Science in China Series B: Chemistry

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One pot synthesis of *N*-ethylaniline from nitrobenzene and ethanol

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A novel method for the one pot synthesis of *N*-alkyl arylamines from nitro aromatic compounds and alcohols is proposed through the combination of the aqueous-phase reforming of alcohol for hydrogen production, the reduction of nitro aromatic compounds for the synthesis of aromatic amine and the *N*-alkylation of aromatic amine for the production of *N*-alkyl arylamine over an identical catalyst under the same conditions of temperature and pressure in a single reactor. In this process, hydrogen generated from the aqueous-phase reforming of alcohols was used *in-situ* for the hydrogenation of nitro aromatic compounds for aromatic amine synthesis, followed by *N*-alkylation of aromatic amine with alcohols to form the corresponding *N*-alkyl arylamines at a low partial pressure of hydrogen. For the system composed of nitrobenzene and ethanol, under the conditions of 413 K and P_{N_2} = 1 MPa, the conversion degrees of nitrobenzene and aniline were 100%, the selectivity to *N*-ethylaniline and N, *N*-diethylaniline were 85.9% and 0%—4%, respectivity, after reaction for 8 h at the volumetric ratio of nitrobenzene∶ethanol∶water = 10∶60∶0. The selectivity for *N*, *N*-diethylaniline production is much lower than that through the traditional method. In this process, hydrogen and aromatic amines generated from the aqueous-phase reforming of alcohols and hydrogenation of nitro aromatic compounds, respectively, could be promptly removed from the surface of the catalyst due to the occurrence of *in-situ* hydrogenation and *N*-alkylation reactions. Thus, this may be a potential approach to increase the selectivity to *N*-alkyl arylamine.

nitrobenzene, ethanol, one pot, N-ethylaniline, combination, N-alkylation, Raney Ni

N-alkyl arylamines are important intermediates in the production of dyes, pharmaceuticals, and pesticides. These compounds are generally synthesized through the formation of aromatic amines from the chemical reduction or liquid phase catalytic hydrogenation of nitro aromatic compounds, and then the aromatic amines are reacted with alkylating agents such as alcohols, ether, and alkyl halides, to form *N*-alkyl arylamines over catalysts. From the viewpoint of environmentally benign, the liquid phase catalytic hydrogenation of nitro aromatic compounds over Raney Ni, Raney Cu and Pd, Pt supported on activated carbon, or Al_2O_3 as catalysts is widely used in the synthesis of aromatic amines[1−4], instead of the chemical reduction using iron, zinc powder, or sodium sulfide, which produce mass wastes[5]. However, some special facilities for hydrogen production, reservation, and transportation are required in the traditional hydrogenation process. Currently, *N*-alkylation of aromatic amines with alkylating agents to produce *N*-alkyl arylamines is accompanied by the great challenge of the rigorous requirements for the equipment, hard purification of the products, and treatment of the

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Received January 31, 2007; accepted March 7, 2007
doi: 10.1007/s11426-008-0032-5

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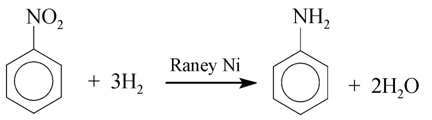
Supported by the Program for New Century Excellent Talents in University (Grant No. NCET-04-0557), and the Specialized Research Fund for the Doctoral Program of High Education (Grant No. SRFDP-20060337001)

waste water due to the occurrence of *N*,*N*-dialkylation using mineral acid, H_2SO_4, H_3PO_4, and hydrochloride as catalysts[6,7]. Gas-phase N-alkylation of aromatic amine using zeolites (ZSM-5, KY, NaX, CaY)[8−11], metallic oxide[12−14] or metallic salt[12,15] instead of mineral acids as catalysts may avoid the equipment corrosion, but it is difficult to obtain an ideal selectivity for the desired product. Furthermore, the high reaction temperature leads to the deactivation of the catalyst and a decreased selectivity for the target product. Recently, a method of synthesis of *N*-alkyl arylamines through a successive occurrence with step-wise hydrogenation of nitro aromatic compounds and the *N*-alkylation of aromatic amines in one reactor over Raney Ni, Pd/C, alumina supported Cu-Mn promoted by rare earth metal, and alkaline hydroxide catalysts has been proposed[16−21]. In this method, nitro aromatic compounds, alkylating agents, and catalysts are added into the batch reactor together. The hydrogenation of nitro aromatic compounds to aromatic amine is then performed at a desired temperature and pressure in hydrogen atmosphere. Subsequently, the reactor is cooled down to room temperature and purged with N_2 for the removal of hydrogen. Finally, the reactor is heated to another desired temperature and pressure in a nitrogen atmosphere for the *N*-alkylation reaction of aromatic amine with alcohol, aldehyde, or ketone. For this process, a high conversion degree of reactants and high selectivity for the desired product could be obtained, and the separation of the aromatic amine after the hydrogenation of nitro aromatic could be avoided. Trotta et al.[22] reported that *N*-alkyl arylamine could be produced through the gas-liquid phase transfer catalysis using dimethyl carbonate as an alkylating agent. However, the hydrogenation of nitro aromatic compounds and the *N*-alkylation of aromatic amine are carried out with step-wise under different conditions in all of the processes mentioned above. In the meantime, the supply of extra hydrogen sources for the hydrogenation of nitro aromatic compounds is certainly needed.

