh was determined from the X-ray diffraction pattern using the Scherrer equation from the (1 1 1) peak of Rh at $2\theta = 40°$.

2.2. Catalytic activity

Hydrogenation of aniline was carried out in a 50 ml stainless steel batch reactors; some details are given elsewhere [10]. Briefly, 0.1 g of catalyst and 0.5 g of the reactant were introduced into the reactor and placed in an oven with a fan heater to maintain the desired temperature. When the reactor reached the set tempera-

ture, H_2 of required pressure was introduced. After that the liquid CO_2 was charged using a high-pressure liquid pump (JASCO) and then compressed to the desired pressure. Finally, the liquid product was separated from the catalyst simply by filtration and identified by GC–MS, followed by quantitative analysis using a GC (HP 6890) equipped with a capillary column and a flame ionization detector. A 30 m × 0.53 i.d. capillary column with a 0.25 μm film thickness (DB-wax; Agilent) was used. The oven temperature program was set to the initial temperature of 50 °C followed by 50–100 °C (hold time 5 min) and 100–230 °C ramps at 10 °C/min (hold time 4 min). Injector and detector were set at 230 °C. Two microlitres of sample was injected in split mode, with a split ratio of 5.6. Quantification of products was obtained by a multipoint calibration curve using standard compounds. For all results reported, the selectivity is defined as follows:

$$\% \text{ selectivity} = \frac{\text{concentration of the product}}{\text{total concentration of products}} \times 100$$

For experiments in an organic solvent, CO_2 was replaced by 5 ml of the organic solvent.

2.3. Phase behaviour studies

Understanding of the phase behaviour is the key to study the reaction in CO_2. The reactor used in this experiment was closed; thus, no observation could be made on the number of phases present during the reaction. Therefore, to mimic the reaction condition, we conducted visual observation of the phase behaviour of aniline separately with a 10 ml high pressure view cell fitted with a sapphire window. However, no catalyst was used in the view cell. The cell was placed over a magnetic stirrer for stirring the content and connected to a pressure controller to regulate the pressure inside the cell; the desired temperature of 80 °C was maintained by a temperature controller. A 0.1 g (1.06 mmol) amount of aniline was introduced into the view cell at a constant H_2 pressure of 4 MPa while CO_2 pressure was varied between 6 and 15 MPa and the phase behaviour of aniline–H_2–CO_2 system was monitored. Similarly, phase behaviours of CHA and DCHA and the mixture of aniline + CHA + DCHA have also been studied. Noteworthy, only a very small amount of CHA (0.098 mmol) was taken, because for 1.0 mmol of CHA, large numbers of solid carbamic acid crystals were found on the sapphire window of the view cell, due to the lower temperature of the window wall in contrast to the reactor wall, which prevented the observation.

3. Results and discussion

Scheme 2 represents a typical reaction profile of aniline hydrogenation. Generally, aniline is considered to be hydrogenated to CHA, followed by the formation of DCHA.

Table 1
Hydrogenation of aniline over different supported noble metal catalysts and in different reaction medium[a].

Entry	Catalyst	Dispersion (%)[d]	TOF (h⁻¹)	Conv. (%)	Selectivity (%)	
					CHA	DCHA
1	5% Pd/C	9.1	50.6	24.2	30.8	69.2
2	5% Pd/Al₂O₃	7.0	81.6	30.0	10.3	89.7
3	1% Pd/MCM-41	5.6	22.0	1.3	100.0	0.0
4	5% Pt/C	8.3	63.1	15.0	100.0	0.0
5	5% Pt/Al₂O₃	4.5	110.3	40.0	61.7	38.3
6	1% Pt/MCM-41	12.0	128.0	8.8	100.0	0.0
7	5% Rh/C	7.9	105.4	45.2	100.0	0.0
8	5% Rh/Al₂O₃	3.6	223.3	95.8	93.0	7.0
9	1% Rh/MCM-41	30.0	57.4	18.7	65.2	34.8
10	5% Rh/Al₂O₃[b]		122.2	52.4	59.5	40.5
11	5% Rh/Al₂O₃[c]		115.6	49.6	60.2	39.8

[a] Reaction condition: Catalyst: 0.1 g, aniline = 0.5 g, $P_{CO_2} = 8$ MPa, $P_{H_2} = 4$ MPa, reaction time = 6 h; Temp. = 80 °C; MCM-41 catalysts are prepared in our laboratory [Ref.: Catal. Lett. 61 (1999) 199]; entry 10, 11 = organic solvent (5 ml).

[b] Ethanol.

[c] Hexane.

