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Ruthenium-Na_2CO_3-catalyzed one-pot synthesis of ring-hydrogenated carbamates from aromatic amines and organic carbonates under H_2

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ABSTRACT

A facile and efficient one-pot procedure for the synthesis of ring hydrogenated carbamates from aromatic amine and alkylene carbonate under H_2 gas pressure has been developed using a heterogeneous catalyst system comprising ruthenium and alkali metal carbonates. The effects of temperature, H_2 pressure, catalyst (types of loaded metal and their supports), molar ratio of substrate/catalyst, and solvent were also investigated. Among the alkali metal carbonates, the sodium carbonate was found as best promoter for nucleophilic attack and ring-opening (NARO) reaction and thus increased the yield of ring hydrogenated carbamate up to 88% when using Ru/C as ring hydrogenation (RH) catalyst. This catalyst system could be reused at least five times without significant loss of activity, which makes this process cost-effective and eco-friendly.

1. Introduction

Carbamates represent an important class of compounds which find wide applications in various areas as pharmaceuticals, agrochemicals such as pesticides, herbicides, insecticides, fungicides etc. and as intermediates in organic synthesis, protection of amino group in peptide chemistry [1–3]. Conventionally, the carbamates have been formed by the Curtius rearrangement [4,5], phosgenation [6], reductive carbonylation [7–9], and oxidative carbonylation [10] (Scheme 1). However, all are suffering from the use of the extremely toxic and highly flammable chemicals, e.g., isocyanates, phosgenes, and carbon monoxide. A direct incorporation of CO_2 with amines and alcohols towards carbamate formation might be considered as benign option [11–14], but not worthy for aromatic amines because it is too weak base to be incorporated with CO_2, especially in the presence of alcohols and furthermore, most of aromatic amine derivatives deeply absorb visible light and are colored reddish yellow or pale yellow, hence they can be hardly used in areas where the absence of coloration is an important requirement [15].

To overcome this drawback and to provide a better alternative technique, we developed a very convenient one-pot synthetic methodology to produce ring-hydrogenated carbamates from aromatic amines using H_2 and organic carbonates as reactants. To the best of our knowledge, this type of reaction has not been previously reported elsewhere in terms of the formation of ring-hydrogenated carbamate as a key product from aromatic amine.

Organic carbonates is classified as a non-toxic, non-flammable polar aprotic solvent and one of the most important green materials as electrolytes for secondary batteries [16]. During the course of our study on the catalytic ring hydrogenation (RH) of aromatic amines (**1**) [17–20] to produce alicyclic amines (**3**), the in-situ generation of **3** was found to be very effective for the nucleophilic attack at the trigonal carbon of the carbonyl group of the PC (**4**) followed by ring opening (NARO) towards carbamate formation [21–23] providing a suitable phosgene-free and non-yellowing synthetic route in a single reactor system. Herein, we report a facile synthesis of

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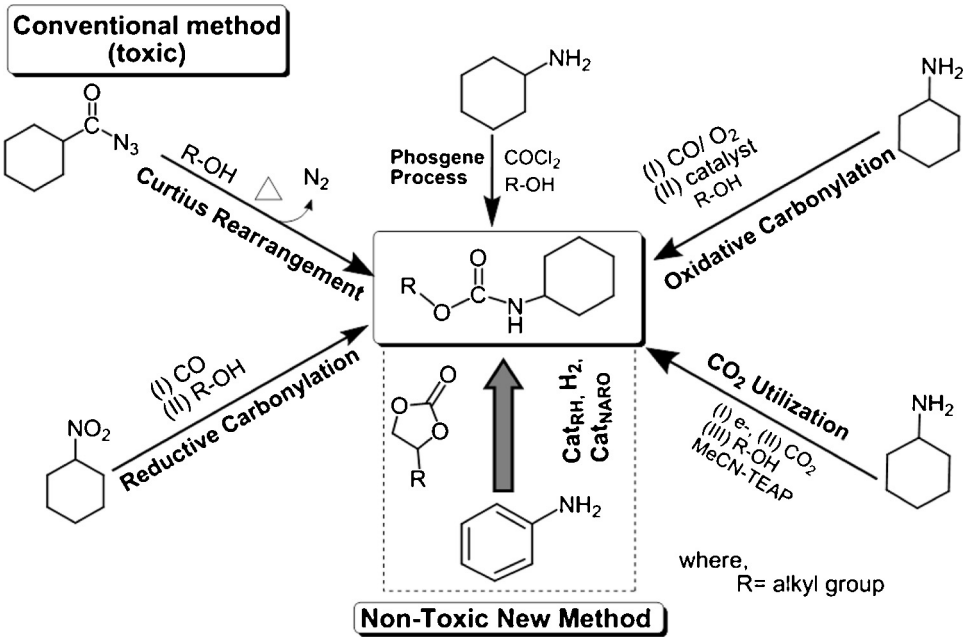


Scheme 1. Formation of carbamates using conventional and new methodology.

alicyclic carbamate such as HPCC from aromatic amine, e.g., aniline using a catalyst system consisting of a catalyst for ring hydrogenation (Cat_{RH}) and a catalyst for nucleophilic attack and ring opening (Cat_{NARO}) and their catalytic activities in terms of variation of reaction parameters therein (Scheme 2).

2. Experimental

2.1. Materials and methods

Aniline, p-phenylene diamine, p-toluidine, p-anisidine, 4-chloroaniline, cyclohexylamine, propylene carbonate, dimethyl carbonate, ethylene carbonate, dicyclohexylamine, $RuCl_3{\cdot}xH_2O$, $RhCl_3{\cdot}xH_2O$, palladium (II) chloride ($PdCl_2$; 99.9%), chitosan, tetraethylorthosilicate (TEOS), 1-butyl-3-methylimidazolium tetrafluoroborate ([Bmim]BF_4), active carbon, imidazole, $NaBH_4$, all the metal salts and solvents were purchased for Aldrich, South Korea.

