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Short Communication

One pot catalytic NO_2 reduction, ring hydrogenation, and *N*-alkylation from nitroarenes to generate alicyclic amines using Ru/C-$NaNO_2$

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ABSTRACT

A report to produce alicyclic amines and subsequent *N*-alkylation with alcohols using Ru/C-$NaNO_2$ catalyzed facile transformation of nitrobenzene was investigated. Effects of solvent, temperature, pressure, reaction time, and molar-ratio of substrate/catalyst on product composition were also studied. These mechanistic studies explain that nitrobenzene undergoes hydrogenation reaction in the following order; $-NO_2$ reduction to $-NH_2$, aromatic ring-hydrogenation to alicyclic, and from the reaction of alcohol to give *N*-alkylated amines. This investigation shed lights on possible application to polyurethane chemistry since these amines are used as important precursors for diisocyanates.

1. Introduction

The efficient synthetic pathway for producing amines has been extensively investigated due to the fact that they are widely used as significant intermediate as well as final product in various chemical industries [1,2]. Especially, the cyclohexylamine (CHA) finds various applications in pharmacology or as agrochemicals in terms of its being raw material for carbamates and isocyanates. Among these, alicyclic diamines also more substantially used feedstock for the synthesis of non-yellowing polyurethanes.

Conventionally, the CHA has been produced from the following two step; i) reduction of nitrobenzene (NB) to aniline [3–9], ii) ring hydrogenation of aniline to CHA [1,2,10–13], which makes the process complicated. Therefore, development of a facile one step synthetic pathway to alicyclic amines from nitroarenes is of great importance with respect to process efficacy.

As to the industrial processes to manufacture aniline through NB hydrogenation, the process generally employs above 240 °C with copper-catalysts in two-stage bed reactor [14]. Recently, Langer et al. reported a low-pressure process for the hydrogenation of aniline to produce CHA with high selectivity using rhodium catalysts [11]. The literature indicates that ruthenium is the most used catalyst for ring-hydrogenation of aromatic amines due to its high activity, selectivity, and reproducibility [10–13]. The *N*-alkylation of amines using non-halide reagent is also an important process because conventional halogenated substances may generate harmful by-products such as HCl [15–17]. To overcome disadvantages, alcohols can be employed as direct alkylating agent for the *N*-alkylation of amines [18–21]. Since there has been no report on one-pot synthesis of CHA or *N*-alkylated amines from the reaction of NB with H_2 and alcohols, this approach might provide much greener pathway from the view point of process efficiency as well as cost saving.

In this context, a direct synthesis of alicyclic amines and their subsequent production of *N*-alkylated amines from the reaction of nitroarenes with H_2 and alcohols in the presence of a catalyst system comprising carbon supported Ru and $NaNO_2$ are presented.

2. Experimental

All the chemicals and catalyst were purchased from Aldrich (South Korea) and used without further purification.

2.1. Hydrogenation reaction

All the hydrogenation reactions were carried out in a 100 ml pressurized reactor with a magnetic stirrer and an electrical heater (Fig. 1). Detailed procedure of hydrogenation reactions is given in supporting information.

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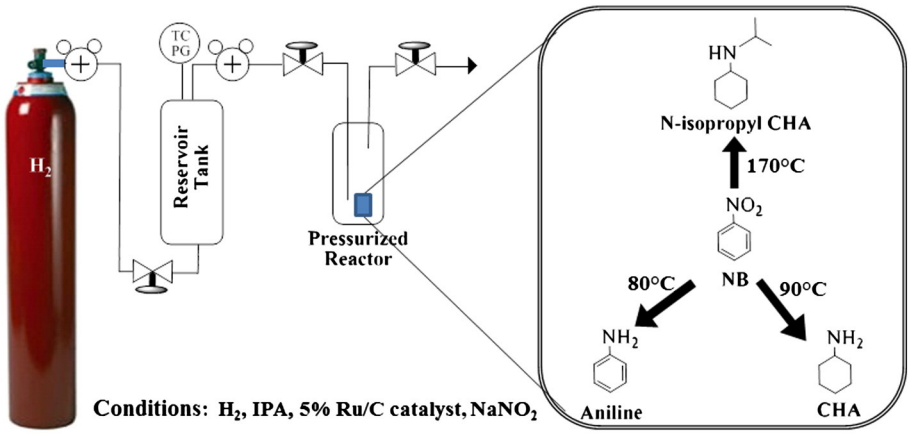


Fig. 1. Process diagram for alicyclic amines from NB.