We have recently reported[23] that the aqueous-phase reforming of alcohols for hydrogen production and the liquid phase hydrogenation of nitro aromatic compounds could be synchronously performed over an identical catalyst under the same conditions of temperature and pressure in a single reactor for the system composed of "nitro aromatic compounds + alcohol + water." For this process, highly selective hydrogenation of nitro aromatic compounds to aromatic amines with hydrogen generated from the aqueous-phase reforming of alcohols was obtained. There is a low hydrogen partial pressure in the gas phase due to the hydrogen produced from the aqueous-phase reforming of solvent methanol, and there are only aromatic amines and alcohol in the liquid phase. Furthermore, the reaction temperature of this process is higher than that of the traditional hydrogenation process. Therefore, synthesis of *N*-alkyl arylamines might take place through the *N*-alkylation reaction between aromatic amines and alcohol in this process under suitable reaction conditions. Based on the comparison of the novel system of liquid phase hydrogenation of nitro aromatic compounds[23] and the *N*-alkylation of aromatic amines with alcohol, under a suitable catalyst and optimized reaction conditions, one pot synthesis of *N*-alkyl arylamine directly from nitro aromatic compounds and alcohols may be obtained. Among the aqueous-phase reforming of alcohols for hydrogen production[24], the hydrogenation of nitro aromatic compounds to aromatic amines, and the *N*-alkylation of aromatic amines with alcohol to *N*-alkyl arylamines, there are good coincidence conditions, i.e., they are usually performed in the liquid phase over an identical types of catalysts such as Raney Ni, Pt/Al_2O_3, Pd/Al_2O_3, and Pd/C, under similar conditions of temperature and pressure, which is as similar as those between the aqueous-phase reforming of alcohols for hydrogen production and the hydrogenation of nitro aromatics. The hydrogen from the aqueous-phase reforming of alcohols is used *in-situ* in the hydrogenation of nitro aromatic compounds to aromatic amines[23]; the aromatic amine is then converted into the corresponding *N*-alkyl arylamines through the *N*-alkylation with alcohol. In these successive reactions, hydrogen generated from the aqueous-phase reforming of alcohol and aromatic amines produced from the hydrogenation of nitro aromatic compounds could be removed promptly; meanwhile, water formed from the hydrogenation of nitro aromatic compounds and the alkylation of aromatic amine with alcohol could be consumed through the aqueous-phase reforming of alcohol. Therefore, this could offer a potential route to increase the conversion rates of nitrobenzene and aniline, and the selectivity to *N*-alkyl arylamine. Alcohol in this system is referred to as "hydrogen source" for the hydrogenation of nitro aromatic compounds, "alkylating reagent" for *N*-alkylation of aromatic amine, and "solvent" for this process. Furthermore, a series of *N*-alkyl arylamine compounds could be synthesized directly from the reactions between different kinds of nitro aromatic compounds and alcohols.

In the present study a novel method for the synthesis of *N*-alkyl arylamine is proposed through a one pot reaction of nitro aromatic compounds and alcohols. For the system of “nitrobenzene + ethanol + water,” the aqueous-phase reforming of ethanol for hydrogen production (1)[24,25], the hydrogenation of nitrobenzene (2), and *N*-alkylation of aniline (3) are performed synchronously for the synthesis of *N*-ethylaniline over an identical catalyst under the same conditions in a single reactor. The reaction mechanism of the one pot synthesis of *N*-ethylaniline directly from nitrobenzene and ethanol is represented in Figure 1, and the global chemical reaction by the following eq. (4).

$$CH_3CH_2OH + 3H_2O \overset{\text{Raney Ni}}{\rightleftharpoons} 2\,CO_2 + 6H_2 \qquad (1)$$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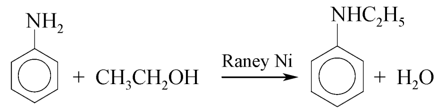
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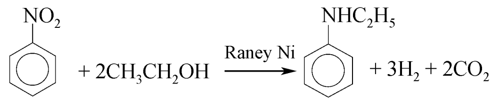

(4)

For this process, the high selective hydrogenation of nitrobenzene with hydrogen generated from the aqueous-phase reforming of ethanol could be performed[23]. The formed aniline will successively react with ethanol to form *N*-ethylaniline.

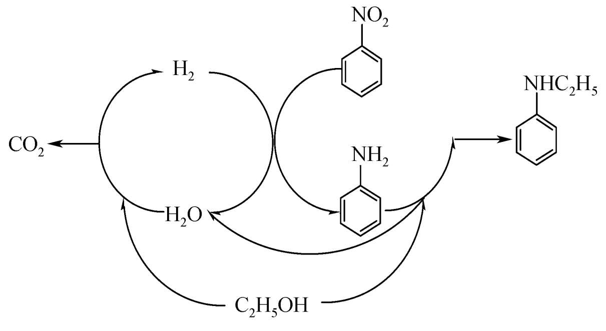


Figure 1 Schematic of the mechanism for one pot synthesis of *N*-ethylaniline from nitrobenzene and ethanol.