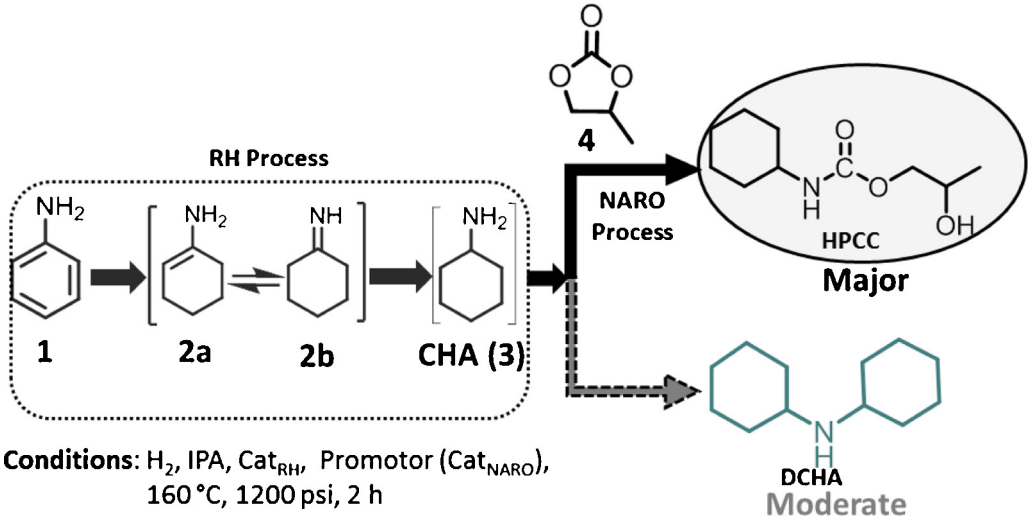
2.2. Preparation of supports and catalysts

2.2.1. Carbon-supported Ru catalyst

A colloidal solution of ruthenium nanoparticles stabilized by polyvinyl alcohol was deposited on activated carbon, using the procedure reported by Porta et al. [24]. Under vigorous stirring an aqueous solution of $RuCl_3{\cdot}xH_2O$ (1.01 g, 5 mmol) was treated with an aqueous solution of polyvinyl alcohol (PVA, 10 ml). To this, a fresh solution of $NaBH_4$ (38 ml, 0.1 M) was added at 50 °C for 2 h. The RuNPs generated were immobilized simply by adding the active carbon (2 g) into the metal dispersion. After 1 h, the resultant slurry was dried for 3 h under vacuum. After being carbonized at 400 °C in a constant N_2 flow with 20 mL min^{-1} for 5 h, black solid could be obtained.

2.2.2. Carbon-supported Rh catalyst

Rhodium supported on carbon catalyst was prepared following the same procedure as described above for ruthenium on carbon using $RhCl_3{\cdot}3H_2O$ (1.02 g, 5 mmol).



Scheme 2. Process diagram for producing HPCC from aniline.

2.2.3. Carbon-supported Pd catalyst

Palladium supported on carbon catalyst was prepared [25] using the following steps: (i) 0.01 M aqueous solution of tetrachloropalladic acid (H_2PdCl_4) was prepared using $PdCl_2$ solution in equivalent amount of hot 0.04 M HCl diluted with distilled water; and (ii) aqueous solution of H_2PdCl_4 was added dropwise on the active carbon support with strong stirring. After 1 h, the resultant slurry was dried for 3 h under vacuum. After being carbonized at 400 °C in a constant N_2 flow with 20 mL min^{-1} for 5 h, black solid could be obtained.

2.2.4. SiO_2-supported Ru catalyst

In a typical procedure [26], $RuCl_3 \cdot xH_2O$ (58.0 mg) was dissolved in BMIm·BF_4 (2.0 g) and ultrasonically treated for 0.5 h. Then, it was mixed with TEOS (10 mL) and ethanol (3.5 mL) was added under magnetic stirring at 60 °C, after the addition of hydrochloric acid (5 mL, 5 M), a brown colloid formed in 0.5 h. The resultant colloid was further aged at 60 °C for 12 h and then treated at 150 °C for 3 h under vacuum. After being carbonized at 400 °C in a constant N_2 flow with 20 mL min^{-1} for 5 h, ≈6 g black solid could be obtained.

2.2.5. γ-Al_2O_3-supported Ru catalyst

First, 0.20 g of $RuCl_3 \cdot xH_2O$ was dissolved in 50 mL of ethylene glycol and then 1.5 g of γ-Al_2O_3 was added to form a suspension. The mixture was stirred for 15 min at RT and the microwave-solvothermal reaction was carried out under mild conditions at 170–180 °C, pressure 5 bar and the hold time of 10 min. After reaction, the vessel was rapidly cooled down in an ice-water bath. A grey solid was filtered off, washed with $NaNO_3$ aqueous solution, next with distilled water to remove the sodium and chloride ions, dried under vacuum at RT and stored in a closed container until used [27].

2.2.6. Chitosan-supported Ru catalyst

Chitosan-supported Ru nanoparticles catalysts were prepared by impregnation method. Granules of chitosan-functionalized polymer were crushed until the fine powders were formed. The fine powders of chitosan were then impregnated into $RuCl_3 \cdot 3H_2O$ solution prepared in ethanol. The mixture was stirred under N_2 atmosphere for a period of 24 h. Finally, catalyst Ru/chitosan was separated by filtration, washed with ethanol and dried to give dark black. Energy dispersive X-ray spectroscopy confirmed that the metal complex was present on the polymer in a metal to saccharide unit ratio of 0.33 (based on the Ru/O ratio), with no loss of chlorine, as observed by the Ru/Cl ratio of 0.47.