[d] Approximate expression of metal dispersion = 0.9/diameter (in nm); [Ref.: M. Boudart, G. Djega-Mariadassou, Kinet. Heterogeneous Catal. React., Princeton University Press: Princeton, NJ, 1984]; Particle diameter (r) was obtained from Scherrer equation: $r = K\lambda/\beta \cos\theta$, where K = Scherrer constant nearly equals to 1, λ = wavelength of X-ray, β = FWHM in radians 2θ; Turnover frequency (TOF) = number of molecules reacted/number of sites × time.

3.1. Catalyst screening

The hydrogenation of aniline was performed over different noble metal catalysts supported on Al₂O₃, C (activated carbon) and MCM-41. Table 1 (entries 1–9) presents the results of aniline hydrogenation. It is evident that Pt and Pd catalysts are less efficient than Rh to achieve targeted high conversion and CHA selectivity. For example, DCHA was the major product over Pd/C and Pd/Al₂O₃ catalysts (entry 1 and 2). Furthermore, CHA was formed with very high selectivity of 100% using Pd/MCM-41 catalysts, but with low conversion (~1%; entry 3). Similar behaviour was also observed for Pt catalysts. Nevertheless, except Rh/MCM-41, all other Rh catalysts were highly active and produced CHA with high selectivity (entries 7 and 8). For instance, Rh/C (entry 7) exhibited 100% selectivity of CHA with the conversion of 45.2%. Table 1 also suggests that irrespective of the metal, Al₂O₃ and C supported catalysts are more efficient than MCM-41. Generally, Al₂O₃ and C are considered acidic, whereas MCM-41 is neutral. It was proposed that acidic sites on the support material can act as the adsorption site for aromatic compounds and, in the region surrounding a metal particle, these adsorbed species can react with H₂ spilt-over from the metal, thus contributing to the overall activity [13]. The inactivity for all the MCM-41 supported catalyst might be due to the neutral nature of the support, or to the low metal content (fewer active sites exposed). This will require a separate study because it is a complicated issue.

3.2. Metal dispersion

Table 1 presents dispersion of metal, which is an important factor to decide the availability of the active phase for reaction. An approximate expression was used to determine the dispersion from the particle diameter, derived using the Scherrer equation. Among the studied catalysts (excluding MCM-41 because its metal content was low), dispersion was varied from ~4% to 10%. For C supported catalysts, the dispersion was Pd ≅ Pt ≅ Rh. However, conversion and the selectivity to CHA followed the order: Rh > Pd > Pt and Rh ≅ Pt > Pd, respectively. On the other hand, metal dispersion of Al₂O₃-supported catalysts shows the order of Pd > Pt > Rh. In contrast to the C support, the exhibited trend of the aniline conversion
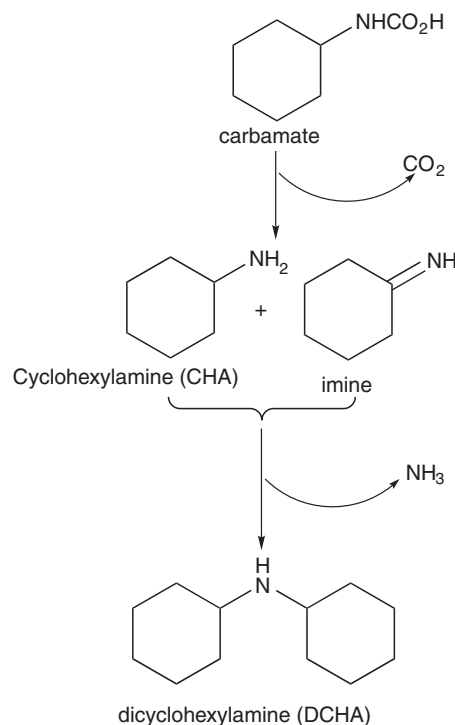
Scheme 3. Schematic representation of the formation of DCHA from CHA.

and selectivity of CHA was Rh > Pt > Pd and Pt > Rh > Pd, respectively. Independent to the metal ion, when the support changes from C to Al₂O₃ (entries 1, 2, 4, 5, 7 and 8), the dispersion was decreased, but conversion increased under the same reaction condition. For example, Rh/Al₂O₃ catalyst was highly active, despite of having a very low dispersion (3.6%; Table 1; entry 7). Results in Table 1 also provide a significant relationship between intrinsic activity in terms of the turnover frequency (TOF) and metal dispersion. An increase in TOF along with the decreasing metal dispersion was observed when the support changes from Al₂O₃ to C (TOF$_{Al_2O_3}$ > TOF$_C$), independent of the metal ion used. Thus, in each case the highest efficiency was achieved over Al₂O₃ support, which might be attributed to the presence of the Lewis acid sites preferably activating the aromatic ring as proved by several theoretical and experimental results [14–17]. Regarding the selectivity, DCHA was the main product on Pd/C and Pd/Al₂O₃ (Table 1; entry 1, 2). However, CHA was obtained with high selectivity using Pt and Rh catalysts (Table 1; entries 4, 5, 7 and 8) irrespective of the support used. The difference in product distribution between Rh and Pd catalysts was observed previously during the hydrogenation of β-myrcene in CO₂ [18]. Similarly, during the liquid phase hydrogenation of aniline, Rh was stated to form CHA (Scheme 3) [19], whereas Pd was strongly inhibited. Hence, no detailed study was available over Pd catalyst. The most striking is that the hydrogenation of aniline in CO₂ also followed a very similar trend when Rh catalyst was used. However, for Pd catalyst, instead of total inhibition such as occurred in organic solvent medium, a moderate conversion of ~30% with the formation of DCHA was observed in CO₂. Thus, judging from the overall activity, we considered Rh/Al₂O₃ as the most effective catalyst concerning the high conversion and selectivity of CHA (conversion = 95.8%, selectivity to CHA = 93%) and we choose it for further study to optimize different reaction parameters. It has to be mentioned that no conversion occurred without a catalyst.