1 Experimental

1.1 Reagents and instruments

Nitrobenzene, aniline, and cyclohexylamine (AR/99.0%) were purchased from Shanghai Chemical Reagents Factory. Dehydrated alcohol (AR/99.7%) was purchased from Anhui Ante Biochemicals Limited Company. Liquid products were analyzed by Gas-Chromatogram (Japan Shimadzu GC-14B) equipped with 30mHP-5 capillary and FID detector, and gaseous products were analyzed by Gas-Chromatogram (Fuli GC-9790) equipped with Porapak Q and TCD detector. The contents of products are determined by the peak area normalization method. The qualitative analysis of products was performed by Gas Chromatograph and Mass Spectrometer (Agilent-6890GC-5973MS).

1.2 Preparation and characterization of catalyst

The preparation of Raney Ni was as previously described[23]. The physical structure parameters and chemical compositions of the three types of Raney Ni catalysts are listed in Table 1.

1.3 One pot synthesis of *N*-ethylaniline from nitrobenzene and ethanol

50—100 mL of dehydrated alcohol, 10 mL of nitrobenzene, 0—15 mL of distilled water, and 21.05 g Raney Ni (wet mass, the Raney Ni catalyst was reversed in dehydrated alcohol solution to remove the water absorbed on the catalyst) were added together into a 500 mL stainless steel autoclave. The autoclave system was then purged with N_2 three times and kept in a nitrogen atmosphere. Subsequently, the autoclave was heated to the temperature of 393—453 K at a nitrogen pressure of 0.8—2.5 MPa. After the reaction was carried out isothermally for 1—8 h, the autoclave was cooled down to room temperature and held at that temperature overnight. The gas and liquid products were analyzed by gas-chroma-

Table 1 Physical structure parameters and chemical composition of the Raney Ni catalysts

Catalyst	Mass fraction (%)		Crystal size (nm)	Particle size (μm)	Surface area (m^2/g)	Pore volume (mL/g)
	Al	Ni				
Raney Ni (A)	15.3	84.7	5.4	1101.2	123.2	0.1147
Raney Ni (B)	5.9	94.1	6.2	22.1	131.0	0.02256
Raney Ni (C)	4.0	96.0	5.5	46.8	130.4	0.09712

tograph.

2 Results and discussion

2.1 Catalytic performances of catalysts

The catalytic performances of the Raney Ni (A, B, C) and Ru-Fe-B/Al_2O_3 catalysts in the one pot synthesis of *N*-ethylaniline (NEA) directly from nitrobenzene and ethanol are listed in Table 2. The selectivity to *N*-ethylaniline over Raney Ni (A) is much higher than those over Raney Ni (B) and Raney Ni (C), which could be attributed to the fact that the Raney Ni (A) is of greater particle size, higher Al content and larger porous size than Raney Ni (B) and Raney Ni (C) as listed in Table 1. Correspondingly, the catalytic activity of the hydrogenation of Raney Ni (A) is much lower than those of Raney Ni (B and C). For example, hydrogenation of 2-nitro-5- methoxyacetaniline under the conditions of temperature 353 K and hydrogen pressure 1 MPa over the Raney Ni (A, B, or C) catalysts was carried out in a 500 mL stainless steel autoclave with a ratio of 2-nitro-5-methoxyacetaniline : methanol : ammonia aqueous solution (w = 25%) : Raney Ni (wet mass) of 30 g : 100 mL : 5 mL : 2 g, respectively. The hydrogenation conversion degrees of 2-nitro-5-methoxyacetaniline over Raney Ni (A), Raney Ni (B), and Raney Ni (C) were 84.8% in 480 min, 100% in 195 min, and 100% in 38 min, respectively. On the other hand, the larger porous size of the Raney Ni (A) could favor the promptly desorption of the products, which suppresses the deep hydrogenation and undesired cyclization reactions. In comparison with the catalytic performance of the Ru-Fe-B/Al_2O_3 catalyst listed in Table 2, it could be suggested that a reasonable catalytic activity of the hydrogenation is essential to increase the selectivity to *N*-ethylaniline for the one pot synthesis of *N*-ethylaniline directly from ethanol and nitrobenzene.

2.2 Effect of reaction conditions on the catalytic performance

One pot synthesis of *N*-ethylaniline from nitrobenzene and ethanol is a complex reaction system, which involves the combination of the aqueous-phase reforming of ethanol for hydrogen production, the *in-situ* hydrogenation of nitrobenzene to aniline, and the *N*-alkylation of aniline to *N*-ethylaniline. Therefore, the reaction temperature, pressure, and the molar ratio of the starting materials would significantly influence the conversion degrees of nitrobenzene and aniline, and the selectivity to *N*-ethylaniline. In the present work, the effects of the reaction conditions on the conversion degrees of nitrobenzene and aniline, and the selectivity to *N*-ethylaniline in the one pot synthesis of *N*-ethylaniline directly from nitrobenzene and ethanol over the Raney Ni (A) catalyst were investigated.