2.3. Characterization of supports and catalysts

^1H and ^{13}C NMR spectra were recorded on a Bruker Avance 300 MHz NMR spectrophotometer in $CDCl_3$ containing TMS as the internal standard. Signals are quoted in parts per million (δ ppm) relative to TMS. The FTIR spectra recorded by from pellets in KBr (AR grade) using a Thermo Scientific Nicolet 6700 FT-IR Spectrometer. The resulting solution after catalytic RH and NARO was analyzed using Agilent 6890N gas chromatograph equipped with a flame ionization detector (FID) and on an Agilent 6890N-5975 MSD-GC Mass spectrometer equipped with HP-5 column (30 m × 0.32 m × 0.25 μm). The product mixture was analyzed using Agilent 6890N gas chromatography (GC) equipped with an FID and HP-5 capillary column. The transmission electron microscopy with microprobe for spectrometry of dispersive X-ray analysis (TEM + EDX) was used aiming at quantifying the main elements found in the catalysts as well as to observing their morphology. The analyses were performed with a JEOL device model JEM-2100F. The initial stage consisted of metalizing the catalyst to form a thin layer of platinum atoms on it with 92 Å film thicknesses. The analyses were performed by employing 3 MA current for 180 s. X-ray photoelectron spectroscopy (XPS) measurements are carried out using a commercial Thermo Fisher K-Alpha XPS system with a focused-beam monochromated K-Alpha source. We use a 180° double focusing hemispherical analyzer with multi-element, high-transmission spectrometer input lens-128-channel detector for high-quality images. The scans are performed with a step size of 0.9 eV and a dwell time of 50 ms/step. The specific surface area (BET) of the catalysts was determined on a BELSORP-max (MP) instrument. The catalyst was pre-treated at 250 °C under vacuum for over 5 h to desorb contaminating molecules (mainly water) from the catalyst surface. For the determination of BET surface area, the value of ρ/ρ_0 in the range $10^{-4} < \rho/\rho_0 \leq 0.997$ was used, and nitrogen was used as the adsorbing gas. The specific surface area of the catalyst was calculated from adsorption isotherms using the standard BET equation. The absolute errors were ≤1%.

2.4. Catalytic tests

All the RH and NARO reactions were carried out together in a 100 mL autoclave reactor with a magnetic stirrer and an electrical heater (Fig. 1). In a typical procedure, 15 mmol of aromatic amine, 7.5 mmol of carbonate, 0.075 mmol of Ru-based catalyst, 0.375 mmol of metal salts as promotor, and 10 mL of isopropanol (IPA) were put into the autoclave together with a magnetic bar. 0.5 mL of isooctane was put into the reactor as an internal standard for a quantitative analysis. The reactor was purged with hydrogen three times to remove any remaining air, followed by pressurizing the reactor with hydrogen gas up to 4 MPa. The reactor was then heated to a specific temperature with addition of hydrogen gas to 8.3 MPa. The pressure was maintained constantly using a reservoir tank equipped with a high-pressure regulator and a pressure transducer to monitor pressure drop during the reaction. After completion of the reaction, the reactor was cooled to RT and the reaction mixture was filtered off to remove catalyst for further reaction. The resulting solution was analyzed on Agilent 6890N gas chromatograph equipped with a flame ionization detector and on an Agilent 6890N-5975 MSD-GC Mass spectrometer equipped with HP-5 column (30 m × 0.32 m × 0.25 μm).

3. Results and discussion

To test the best RH catalyst, we loaded various metals (ruthenium, rhodium, and palladium) on carbon, silica, alumina, and chitosan. The preparation method of these catalysts was mentioned in Section 2. In order to confirm the particle size of the loaded metal over support and the amount of the catalyst loading, microscopic analyses were carried out using TEM-EDX (Figs. 1 and 2) and X-ray photoelectron spectroscopy (XPS), respectively, and it was found that the particle size of the dispersed ruthenium was ranging from 2.0 to 5.0 nm and 5 wt%, indicating that they were all properly loaded according to the prepared method with equally distributed on the these solid supports.

To choose proper catalyst for RH reaction, a series of reactions were done using transition metal catalysts with various supports and $NaNO_2$ as a fixed promoter. The reason to choose $NaNO_2$ as promoter in this system is that it has already been proved as a best promoter for RH reaction of aromatic amine to produce ring-hydrogenated amine in our previous article [18]. For this purpose, reactions were carried out by employing aniline as a model aromatic amine as a substrate and PC as reactant (molar ratio of aniline:PC:Cat_{RH}:Cat_{NARO} = 200:200:1:5) to investigate product composition at 160 °C under 8.3 MPa of H_2 in isopropanol (IPA)