3. Results and discussions

3.1. Effect of polar aprotic and protic solvents

Catalytic reduction of $-NO_2$ group and ring hydrogenation reaction of NB were carried out over Ru/C catalyst in the presence of various polar aprotic and alcoholic solvents at 170 °C. This temperature was used to figure out all the possible products from these harsh reaction conditions. The results summarized in Fig. 2 show that NB conversion was observed as 100% (data not shown) regardless of solvent used probably due to the high temperature. Among polar aprotic solvents, only NMP showed 100% selectivity toward CHA (entry 1, Fig. 2). On the other hand, DMF and acetonitrile delivered aniline as major product, which suggests that reaction is retarded in these solvents thus reaction did not continue further (entries 2–3, Fig. 2). It is generally accepted that the reaction rate of the reduction of $-NO_2$ group is regarded as faster than that of ring hydrogenation and it is somewhat supported from the results of very small amount of CHA in the reaction mixtures (entries 2–3, Fig. 2). In contrast, THF, diethyl ether, and diisopropyl ether produced considerable amount of CHA and dicyclohexylamine (DCHA) without the existance of aniline (entries 4–6, Fig. 2), giving a clue that they facilitate the reaction to undergo ring hydrogenation as well as $-NO_2$ reduction. From these results, NMP was found to be the most favorable polar aprotic solvent at 170 °C in terms of production of CHA and the rate of hydrogenation reaction is much influenced according to the solvent used.

However, when we employed polar protic solvents, the products were identified as CHA, DCHA, and *N*-alkyl CHA whilst the aniline was not detected, suggesting that due to high solubility of hydrogen gas in alcohols, these solvents accelerate both the ring hydrogenation and $-NO_2$ reduction. Among those solvents, it is interesting to note that IPA showed best result for obtaining ring-hydrogenated product, *N*-isopropyl CHA (IP-CHA) almost quantitatively at 170 °C (entry 9, Fig. 2). The facile synthesis of *N*-alkyl CHA is also significant since they are used as important intermediates in the fine chemical industry, especially when obtained directly from nitroarenes.