2.2.1 Effect of reaction time. The curves of the conversion degrees of nitrobenzene and aniline, and the selectivity to *N*-ethylaniline and by-products with the reaction time are shown in Figure 2. In the reaction system composed of “nitrobenzene and ethanol,” the hydrogenation of nitrobenzene into aniline with the hydrogen generated from the aqueous-phase reforming of ethanol is a fast reaction. The conversion degree of nitrobenzene reached 95% after reaction for 3 h and reached 100% after reaction for 6 h. Meanwhile, the conversion degree of intermediate aniline reached 95% after reaction for 6 h, and reached higher than 98% after reaction for 8 h. The selectivity to *N*-ethylaniline reached up to 45% after reaction for 1 h, and further increased gradually to higher than 82% after reaction for 8 h. While the selectivity to *N*, *N*-diethyl aniline changed slightly during the period of reaction, it was always maintained at 0—4%. These experimental results indicated that the deep *N*-alkylation reaction of aniline could be highly suppressed in the on pot synthesis of *N*-ethylaniline directly from nitrobenzene and ethanol, and the selectivity to *N*, *N*-diethylaniline is much lower than that with the traditional method[26,27].

2.2.2 Effect of temperature. Generally, the aqueous phase reforming of alcohol over Raney Ni takes place at

Table 2 One pot synthesis of *N*-ethylaniline from nitrobenzene and ethanol over various catalysts

Catalyst	Conversion (%)		Selectivity (%)					
	nitrobenzene	aniline	NEA	NNEA	RH	BTA	quinoline	others
Raney Ni (A)	100	100	85.9	2.4	11.7	0	0	0
Raney Ni (B)	100	99.3	57.2	1.1	4.6	4.0	15.2	17.9
Raney Ni (C)	100	97.3	58.3	0.7	3.7	4.1	13.8	19.4
Ru-Fe-B/Al_2O_3	35.7	93.6	95.6	0	1.1	0.3	0.7	2.3

NEA: *N*-ethylaniline; NNEA: *N*, *N*-diethylaniline; RH: ring hydrogenated product; BTA: *p*-butylaniline. Reaction conditions: nitrobenzene 10 mL, ethanol 60 mL, Raney Ni 21.05 g or Ru-Fe-B/Al_2O_3 2.05 g, T = 413 K, P = 1—1.2 MPa, t = 8 h.

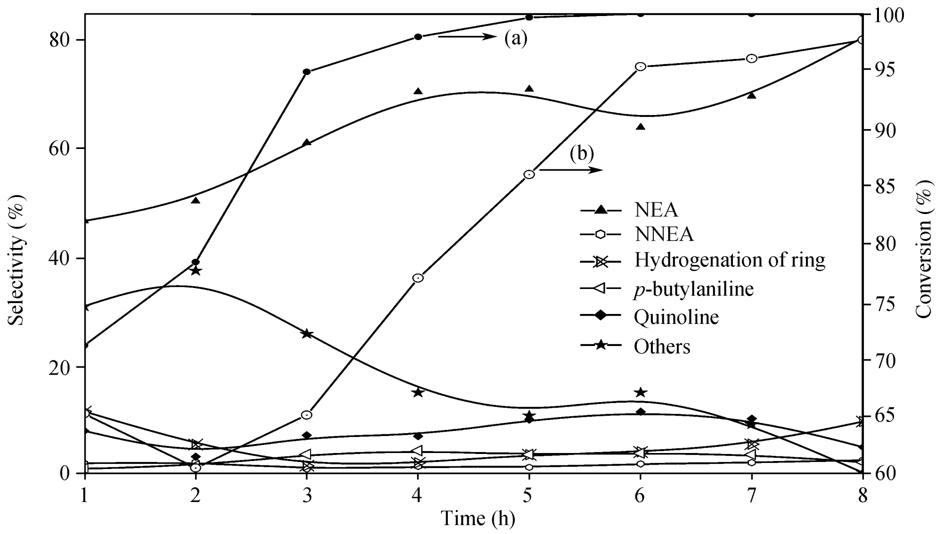


Figure 2 Effect of reaction time on the one pot synthesis of *N*-ethyl aniline from nitrobenzene and ethanol. (a) Nitrobenzene; (b) aniline. Reaction conditions: nitrobenzene 20 mL, ethanol 120 mL, Raney Ni 42 g, $T = 413$ K, $P = 1-1.2$ MPa.