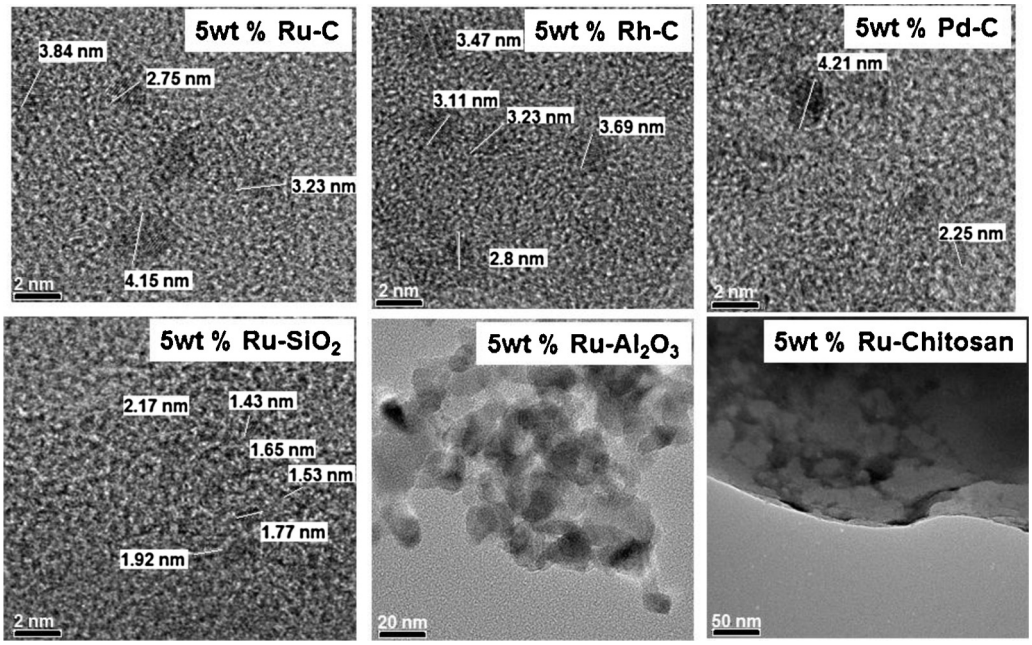


Fig. 1. TEM images of catalysts.

as a solvent for 2 h and the results are listed in Table 1. Among the carbon-supported transition metal catalyst (entries 1–3), Ru/C was best for the production of the ring-hydrogenated hydroxypropyl carbamate (HPCC). We also prepared different supports loaded with ruthenium metal such as silica, alumina, and chitosan (entries 4–6), however, none of them showed better activity toward the HPCC than Ru/C (13%; entry 3), which presents a signal for obtaining HPCC from aniline through the reaction of in-situ generated cyclohexylamine (**3**, CHA) and PC. The catalytic activity of the loaded metal on these supports was found in the following order: Ru/C > Rh/C > Pd/C > Ru/silica > Ru/alumina > Ru/chitosan and these results were also correlated with the Brunauer–Emmett–Teller (BET) specific surface area analysis (Fig. 3). These results imply that the yield of product (HPCC) might be enhanced by tuning the reaction conditions or by replacing $NaNO_2$ with one that is more able to facilitate NARO reaction.

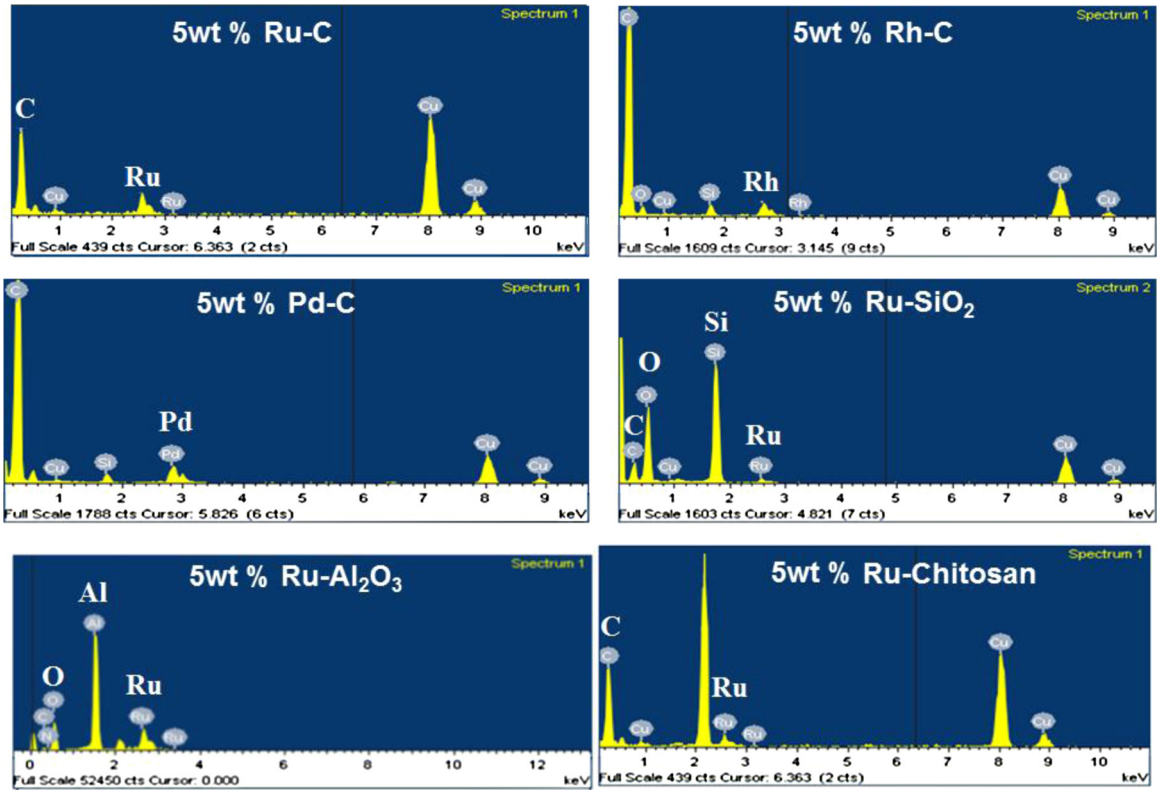


Fig. 2. TEM-EDX chromatogram images of catalysts.

Table 1
Effect of catalyst on the product composition.[a]

Entry	Catalyst	Specific surface area ($m^2\ g^{-1}$)	Ani. conv. (%)	PC conv. (%)	HPCC yield[b] (%)	DCHA yield (%)	Remain-CHA (%)
1	5 wt% Pd/C	226	50	20	1	17	7
2	5 wt% Rh/C	836	85	60	10	8	32
3	5 wt% Ru/C	876	90	68	13	7	28
4	5 wt% Ru/SiO_2	110	78	58	04	0	30
5	5 wt% Ru/Al_2O_3	105	74	19	03	6	67
6	5 wt% Ru/chitosan	001	10	10	0	0	2

[a] Reaction conditions: aniline (15 mmol), PC (15 mmol), catalyst (0.075 mmol), $NaNO_2$ (0.375 mmol), IPA solvent (15 ml), $T = 160\ ^\circ C$, $P = 8.3$ MPa, $t = 2$ h.
[b] HPCC yield is calculated based on PC.