3.3. Effect of CO₂ pressure

For optimization of reaction parameters, CO₂ pressure is an effective variable. Aniline hydrogenation was carried out under dif-
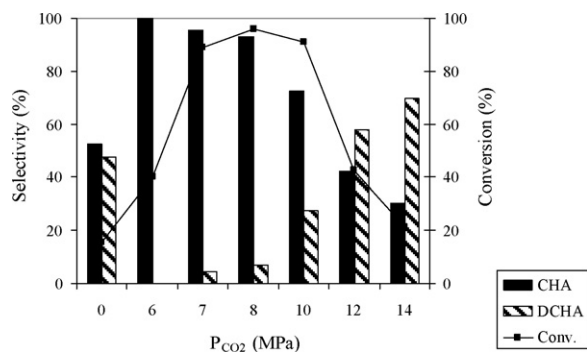
Fig. 1. Effect of CO_2 pressure on the conversion and selectivity of aniline hydrogenation. Reaction conditions: catalyst = 0.1 g, substrate = 0.5 g, temperature = 80 °C, P_{H_2} = 4 MPa, time = 6 h.

ferent CO_2 pressure values at the fixed hydrogen pressure of 4 MPa and the temperature of 80 °C (Fig. 1). Results show that with the increase in pressure from 6 to 8 MPa, the conversion was changed from 40.2% to 95.8% and then decreased to 21.2% when the pressure reached 14 MPa. To explain this observation, we studied phase behaviour of aniline, CO_2 and H_2 in a view cell (details in the experimental section) and images are shown in Fig. 2(a–f). Fig. 2a presents the image of only aniline in the view cell. After the introduction of CO_2, at the lower pressure (Fig. 2b and c), the system was biphasic. On the other hand, the meniscus between two phases disappeared and the system attained a single phase (aniline–CO_2–H_2) (Fig. 2d and e) when the CO_2 pressure was above 12 MPa. Therefore, according to the phase behaviour, the highest conversion of aniline and CHA selectivity were achieved in the biphasic condition. Increased conversion and selectivity in the biphasic condition is an unusual observation for hydrogenation in scCO_2. However, Hitzler et al. [20] described a similar example of fast hydrogenation in a biphasic mixture containing high-pressure CO_2. Chouchi et al. [21] provide another example of high reaction efficiency at the biphasic condition during the hydrogenation of pinene in scCO_2. Authors interpreted their results based on the assumption that the reaction is controlled by the adsorption of substrate on the catalyst surface as the substrate is more concentrated in the liquid rich phase around the catalyst, which represents a good model of CO_2-expanded liquids [21,22]. It has been reported that CO_2 has a tendency to add to organic liquids [23] and the combination act as CO_2-expanded liquid. The solubility of H_2 is greater in the CO_2-expanded liquid than
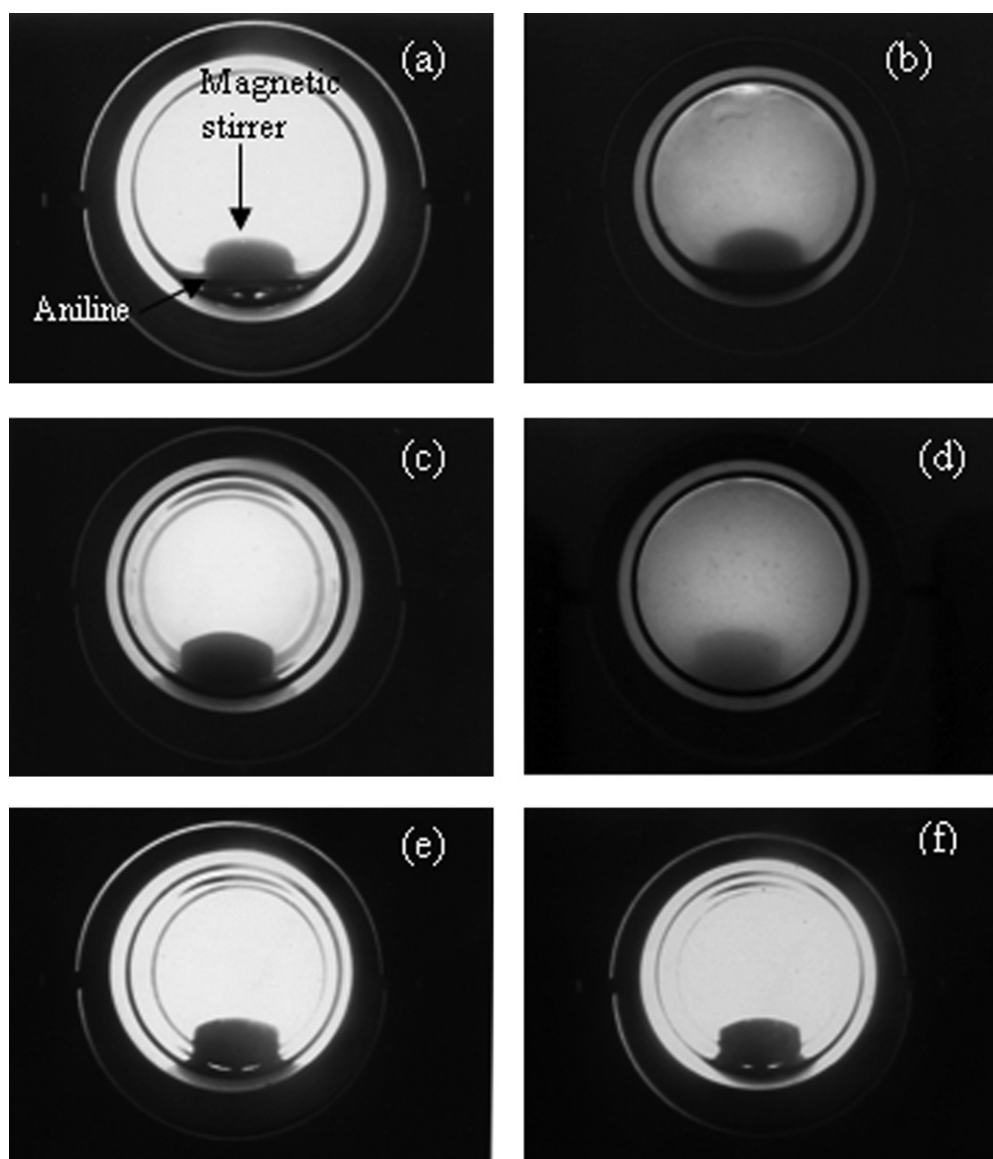