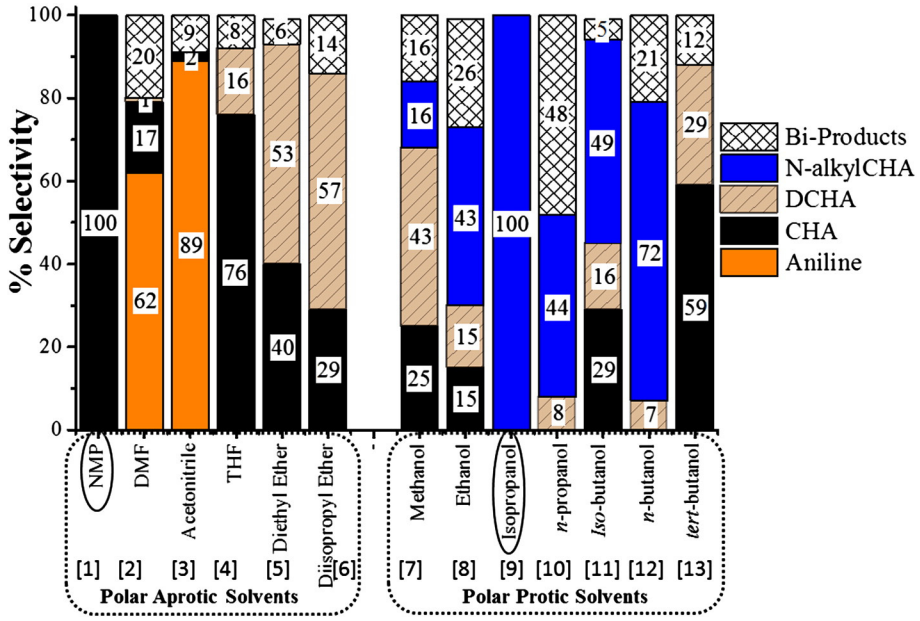


Fig. 2. Effect of various solvents on product composition: NB (7.5 mmol), 5 wt.% Ru/C (0.19 mmol of Ru), solvent (15 ml), $T = 170$ °C, $P = 8.3$ MPa, $t = 4$ h.

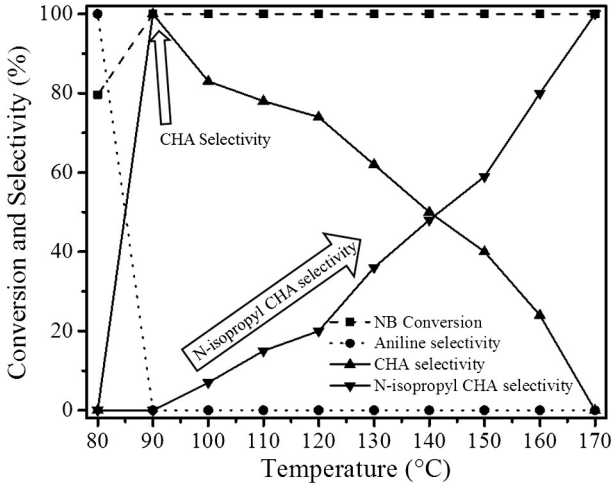


Fig. 3. Effect of temperature on product composition; NB (7.5 mmol), 5 wt.% Ru/C (0.19 mmol of Ru), IPA (15 ml), $P = 8.3$ MPa, $t = 4$ h.

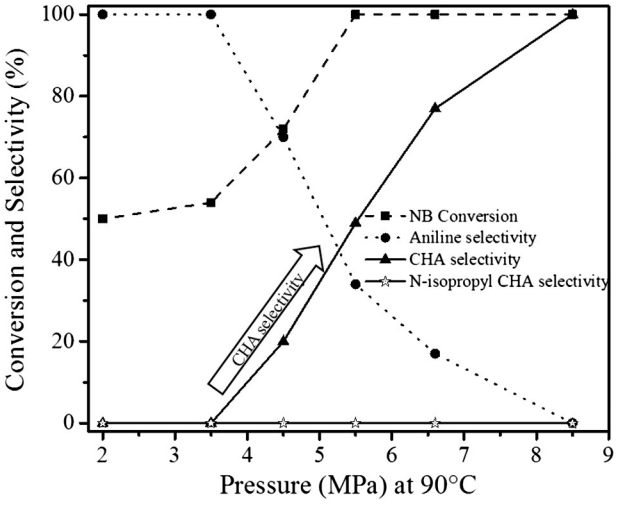


Fig. 4. Effect of pressure on product composition; NB (7.5 mmol), 5 wt.% Ru/C (0.19 mmol of Ru), IPA (15 ml), $T = 90$ °C, $t = 4$ h.

Table 1
Effect of reaction time on the product compositional change.[a]

Time	Conversion and selectivity (%)			
	NB conversion	Aniline selectivity	CHA selectivity	IP-CHA selectivity
1 h	49.7	100	0	0
2 h	100	0	89	0
3 h	100	0	100	0
4 h	100	0	100	0

[a] Reaction conditions: NB (7.5 mmol), 5 wt.% Ru/C (0.19 mmol of Ru), IPA (15 ml), $T = 90$ °C, $P = 8.3$ MPa.