Table 2
Effect of aniline and PC ratio on the product composition.[a]

Entry	Ani:PC	Ani. conv. (%)	PC conv. (%)	HPCC yield[b] (%)	DCHA yield (%)	Remain-CHA (%)
1	**1:1**	90	68	13	7	28
2	**1:2**	81	68	8	15	30
3	**1:3**	72	60	4	25	33
4	**2:1**	**95**	**88**	**39**	**14**	**12**
5	**3:1**	100	82	18	15	34

[a] Reaction conditions: aniline (15 mmol), PC (5–45 mmol), Cat_{RH} (0.075 mmol), $NaNO_2$ as Cat_{NARO} (0.375 mmol), IPA (15 ml), $T = 160\ ^\circ C$, $P = 8.3$ MPa, $t = 2$ h.
[b] HPCC yield is calculated based on PC.

Although the HPCC yield was not high enough at this moment (Table 1, entry 3), it shed some light for more generation of HPCC because there is still room when considering the remaining amount of in-situ generated **3** (28%). It is not clear that why the NARO reaction to produce HPCC did not take place more rapidly; however, it is probably because the existence of PC renders the reaction medium less basic, which played a certain role in quenching of Cat_{NARO} activity. Therefore, to find out appropriate cause and to improve the yield of HPCC, various equimolar ratios between aniline and PC were tested and the results were summarized in Table 2. The results show that the increase in the amount of PC from 1 to 3 equimolar, conversion of aniline decreased and the production of HPCC also decreased from 13 to 4% due to the increased acidity arising from PC while the unutilized amount of **3** and yield of DCHA increased concomitantly (Table 2, entries 1–3). For clarifying the role of increased basicity by adding more aniline for obtaining higher yield of HPCC, a couple of more experiments were conducted using 2 and 3 equimolar of aniline compared to PC if the excess amount of amine may act as base during the reaction to facilitate the formation of HPCC. Experimental results demonstrated that the 2 equimolar ratio of aniline showed the most promoting effect for the synthesis of HPCC yield (39%, Table 2, entry 4). In contrast, using 3 equiv. of aniline rather decreased the yield of HPCC, indicating that there is certain optimized ratio of aniline to PC for the best result. With using this molar ratio, the following investigation was undertaken to improve the productivity of HPCC.

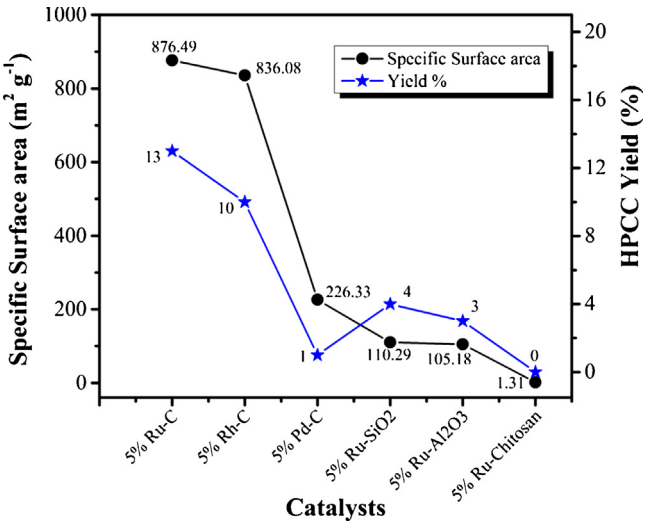


Fig. 3. Specific surface area correlation with respect to catalytic reactivity for HPCC formation.

In our previous article, we have reported that $NaNO_2$ was found as the best promoter for producing CHA (**3**) from nitrobenzene in the presence of Ru/C as a main catalyst and IPA as solvent [18] but the use of PC as a reactant retarded the NARO reaction, affording only 39% yield of HPCC (Table 2, entry 4). To overcome this low productivity, various alkali metal and alkali earth metal salts such as halides, bicarbonates, nitrites and nitrates, carbonates, silicates, phosphates, and hydrogen phosphates were tested as a new promoter (Cat_{NARO}, 5 equiv. to Cat_{RH}) in the Ru/C-catalyzed HPCC formation reaction and the results are listed in Table 3. The absence of metal salts (Table 3, entry 1) did not show any activity both for RH of aniline and NARO reaction with PC. When adding a promoter, the aniline and PC conversion retained approximately 73–100%. KH_2PO_4, $CaNO_3{\cdot}4H_2O$, $MgNO_3{\cdot}6H_2O$, and Li_2CO_3 showed moderately promoting effect, while others showed negligible effect. Among all the used Cat_{NARO} for HPCC synthesis, Na_2CO_3 (entry 13) was found to show most promoting effect to increase the yield of HPCC up to 88% using Ru/C as Cat_{RH} in the presence of IPA. These results clearly indicate that the HPCC yield was largely influenced by the types of added promoter in this reaction, resulting in that sodium carbonate was found to be the best Cat_{NARO}.