Fig. 2. Phase behaviour of aniline–H_2–CO_2 at 80 °C; (a) aniline in the view cell, in presence of CO_2 (b) 8 MPa, (c) 12 MPa, (d) 14 MPa, (e) 15 MPa and (f) 8 MPa at 35 °C.
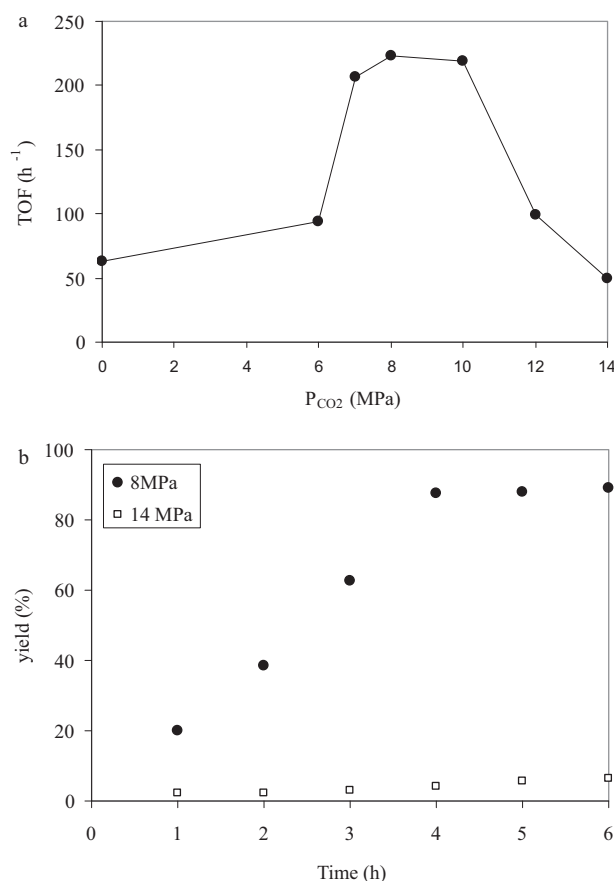
Fig. 3. (a) TOF of aniline hydrogenation at various CO_2 pressures and (b) comparison of the yield (%) of CHA at 8 and 14 MPa of CO_2 pressure.

that in the absence of CO_2 [18,24], which can explain the increased reaction efficiency in the biphasic condition. On the contrary, in the single phase condition, conversion and selectivity were reduced considerably, due to the dilution effect.