423—530 K[24,25], while the hydrogenation of nitro aromatic compounds and *N*-alkylation of aromatic amine over Raney Ni operate at 333—393 K[2−5] and 393—453 K[16−20], respectively. Therefore, the optimization of reaction temperature is important to achieve a good coincidence of these three reactions in the system composed of "nitrobenzene + ethanol." The effect of temperature on the selectivity for the products in the one pot synthesis of *N*-ethylaniline is shown in Figure 3. With an increase in temperature the selectivity to *N*-ethylaniline increases and then decreases. The highest selectivity of 85.9% to *N*-ethylaniline is obtained at 413 K. These experimental results could be attributed to the fact that the increase of temperature favors the aqueous phase reforming of alcohols for hydrogen production[24,25], while it suppresses the *N*-alkylation of aromatic amine[16−19], which results in the decrease of the selectivity to *N*-ethylaniline. Meanwhile, the increase of temperature will cause the increase of hydrogen partial pressure in the system due to the acceleration of hydrogen generation rate from the aqueous reforming of ethanol, and eventually increases the selectivity of by-products due to the occurrence of deep hydrogenation. Additionally, the increase of temperature is also favorable for the occurrence of *C*-alkylation[7] and *N*, *N*-dialkylation[16].

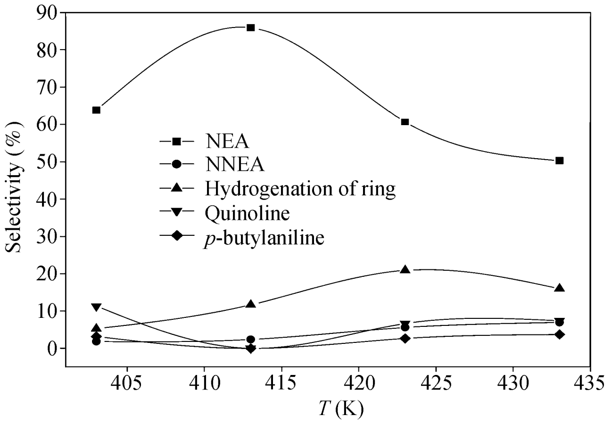


Figure 3 Effect of temperature on the one pot synthesis of *N*-ethylaniline from nitrobenzene and ethanol. Reaction conditions: nitrobenzene 10 mL, ethanol 60 mL, Raney Ni 21.05 g, $P = 1-1.2$ MPa, $t = 8$ h.

2.2.3 Effect of pressure. To investigate the effect of system total pressure on the selectivity to the products, the autoclave system was fed with nitrogen before the reaction. To investigate the effect of hydrogen partial pressure on the selectivity to the products, in the case of a hydrogen partial pressure lower than 1.0 MPa the autoclave system was fed with hydrogen up to the desired partial pressure, and then nitrogen was added up to the desired partial pressure, and then nitrogen was added up to the desired total pressure, while in the case of a hydrogen partial pressure greater than 1.0 MPa the autoclave system was fed with hydrogen only.

The effects of system total pressure and hydrogen partial pressure on the product selectivity for this process are shown in Figure 4. As shown in Figure 4(a), with the increase of the system total pressure the selectivity to *N*-ethylaniline decreases and is then maintained at a constant value, while the selectivity to quinoline and other by-products increases and is then maintained at a constant value. The selectivity to the products of ring

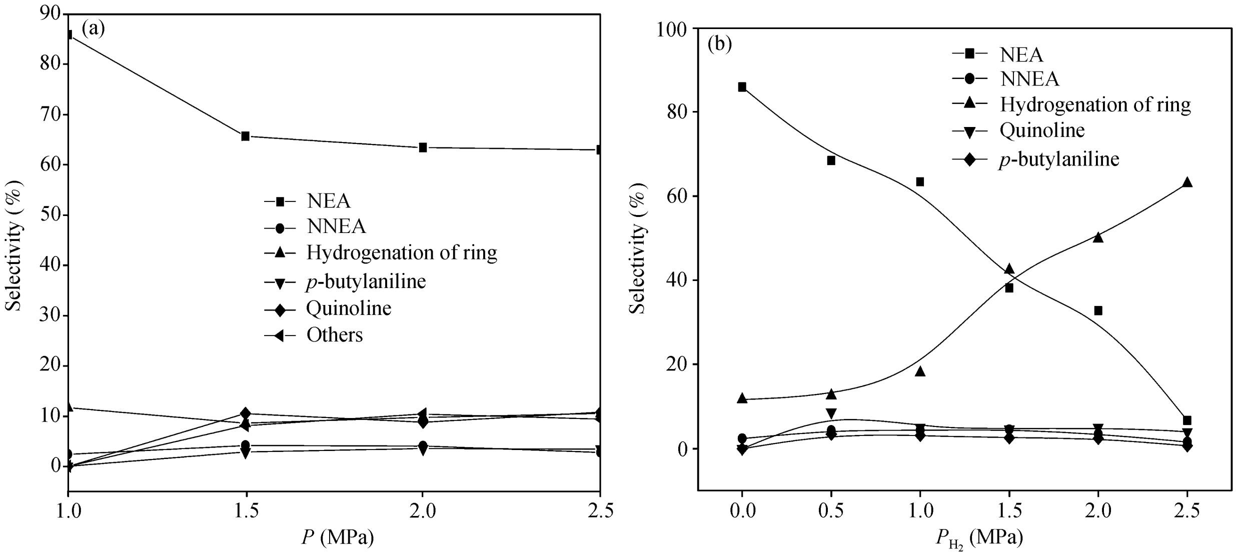


Figure 4 Effect of temperature on the one pot synthesis of *N*-ethylaniline from nitrobenzene and ethanol. (a) System pressure, the system pressure was increased by adding nitrogen to the desired pressure; (b) hydrogen partial pressure, if the hydrogen partial pressure is lower than 1 MPa, hydrogen and nitrogen coexisted in the system, when the hydrogen partial pressure is over 1 MPa, there is only hydrogen in the system. Reaction conditions: nitrobenzene 10 mL, ethanol 60 mL, Raney Ni 21.05 g, $T = 413$ K, $t = 8$ h.