In order to have a better understanding of the adding Na_2CO_3 (Cat_{NARO}) effect on the yield of HPCC with respect to ruthenium catalyst (Cat_{RH}), various experiments were carried out and results were highlighted in Fig. 4. The results show that the conversion of aniline increased with increasing amount of Na_2CO_3 and the yield of the HPCC increased with the simultaneous decrease in DCHA by the addition of Cat_{NARO} from 1 to 5 equiv. to ruthenium, but thereafter the yield of HPCC decreased with the concomitant increase in side product. This result implies that the addition of Cat_{NARO} plays a significant role in promoting the NARO reaction but has a certain limit. The exact role of Na_2CO_3 is not clear at this moment but it seems that an interaction between IPA and Na_2CO_3 plays an certain

Table 3
Effect of Cat_{NARO} on the product composition.[a]

Entry	Cat_{NARO}	Ani. conv. (%)	PC conv. (%)	HPCC yield[b] (%)	DCHA yield (%)	Remain-CHA (%)
1	None	0	50	0	0	0
2	KCl	86	81	1	4	6
3	NaI	75	85	4	12	4
4	LiCl	89	84	43	28	23
5	$NaHCO_3$	84	89	24	11	9
7	$KHCO_3$	88	85	48	16	13
8	$CaNO_3{\cdot}4H_2O$	98	90	60	60	26
9	KNO_3	90	78	48	14	26
10	$MgNO_3{\cdot}6H_2O$	90	90	57	16	12
11	$AlCl_3$	90	94	50	20	15
12	Li_2CO_3	99	87	63	20	18
13	**Na_2CO_3**	**100**	**95**	**88**	**10**	**16**
14	K_2CO_3	73	91	19	13	9
15	Cs_2CO_3	48	72	9	4	3
16	K_2HPO_4	84	100	17	25	6
17	KH_2PO_4	99	87	64	16	18
18	$Na_2SiO_3{\cdot}5H_2O$	97	99	51	20	22

[a] Reaction conditions: aniline (15 mmol), PC (7.5 mmol), Cat_{RH} (0.075 mmol), Cat_{NARO} (0.375 mmol), IPA (15 ml), T = 160 °C, P = 8.3 MPa, t = 2 h.
[b] HPCC yield is calculated based on PC.

role in promoting not only RH reaction by the in-situ formation of active species like $NaOCH(CH_3)_2$ [17], but also NARO reaction by rendering the reaction media more basic to facilitate nucleophilic attack of amino group of CHA to carbonyl carbon of PC.

To find out the effect of temperature on the RH and NARO reaction, a series of reactions were performed in the temperature range of 80–200 °C and the results were demonstrated in Fig. 5. Aniline disappeared completely at 160 °C and the HPCC yield was highest (88%), but thereafter a sharp decrease was observed with the increase in the by-product formation, indicating the strong dependency on the reaction temperature.

The results also suggest that above 160 °C, the reaction rates of deamination and *N*-alkylation of isopropyl alcohol are facilitated and might be higher than that of NARO and thus the formation of by-products such as DCHA, *IP*-CHA, and 1,2-propanediol increased with increasing temperature.

To study the influence of H_2 pressure on the product composition, separate reactions were carried with a varying pressure range of 1.4–14.0 MPa for 2 h at a constant reaction temperature of 160 °C. The results show that H_2 gas does not seem to have a significant effect on the hydrogenation as long as the reaction pressure is maintained above 5.5 MPa (data not shown). Below 5.5 MPa, the rate of the reaction becomes slower, but the effect on the rate is much less pronounced than in the case of temperature.

Inspired by these promising results and to broaden the scope of the RH and NARO reaction, various aromatic amines and organic carbonates were examined for the formation of ring-hydrogenated carbamates using ruthenium-Na_2CO_3 catalyst system. To check the performance of aromatic amine, we have chosen a variety of aromatic amines like aniline, *p*-phenylene diamine (PPDA), *p*-toluidine, *p*-anisidine, and 4-chloroaniline. The results in Table 4 show that PC and ethylene carbonate (EC) show near about similar reactivity with all the aromatic amines but their reaction with dimethyl carbonate (DMC) was quite lower at 160 °C and a large number of *N*-alkylated derivatives were observed with less formation of carbamate products (entries 3, 7, 10, 13, and 16). The reason for this lower yield may be due to the fast methylation ability of DMC than others under this operating conditions [28]. It is observed that the selectivity of the carbonates was found in following orders: PC > EC > DMC.

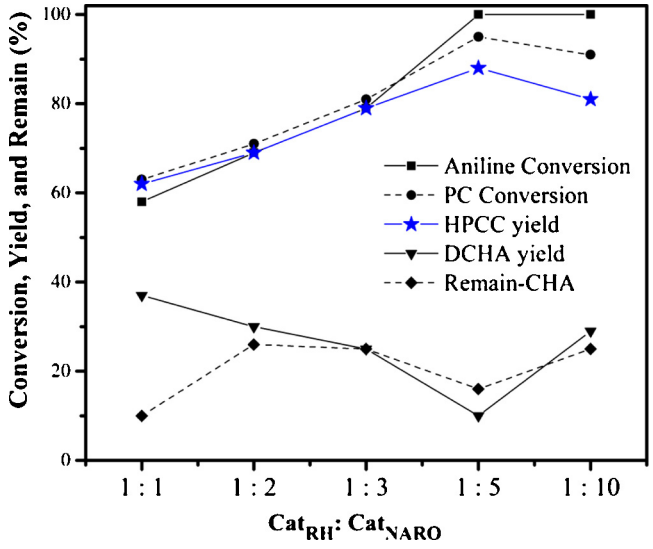


Fig. 4. Effect of molar ratio of Cat_{NARO} on the product composition: [a]Aniline (15 mmol), PC (7.5 mmol), Cat_{RH} (0.075 mmol), Cat_{NARO} (0.075–0.75 mmol), IPA (15 ml), T = 160 °C, P = 8.3 MPa, t = 2 h; [b]HPCC yield is calculated based on PC.