Fig. 3a represents TOF of aniline hydrogenation at different CO_2 pressures, and shows a faster reaction rate (higher TOF) in the biphasic condition when aniline is present in the liquid rich phase. Again, Fig. 3b is a plot of CHA yield (%) versus reaction time at 8 and 14 MPa pressure, which evidenced a clear difference in the rate of formation of CHA. The reaction is much faster towards the formation of CHA in the biphasic condition than in the diluted single phase. Thus, hydrogenation of aniline to CHA in CO_2 medium prefers liquid rich aniline phase rather than single phase contacted to the catalyst; this result fits the explanation of Chouchi et al. [21]. According to the results, a change in CO_2 pressure was also coupled with the drastic change in product selectivity. When the pressure increased from 8 to 14 MPa, the selectivity of CHA and of DCHA was changed from 93% and 7% to 30.5% and 69.5%, respectively. The tuning of the pressure is related to the number of phases present in the system. Under the biphasic condition, aniline hydrogenation towards the formation of CHA seems to dominate and further conversion of CHA to DCHA was minimized, but in the single phase condition (∼14 MPa) selectivity of DCHA increased. To explain this observation, phase behaviour of CHA, DCHA and the mixture of aniline + CHA + DCHA corresponding to the composition of 8 and 14 MPa were studied separately at 80 °C (Fig. 4). At 8 MPa, CHA existed as a separate phase (Fig. 4b) due to the low solubility in CO_2. Therefore, a phase separation at the lower pressure of 8 MPa could be the cause of the high selectivity of CHA (Fig. 4b). Moreover, at a higher pressure the solubility of CHA was increased, whereas DCHA

(Fig. 4f) and aniline (Fig. 2d) show complete solubility. As mentioned before, the conversion of aniline was substantially decreased at the higher pressure of CO_2. We speculated that the produced CHA, which was present in the same phase of aniline, converted to DCHA (Scheme 3) [19]. This explanation could be supported by the phase behaviour image of aniline + CHA + DCHA corresponding to the composition of 8 (Fig. 4g) and 14 MPa (Fig. 4h), respectively, which indicates the difference in the number of phases present in the system. Thus, the conversion and selectivity of aniline hydrogenation were strongly influenced by the phase behaviour under the studied reaction conditions.

In the absence of CO_2, the conversion of aniline was reduced to 16% and almost a 1:1 mixture of CHA and DCHA was produced (Fig. 1), under the similar reaction condition, which again confirmed the potential of using CO_2 as a reaction medium.

3.4. Variation of reaction time

The effect of reaction time on the hydrogenation of aniline in CO_2 at 8 MPa (biphase) is shown in Fig. 5. It can be seen that the conversion and selectivity were strongly influenced by the reaction time. The conversion of aniline was increased linearly from 5.4% to 95.8% as time changes from 0.5 to 6 h. On the other hand, CHA was sole product in the beginning, but as the conversion increased, the selectivity of CHA decreased from 100% to 93% with the formation of DCHA. An attempt was made to check the effect of prolonged reaction time (18 h), the result indicated a considerable change in the product distribution. Although the conversion of aniline reached to 100%, the selectivity of CHA and DCHA changed from 93% to 44% and 7% to 56%, respectively. Thus, an optimum reaction time of 6 h was chosen for all the measurements.

3.5. Influence of H_2 pressure

To check the influence of H_2 pressure in the biphasic condition, we performed aniline hydrogenation at a fixed temperature of 80 °C and the CO_2 pressure of 8 MPa in accordance with the observed highest conversion and selectivity (Fig. 6a). H_2 pressure was varied from 1 to 4 MPa. Results show that the conversion of aniline was increased from 25.2% to 95.8% as the pressure changes from 1 to 4 MPa. The reason behind the enhancement of conversion was generally given as the increased solubility of H_2 in CO_2-expanded liquid [24,25]. Recently, it was suggested that the hydrogenation in CO_2-expanded liquid catalyzed by Rh and Ru is influenced by the phase equilibrium, related to the distribution of H_2 between vapour and liquid and the volumetric expansion of the liquid substrate due to the presence of CO_2 [26]. However, plots of the yield of CHA versus reaction time at 1 and 4 MPa H_2 pressure (Fig. 6b) revealed that the effect of H_2 pressure was insignificant for the present case. Thus, aniline hydrogenation under the studied reaction condition is independent of the amount of H_2, present in large excess in the reaction medium.