hydrogenation, *p*-butyl aniline, and *N*, *N*-diethyl aniline is almost independent of the system total pressure. As shown in Figure 4(b), with the increase of hydrogen partial pressure, the selectivity to *N*-ethylaniline is decreased, the selectivity to the products of ring hydrogenated increased linearly, while the selectivity to other products is kept at a constant value. These results indicate that the hydrogen partial pressure has a significant effect on the selectivity to *N*-ethylaniline and the ring hydrogenated products, while it has almost no effect on the selectivity to other by-products. Therefore, the decrease of system total pressure and hydrogen partial pressure would be favorable for the formation of *N*-ethylaniline in the case of the occurrence of reactions in liquid phase.

2.2.4 Effect of the ratio of starting materials. The effect of the volume ratio of “nitrobenzene : ethanol : water” on the conversion degrees of nitrobenzene and aniline and the selectivity to the products in the one pot synthesis of *N*-ethylaniline directly from ethanol and nitrobenzene is listed in Table 3. When the volume ratio of “nitrobenzene : ethanol : water” is equal to 10 : 60 : 0, the highest selectivity (85.9%) to *N*-ethylaniline is reached. With the further increase of ethanol content, the selectivity to *N*-ethylaniline will be decreased and the selectivity of the by-products *p*-butylaniline and quinoline highly increased, as the reactions, such as the dehydrogenation of ethanol to acetone, induced from ethanol take place easily. When the volume of ethanol is 90 mL, the selectivity to the by-product quinoline is up to 20.1%, but no high effect of the ethanol content on the selectivity to products of deep ring hydrogenation is observed. The experimental results mentioned in Section 2.2.3 indicated that hydrogen partial pressure has a profound effect on the selectivity to ring hydrogenated products. Thus, it could be concluded that the increase of ethanol ratio in the feeds should have no effect on the hydrogen partial pressure in this reaction system. Furthermore, the experimental results in Table 3 also indicate that the presence of a small amount of water will result in the large decrease of the selectivity of *N*-ethylaniline. With the increase of water content, the selectivity to quinoline and its derivatives will be increased, and the selectivity to the ring hydrogenated products will be decreased, which also indicates that the presence of water suppresses the formation of *N*-ethylaniline.

2.3 Analysis on the reaction mechanism and side reactions

2.3.1 Combination reaction process. Generally, the reaction process of the hydrogenation of nitro aromatic compounds and the successive *N*-alkylation of aromatic amine with alcohol from nitrobenzene and ethanol over Raney Ni has been thought as follows[16,17]: nitro aromatic compounds are hydrogenated into aromatic amine in the first step, and in the meantime alcohols are dehy-

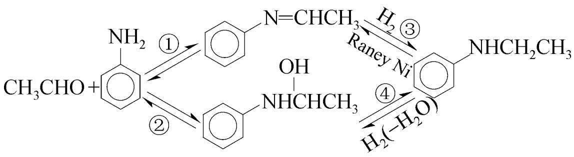
Table 3 Effect of starting materials composition on the one pot synthesis of *N*-ethylaniline from nitrobenzene and ethanol

Material (mL)		Conversion (%)		Selectivity (%)					
Ethanol	water	nitrobenzene	aniline	NEA	NNEA	RH	BTA	quinoline	others
50	0	100	99.9	74.2	2.2	8.5	7.8	7.0	0.3
60	0	100	100	85.9	2.4	11.7	0	0	0
70	0	100	99.6	69.8	3.8	3.9	7.9	10.7	3.9
80	0	100	92.3	70.8	2.1	4.0	9.6	9.9	3.6
90	0	100	98.7	60.6	1.7	6.4	6.8	20.1	4.4
60	5	100	99.7	55.1	2.4	10.7	3.0	16.7	12.1
60	10	100	97.9	66.2	0.3	9.6	2.2	18.5	3.2
60	15	97.8	50.2	44.3	0.3	1.1	2.3	36.3	15.7

NEA: *N*-ethylaniline; NNEA: *N*, *N*-diethylaniline; RH: ring hydrogenated product; BTA: *p*-butylaniline. Reaction conditions: nitrobenzene 10 mL, Raney Ni 21.05 g, $T = 413$ K, $P = 1-1.2$ MPa, $t = 8$ h.