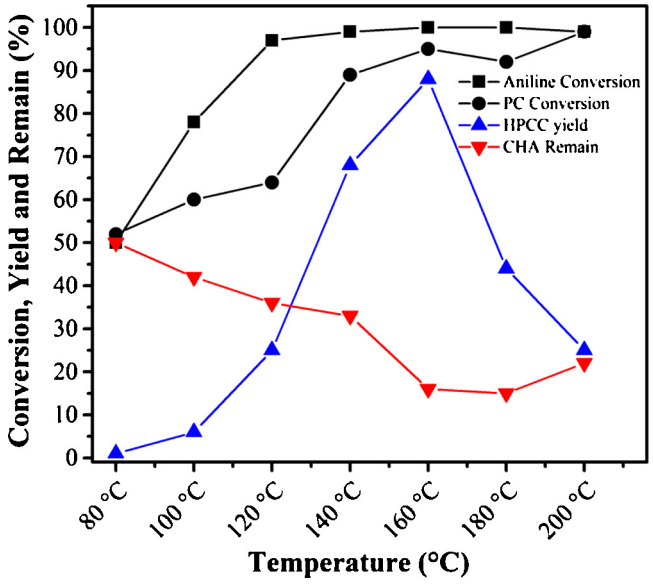


Fig. 5. Effect of temperature on the product composition: [a]Aniline (15 mmol), PC (7.5 mmol), Cat_{RH} (0.075 mmol), Cat_{NARO} (0.375 mmol), IPA (15 ml), T = 80–200 °C, P = 8.3 MPa, t = 2 h. [b]HPCC yield is calculated based on PC.

Table 4
Scope of RH and NARO reaction for various aromatic amines and carbonates.[a]

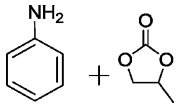
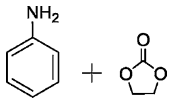
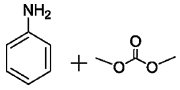
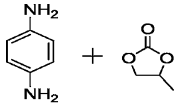
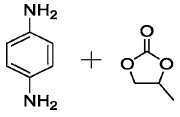
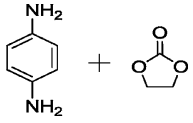
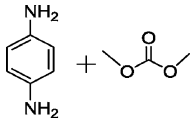
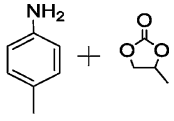
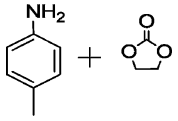
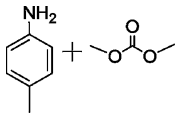
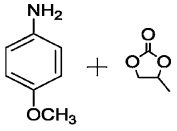
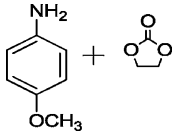
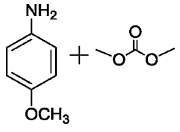
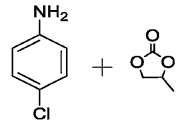
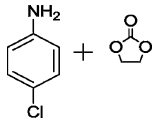
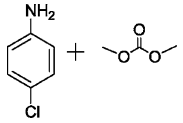
Entry	Reactants	Amine conv. (%)	Carbonate conv. (%)	Carbamate yield[b] (%)	Remaining ring-hydrogenated amine (%)
1		100	95	88	16
2		100	100	85	15
3		95	88	20[c]	18
4	 PPDA	92	94	78[d]	15
5		85	75	52[d,e]	20
6		77	79	74[d]	16
7		68	74	23[d]	30
8	 *p*-toluidine	88	100	71[d]	14
9		89	90	70[d]	16
10		89	70	11[d]	26
11	 *p*-anisidine	100	95	70[d]	19
12		100	79	68[d]	21
13		97	83	18[d]	25

Table 4 (*Continued*)

Entry	Reactants	Amine conv. (%)	Carbonate conv. (%)	Carbamate yield[b] (%)	Remaining ring-hydrogenated amine (%)
14	 4-chloroaniline	95	100	80[d]	12
15		94	81	76[d]	15
16		90	95	15[d]	23

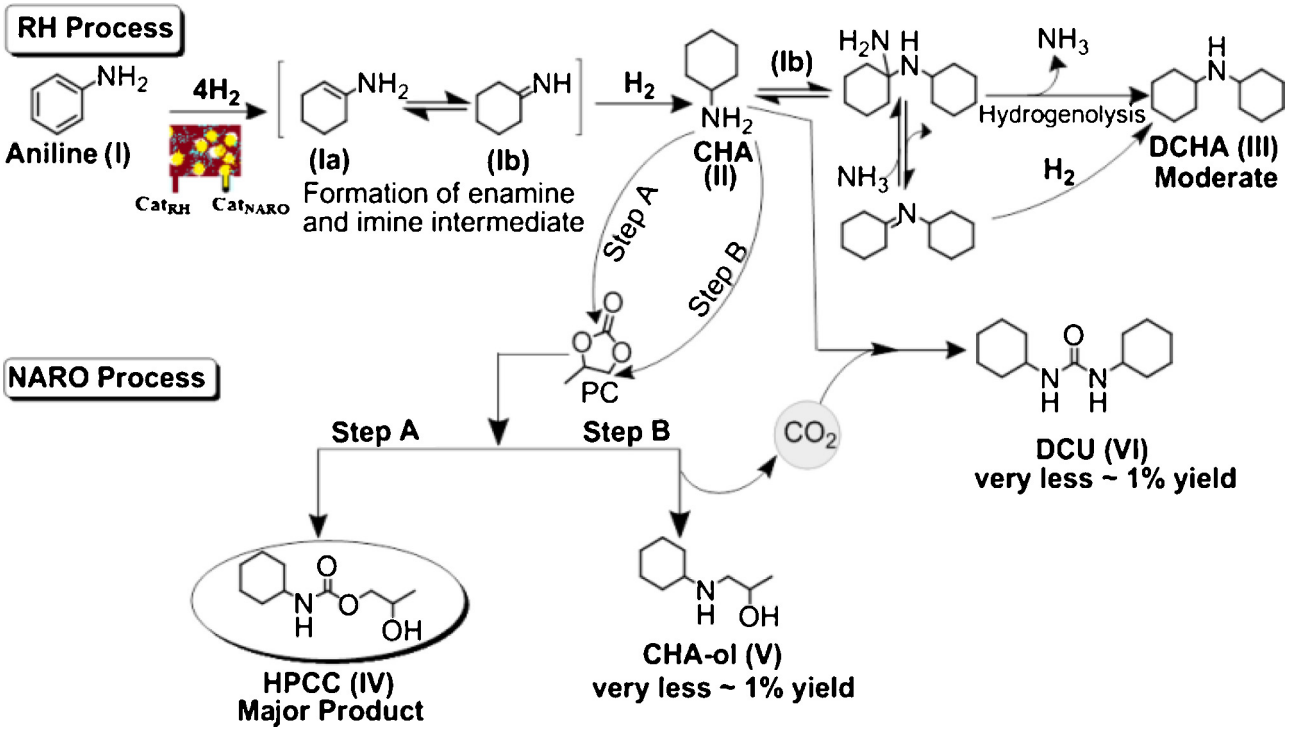
[a] Reaction conditions: amines (15 mmol), carbonates (7.5 mmol), Cat_{RH} (0.075 mmol), Cat_{NARO} (0.375 mmol), IPA (15 ml), $T = 160\,^{\circ}C$, $P = 8.3$ MPa, $t = 2$ h.
[b] Carbamate yield is calculated based on carbonates.
[c] So many by-products (e.g. 5–6 types of alkyl amines).
[d] Data are based on GC-FID area (%).
[e] 1:1 ratio of amine and PC because of two amino groups available in moiety (mixture of carbamate formed).