These experimental results led us to a hypothesis that a fine tuning of the reaction conditions using IPA as solvent may result in producing preferred amine compounds selectively, e.g., aniline, CHA, and *N*-alkyl CHA. Thus to correlate above hypothesis, the effects of solvents, temperature, pressure, and the molar ratio of substrate/catalyst on the product composition were investigated.

3.2. Effect of temperature

Fig. 3 shows the effect of temperatures on product composition produced from hydrogenation of NB using IPA as solvent. The main products were found to be hydrogenated compounds such as aniline, CHA, and IP-CHA.

The NB conversion and aniline selectivity were 79.6% and 100%, respectively at 80 °C whilst 100% of NB was converted to CHA at 90 °C, indicating that temperature barrier between the products of $-NO_2$ reduced and ring-hydrogenated is very slight. As temperature increased above 90 °C, CHA decreased gradually and IP-CHA started to generate, and eventually, the CHA was completely converted to IP-CHA at 170 °C. These results suggest that the hydrogenation of NB undergoes i) aniline formation, ii) CHA formation, and iii) *N*-alkylated CHA formation pathway, therefore all intermediate compounds such as aniline, CHA, and IP-CHA can be synthesized selectively by simply varying the reaction temperature in IPA.

3.3. Effect of pressure

To investigate the effect of pressure on the product composition, same hydrogenation reaction of NB was carried out in IPA at 90 °C for 4 h with varying pressure. Fig. 4 described that NB conversion gradually increased up to 100% with increasing pressure ranging from 2.06 to 5.50 MPa. At this pressure range, a sharp decrease in the selectivity of aniline was observed with a simultaneous increase in the formation of CHA, and finally, the 100% CHA selectivity was achieved without the formation of IP-CHA even at 8.3 MPa, probably ascribing to the relatively low temperature (90 °C).

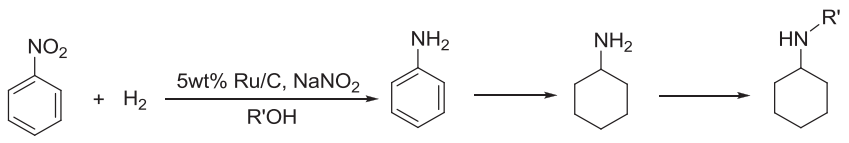
3.4. Effect of reaction time

To study the product compositional change as a function of time, hydrogenation reaction was performed in IPA at 90 °C and 8.3 MPa with varying reaction time. As shown in Table 1, the conversion of NB remained 50.3% until 1 h, producing aniline with 100% selectivity. When the reaction time is retained for 2 h, conversion reached 100% with a parallel disappearance of aniline while the CHA was formed with 89% selectivity, and after 3 h, the CHA was obtained almost quantitatively (both conversion and selectivity = 100%).

These results are again clearly supporting that hydrogenation of NB undergoes following step: i) reduction of $-NO_2$ to $-NH_2$; ii) aromatic ring hydrogenation to alicyclic; iii) alkylation with alcohol to give corresponding *N*-alkylated amine as shown in Scheme 1.

3.5. Effect of catalyst molar ratio

To investigate the effect of catalyst loading, various molar ratios (NB/catalyst) ranging from 40:1 to 2000:1 were tested at 140 °C, 8.3 MPa for 4 h (Fig. 5). The substrate conversion retained 100% until the molar ratio was 400, and thereafter a sharp decrease was observed. The selectivity of aniline increased very rapidly until the molar ratio reached 1000 and thereafter a gradual decrease was observed while the selectivity of CHA increased sharply until the molar ratio of 200:1 then deep decrease was observed. The overall decrease in the NB conversion as



Scheme 1. Reaction pathway for the hydrogenation of NB.