3.6. Effect of temperature

Variation of temperature is also a critical parameter to describe the aniline hydrogenation in $scCO_2$ because (i) it affects the phase behaviour and (ii) the formation of carbamic acid. In this work, the hydrogenation of aniline was studied at 35, 50, 60, 70 and 80 °C at the fixed pressure of H_2 (4 MPa) and CO_2 (8 MPa) (Fig. 7). The temperature was found to influence the conversion of aniline. At 70 °C, the conversion of 60% could be observed; this value dropped to <20% as the temperature decreased. While it is normal for a reaction conversion to decrease with decreasing temperature, the steepness of the observed drop suggests that phase behaviour rather than reaction kinetics is responsible. Visual inspection of the phase
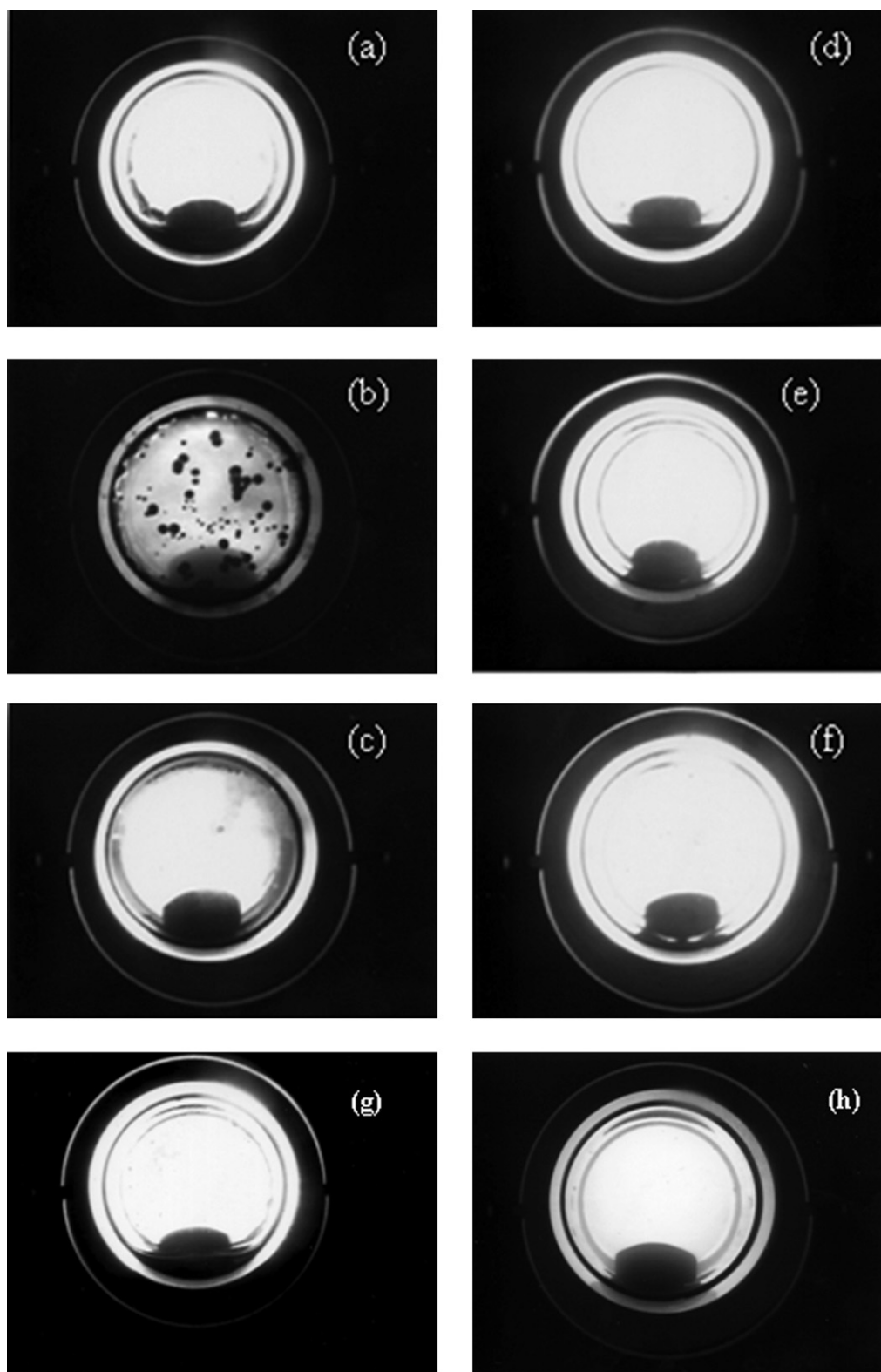
Fig. 4. Visual observation of phase behaviour of CHA (a–c); (a) only CHA; in the presence of CO_2 (b) 8 MPa, (c) 14 MPa and DCHA (d–f); (d) only DCHA; in the presence of CO_2 (e) 8 MPa, (f) 14 MPa of at 80 °C; mixture of aniline + CHA + DCHA (g) 8 and (h) 14 MPa.