To test the possibility of recycling the catalyst for the RH with NARO reaction from PC, experiments have been conducted with the same catalyst system at 160 °C and 8.3 MPa for 2 h which were responsible for 88% yield of HPCC from aniline (Fig. 6). After completion of the reaction, the product mixture was filtered to isolate the insoluble Ru/C catalyst and dried for 12 h for further use of the RH and NARO reactions.

The recycling experiments were repeated five times and all the recovered catalysts were collected to make every run use equal amount (0.19 mmol) of catalyst to exclude a factor arising from catalyst loss after filtration. The recycling study revealed that the catalyst could be recycled five times without any loss of its original reactivity, but at fifth recycle, only 75% HPCC was obtained.

4. Reaction mechanism

On the basis of overall results and discussion, a reasonable mechanism for the production of ring-hydrogenated carbamate is proposed in Scheme 3 and it distributes the overall mechanism into two processes based on the RH and NARO reaction. The first step goes through the catalytic RH reaction of the aniline (**I**) into CHA (**II**). The catalytic RH reaction probably proceeds stepwise with the



Scheme 3. Plausible mechanism for the formation of HPCC through RH and NARO reaction.

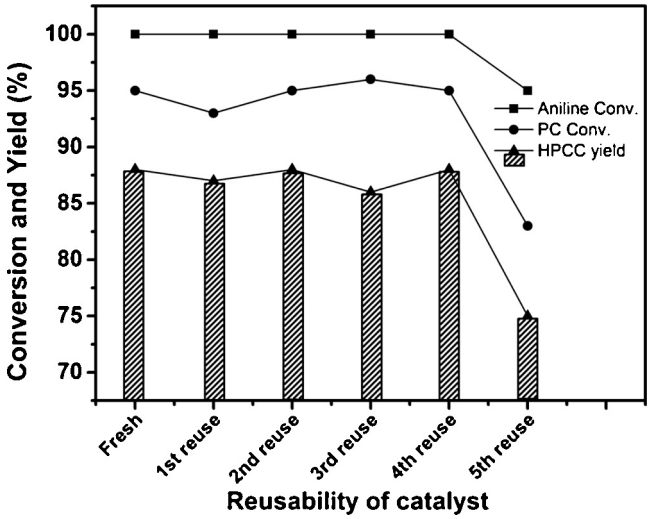


Fig. 6. Catalytic reusability tests. Reaction conditions: aniline (15 mmol), PC (7.5 mmol), Cat_{RH} (0.075 mmol), Cat_{NARO} (0.375 mmol), IPA (15 ml), $T = 160\,^{\circ}C$, $P = 8.3$ MPa, $t = 2$ h. [b]HPCC yield is calculated based on PC.

formation of enamine (**Ia**) and imine (**Ib**) intermediates [29]. This **Ib** might sometimes go towards the formation of side product, i.e. dicyclohexylamine (DCHA, **III**) by addition with another **II**, followed by hydrogenolysis with evolving ammonia.

In the next step, i.e. NARO process, the in-situ generated CHA, **II**, would work as a stronger nucleophile and readily react with PC. During the reaction, **II** has some possibilities to attack on a different position on PC due to its dual electrophilic character [30]. The first favorite route (path A) is the nucleophilic attack of amino group of **II** on the carbonyl group of PC to produce HPCC, resulting in ring-hydrogenated carbamate (**IV**) as a major product in this reaction. Another probable but unfavorable route [16,31] is hydroxyalkylation (path B) by nucleophilic attack on methylene carbon of PC to form cyclohexyl amino alcohol (**V**) in approx. 1–2% yield with evolving CO_2. This evolved CO_2 might further interact with **II** to generate dicyclohexylurea (DCU, **VI**) in a trace amount. During this reaction, all the by-products were observed in trace amount and helped us to support a plausible mechanism of RH and NARO reaction simultaneously.

5. Conclusions

In summary, a Na_2CO_3-promoted Ru/C catalyst system is very promising for the single-step synthesis of ring-hydrogenated carbamates with good yield using one-pot system from various aromatic amines, organic carbonates, and H_2. This reaction develops a facile environment-friendly route without the use of any toxic chemical like phosgene, CO, or acid azides. This methodology is quite sufficient to fulfill the required market demanding alicyclic amines and endows facile synthesis of direct production of ring-hydrogenated carbamates with good yields. Because of these points, this methodology will increase the importance and its scope for industrial applicability since the carbamates find wide applications in various areas such as pharmaceuticals, agrochemicals, intermediates in organic synthesis, protection of amino group in peptide chemistry, and especially, important precursor for isocyanates, a platform chemical for polymer chemistry.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.apcata.2014.09.013.

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