drogenated to aldehyde; then the aromatic amine reacts with aldehyde to form a Schiff base; finally, the Schiff base is further hydrogenated to form *N*-alkyl arylamine. One pot synthesis process of *N*-ethylaniline directly from nitrobenzene and ethanol through the combination of the hydrogen formation from aqueous phase reforming of ethanol, the hydrogenation of nitrobenzene and *N*-alkylation of aromatic amine with ethanol might also have been thought to occur via the formation process of the Schiff base intermediate. The main reactions[16−19] are as follows, where the reactions (1), (2), and (5)—(7) are the process of successive occurrence:

$$2CH_3CH_2OH \overset{\text{Raney Ni}}{\rightleftharpoons} 2CH_3CO + 3H_2 \qquad (5)$$



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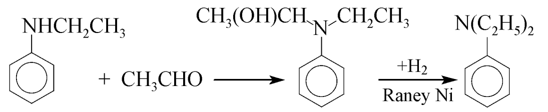
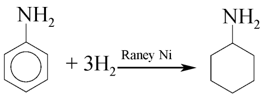


(7)

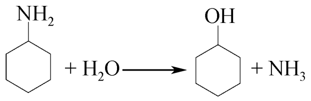
In the absence of water, the partly hydrogenation of nitrobenzene to aniline and H_2O by the hydrogen adsorbed on the Raney Ni from the reduction process is an initiative step for the one pot synthesis of *N*-ethylaniline directly from nitrobenzene and ethanol[28]. H_2O generated from the hydrogenation of nitrobenzene in the initiative step, and the *N*-alkylation of aromatic amine with alcohol is then used as the starting material for the aqueous-phase reforming of alcohols to produce hydrogen. The hydrogen generated from the aqueous-phase reforming is further used for the hydrogenation of nitrobenzene. Subsequently, acetaldehyde generated from the dehydrogenation of alcohols reacts with aniline to form Schiff base over Raney Ni; finally, *N*-ethylaniline is formed via the hydrogenation of Schiff base. After the reactions have been carried out for 2 h, the presence of 0.86% H_2, 7.60% CO_2, and 12.74% CH_4 also indicates the occurrence of the aqueous-phase reforming of ethanol[24]. In the process of one pot synthesis of *N*-ethylaniline, the dehydrogenation of ethanol to acetaldehyde should be a pivotal process of the conversion of aniline into *N*-ethylaniline[19]. A high activity of the Raney Ni catalyst for hydrogen production and hydrogenation will be of benefit to the occurrence of reaction (1) and (2), but will suppress the dehydrogenation of alcohol to acealdehyde, which results in the decrease of the selectivity to *N*-ethylaniline. For the *N*-alkylation reaction (6) of aniline and acetaldehyde for the production of *N*-ethylaniline, there are a couple of possible routes, via ①→③ to form Schiff base and via ②→④ to form hydroxylamine, respectively. The process of ②→④ route is always performed at a high temperature and pressure, while the process of ①→③ route is performed at a low temperature and pressure. *N*-ethylaniline is a secondary amine with just one H atom on the N, in which Schiff base could be not formed via the reaction of aromatic amine with acelaldehyde. However, the process of ②→④, i.e., only via the formation of hydroxylamine, will produce *N*, *N*-diethylaniline (reaction (7)). Therefore, high temperature and pressure will accelerate the formation of *N*, *N*-diethylaniline, which indicates that the high selectivity to *N*-monoalkyl aromatic amine via *N*-alkylation of aniline could be achieved through the optimization of the reaction conditions. This should be an important advance for the process of one pot synthesis of *N*-monoalkyl aromatic amine over the traditional method.

2.3.2 Analysis of side reactions. The main four kinds of by products in the procedure of one pot synthesis of

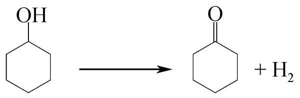
N-ethylaniline from nitrobenzene and ethanol are as follows: (1) ring hydrogenated products, such as cyclohexanol, cyclohexanone, cyclohexylamine, *N*-ethylcyclohexylamine, and *N*, *N*-diethyl cyclohexylamine; (2) p-butylaniline; (3) quinoline and its derives such as 2-methylquinoline mainly, and 2-methyl-1,2,3,4-tetrahydroquinoline; and (4) *N*, *N*-diethylaniline. The production mechanism of *N*, *N*-diethylaniline was described in Section 2.3.1, and the formation of cyclohexanol, cyclohexanone, and cyclohexylamine were shown as the reactions (1) and (8)—(13). To determine the formation mechanism of other by-products, aniline, cyclohexylamine, and *N*-ethylaniline are used as starting materials, instead of nitrobenzene, in the *N*-alkylation reaction. The experimental results are listed in Table 4. The results indicate that *p*-butyl aniline is not produced through the *C*-alkylation of aniline or nitrobenzene; it should be generated from the *C*-alkylation of hydroxylamine that is an intermediate formed during the reduction process of nitrobenzene to aniline[7]. Meanwhile, *N*-ethyl and *N*, *N*-diethyl cyclohexylamine are formed undergoing the hydrogenation of *N*-ethyl and *N*, *N*-diethyl aniline and *N*-alkylation of cyclohexylamine. Quinoline and its derives are formed through the reaction of the intermediate formed in the hydrogenation of nitrobenzene with acetaldehyde catalyzed by H^+, which is also approved by the formation of a large amount of acetic acid in the aqueous-phase reforming of ethanol. Wu Zuwang et al.[17,18] also reported that quinoline and its derivatives have not been detected in the products of the *N*-alkylation preparation via successive hydrogenation of nitrobenzene and the *N*-alkylation of aniline, which were carried out in one reaction under different temperatures and pressures. Further studies on the formation mechanism of quinoline and its derivatives are certainly required. The reactions for the formation of by products are shown in eq. (8)—(16)[16−19].