behaviour revealed that the change in temperature is associated with the change in the number of phases present in the system. Fig. 2f evidences a clear difference in the phase behaviour of aniline between 35 and 80 °C (Fig. 2b). At 35 °C the system existed as single phase (aniline–H_2–CO_2) with the disappearance of all the liquid phase, whereas at 80 °C a biphasic system is revealed; ani-

line hydrogenation preferred a biphasic system rather than a single phase for higher conversion. Again, in the presence of catalyst, aniline was converted to cyclohexylamine, and might be deposited as a white solid due to the lower temperature. A separate experiment was conducted on the visual observation of the phase behaviour of CHA at 35 °C (Fig. 8), the result clearly demonstrated the deposi-
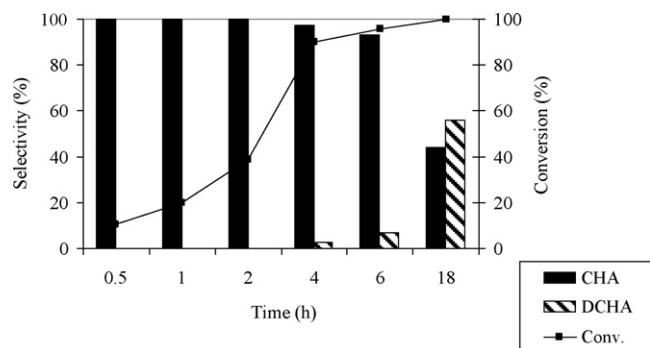
Fig. 5. Variation of reaction time on aniline hydrogenation; Reaction condition: catalyst = 0.1 g, substrate = 0.5 g, temperature = 80 °C, $P_{CO_2} = 8$ MPa, $P_{H_2} = 4$ MPa.

Fig. 7. Effect of temperature on the conversion and selectivity of aniline hydrogenation; Reaction condition: catalyst = 0.1 g, substrate = 0.5 g, $P_{CO_2} = 8$ MPa, $P_{H_2} = 4$ MPa, time = 6 h.

tion of solid carbamic acid through the interaction between CHA and CO_2, and this scenario continued until 60 °C. The formation of the solid, results diminished contact between aniline and the catalyst, which inhibited the reaction rate. When the temperature was above 60 °C, solid carbamate was converted to liquid and the conversion increased sharply from 18.2% to 61%, as depicted in Fig. 7. Temperature also played a prominent role in determining the product distribution. Concerning the selectivity, only CHA (selectivity = 100%) was observed from 35 to 60 °C. Therefore, temperature selection for optimization was a crucial part to the aniline hydrogenation in CO_2. Due to the limitations of the reactor, measurement over 80 °C was not undertaken.
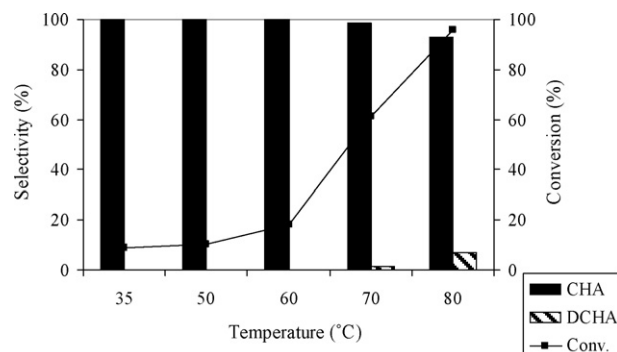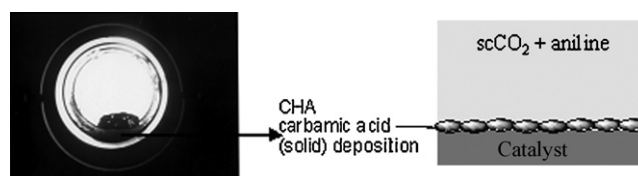

Fig. 8. Formation and deposition of solid carbamic acid at low temperature of 35 °C.

3.7. Reaction in organic solvent

In order to gain farther insight into the role of CO_2 in aniline hydrogenation, we conducted the reaction in organic solvent under similar reaction conditions; the results are shown in Table 1 (entry 10 and 11). Similar to the CO_2 medium, aniline was hydrogenated to CHA and DCHA in organic solvents under the same condition. In ethanol and hexane the conversion of aniline was ~50% and the selectivity of CHA was ~60% (entry 10 and 11), which was lower in comparison to CO_2 medium. The use of CO_2 caused a marked increase in the product selectivity and TOF (Table 1; entry 10 and 11), which again confirmed the efficiency of CO_2-expanded substrate. Conventional solid catalyzed hydrogenation in organic solvents is mainly H_2 concentration dependent and is often controlled by the transport rate, which requires more energy to get a reasonable rate of reaction. Moreover, the liquid phase reaction also suffers from the additional requirement of removing the solvents from the product.