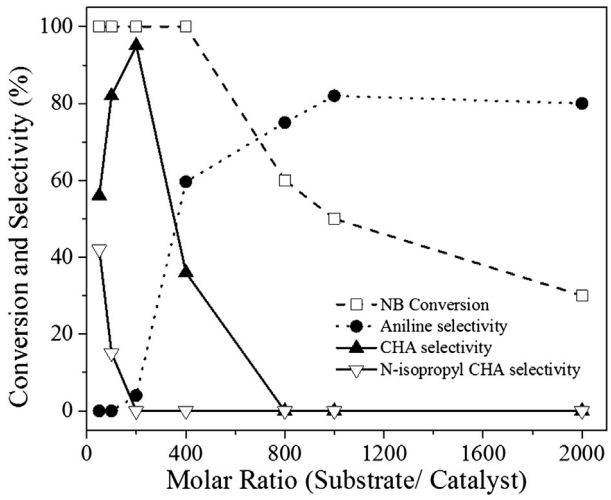


Fig. 5. Effect of molar ratio on product composition; 5 wt.% Ru/C (0.19 mmol of Ru), IPA (15 ml), $T = 140$ °C, $P = 8.3$ MPa, $t = 4$ h.

the increase in the molar ratio is mainly due to the fact that the chances of the interactions between catalyst with substrate are greatly diminished at the molar ratios higher than 200 under these reaction conditions.

3.6. Scope of hydrogenation reaction for dinitroarenes and aromatic diamines

To broaden the hydrogenation scope, various dinitroarenes and diamines were examined for the formation of alicyclic diamines. The results in Table 2 show that conversions were mostly high but this catalyst system was not able to properly hydrogenate dinitroarenes to give corresponding alicyclic diamines whereas 2,4 and 3,4-dinitrotoluenes were reduced to give a quantitative yield (100%) of corresponding diamino toluenes (entries 1,2). The low selectivity of 2,6-diaminotoluene (66.4%, entry 3), is likely ascribed to the steric hindrance arising from the 2,6 position of nitro group. Among the diamino compounds, 4,4 -methylene dianiline (MDA) was converted to di(4-aminocyclohexyl)methane in excellent yield even at 110 °C (entry 4) while others (entries 5,6) showed very low selectivity toward ring-hydrogenated product even at elevated temperatures.

3.7. Reusability of catalyst for hydrogenation

The recycling study revealed that the catalyst was able to be reused five times without any loss of its original reactivity, at sixth recycling, however, the yield of CHA reduced slightly down to 94.1% (Table S1). Details are given in supporting information.

4. Conclusions

Ru/C-$NaNO_2$ catalyst system is found to catalyze various nitroarenes to produce corresponding alicyclic or aromatic amines in high yield. The hydrogenation reaction undergoes following steps; NO_2 reduction, ring hydrogenation, and continuing to *N*-alkylation depending on the reaction conditions used. The more severe reaction conditions, the further the reaction proceeded thus any compound out of the three, e.g., aniline, CHA, *N*-alkylated CHA, could be produced almost quantitatively by simply altering the reaction conditions. The effects of solvent, temperature, pressure, reaction time, and molar ratio on the product composition were studied using NB as substrate. Among the reaction parameters, temperature showed highest dependency on product composition. The catalyst reuse study revealed that this catalyst system was able to catalyze 5 times without any loss of activity. Various aromatic dinitro and diamines were tested using same catalyst system which produced corresponding aromatic diamines in high yield but not delivered alicyclic diamines.

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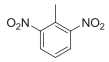
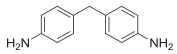
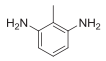
Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.catcom.2013.09.012.

Table 2
Hydrogenation of various aromatic dinitro and diamine compounds.[a]

Entry	Substrate	T.	Conv.(%)	Selectivity (%)		
				$-NH_2$	Ring-hydrogenated	*N*-alkylated
1		110	100	100	0	0
2		150	100	100	0	0
3		130	100	66.4	0	0
4		110	100	N/A	100	0
5		150	100	N/A	trace	22.9
6		170	100	N/A	24.8	45.2

[a] Substrate (7.5 mmol), 5 wt.% Ru/C (0.19 mmol of Ru), IPA (15 ml), $P = 8.3$ MPa, $t = 4$ h.

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