(8)

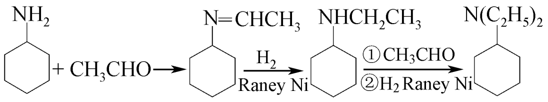


(9)

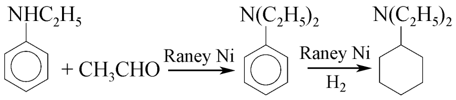


(10)

$$NH_3 + 3CH_3CH_2OH \xrightarrow{\text{Raney Ni}} N(C_2H_5)_3 + 3H_2O \quad (11)$$

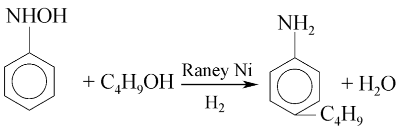


(12)

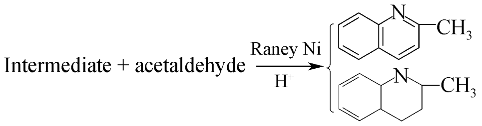


(13)

$$2\ CH_3CH_2OH \xrightarrow{\text{Raney Ni}} CH_3CH_2CH_2CH_2OH \quad (14)$$



(15)



(16)

3 Conclusion

In the present study a novel method for the one pot synthesis of *N*-alkyl arylamines from nitro aromatic compounds and alcohols over a Raney Ni catalyst under the same conditions of temperature and pressure in a single reactor is proposed through the combination of the aqueous-phase reforming of alcohols for hydrogen production, the liquid phase hydrogenation of nitro aromatic compounds into aromatic amines, and the *N*-alky-

Table 4 Experimental results for different starting material

Materials	Results
Aniline, ethanol	Aniline conversion: 99.4%, products: *N*-ethylaniline 82.0%, ring hydrogenated products 14.5%, and N, *N*-diethylaniline 3.2% No *p*-butylaniline and quinoline and its derivatives
Cyclohexylamine, ethanol	Main products: *N*-ethyl cyclohexylamine and *N*, *N*-diethyl cyclohexylamine No quinoline and its derivatives
N-ethylaniline, acetaldehyde	*N*-ethylaniline conversion 27.8%, main products: *N*, *N*-diethylaniline 30.3% and *N*, *N*-diethyl cyclohexylamine 52.1% No p-butylaniline and quinoline and its derivatives
Nitrobenzene, ethanol, and acetic acid 5 mL	Nitrobenzene conversion 100%, aniline conversion 96.9%, main products: *N*-ethylaniline 41.2%, ring hydrogenated products 4.33%, quinoline and its derivatives 28.1%, *N*, *N*-diethylaniline 2.1%, and other side products 23.8%
Ammonia solution 5 mL, ethanol	Main product: triethylaniline

Nitrobenzene, aniline, cyclohexylamine or *N*-ethylaniline 10 mL, and ethanol or acetaldehyde 60 mL were placed into a 200 mL autoclave; reaction conditions: Raney Ni 21.05 g, $T = 413$ K, $P = 1—1.2$ MPa, $t = 8$ h.

lation of aromatic amine. In this process, the active hydrogen generated from the aqueous-phase reforming of alcohols is used *in-situ* for the hydrogenation of nitro aromatic compounds into the corresponding aromatic amine, and then the aromatic amines react with alcohols via the successive occurrence of *N*-alkylation to form *N*-alkyl arylamine at a low partial pressure of hydrogen. This process could be a potential route to increase the conversion rates of nitro aromatic compounds and aromatic amine and the selectivity to *N*-alkyl arylamines. Furthermore, it will simplify the working process, because some special facilities for hydrogen generation, storage and transportation in traditional liquid phase hydrogenation industrial processes are yet not needed. For the one pot synthesis of *N*-ethylaniline in the system of "nitrobenzene + ethanol," both the nitrobenzene and aniline are completely converted (100%), the selectivity to *N*-ethylaniline and *N*, *N*-diethylaniline are 85.9% and 0%—4%, respectively, under the reaction conditions of nitrobenzene : alcohol : water = 10 : 60 : 0, T = 413 K, P = 1 MPa, t = 8 h, in which the selectivity to *N*, *N*-diethylaniline is much lower than that via the traditional method. However, this novel method for the one pot synthesis of *N*-alkyl directly from nitro aromatic compounds and alcohols is a comprehensive combination process of the three reactions; therefore, further optimization of the reaction conditions and catalyst, and analysis of the reaction mechanisms are required.

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