3.8. Catalyst recycling

Recycling of the catalyst is the most important criterion for heterogeneous catalytic reaction. The catalyst was recycled for four successive runs after the reaction followed by separation through filtrations; the results are shown in Table 2. The yield of CHA was decreased from 89% to 84% after the 4th recycle.

Table 2
Recycling of the catalyst[a].

Entry	Catalyst	Yield (%)	
		CHA	DCHA
1	Fresh	89.0	6.7
2	Recycle-1	89.4	6.5
3	Recycle-2	87.4	6.5
4	Recycle-3	85.6	6.6
5	Recycle-4	84.4	6.5

[a] Reaction conditions: Catalyst: 0.1 g, aniline = 0.5 g, $P_{CO_2} = 8$ MPa, $P_{H_2} = 4$ MPa, reaction time = 6 h; Temp. = 80 °C.
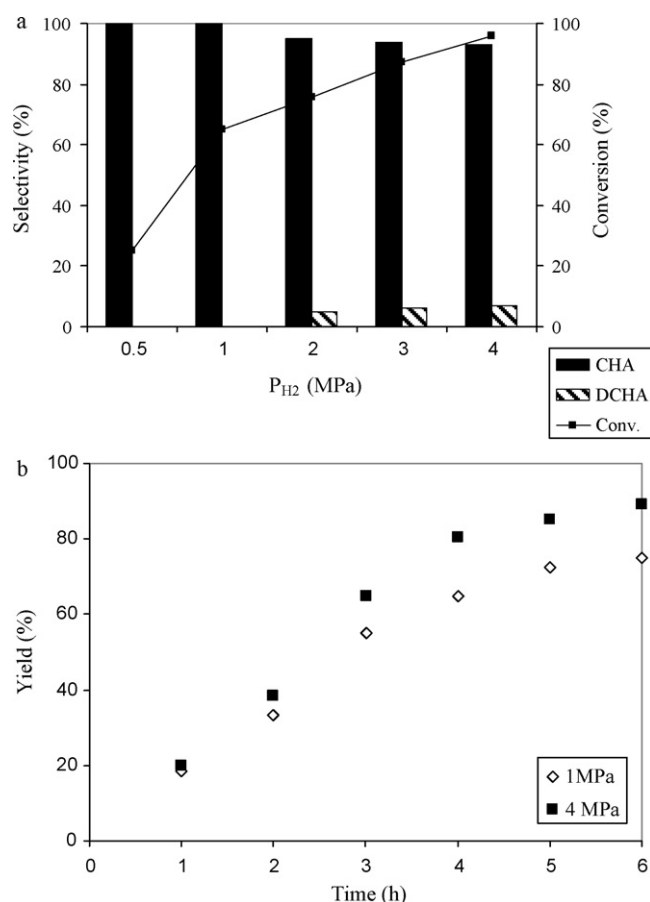

Fig. 6. (a) Variation of H_2 pressure on the hydrogenation of aniline; Reaction condition: catalyst = 0.1 g, substrate = 0.5 g, temperature = 80 °C, $P_{CO_2} = 8$ MPa, time = 6 h and (b) comparison of the yield (%) of CHA at 1 and 4 MPa of H_2 pressure.

4. Conclusions

In conclusion, this study demonstrated that CO_2 is an efficient reaction medium for hydrogenation of aniline to CHA. Different reaction parameters such as temperature, pressure (CO_2 and H_2) and reaction time were studied to optimize reaction conditions. Under the optimized conditions, the conversion of aniline and the selectivity of CHA were remarkably high in comparison to those for an organic solvent, which reflected the advantageous role of CO_2 as reaction medium. To enhance the selectivity of CHA, no by-product suppressor was used, which is a common feature in the classical organic solvent. A remarkable effect of phase behaviour on the conversion and selectivity of the reaction was noticeable. According to the present reaction condition, the reaction occurred in the gas–liquid biphasic system. When pressurized by CO_2, aniline expanded and the dissolution of H_2 was promoted, resulting in high TOF. Furthermore, controlling the temperature is another important parameter to achieve high aniline conversion and CHA selectivity. At lower temperature, high selectivity of CHA (100%) was achieved due to the formation of carbamate, but the conversion decreased substantially. On the other hand, at higher temperature, product distribution changed depending on the CO_2 pressure. High product selectivity and high TOF in CO_2 revealed the importance of CO_2-expanded substrate. This study further suggested that CO_2 is an ideal "replacement" solvent for hydrogenation with a lot of advantages such as high selectivity, clean product separation and lesser catalyst deactivation in "green" and mild conditions.

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