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A green and recyclable ligand-free copper (I) catalysis system for amination of halonitrobenzenes in aqueous ammonia solution



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ABSTRACT

The amination of halonitrobenzenes is an important reaction to produce the corresponding nitroanilines. Direct amination of *p*-chloronitrobenzene (*p*-CNB) to *p*-nitroaniline (*p*-NAN) with aqueous NH₃ solution was investigated over various transition metal salts in the absence of ligand, inorganic base and organic solvent. It was found that CuI is the most effective catalyst with respect to *p*-CNB conversion, *p*-NAN selectivity ($\approx 100\%$) and the post-reaction separation and recycling. A high *p*-NAN yield of 97% could be obtained at 200 °C in 6.5 h with molar ratios of NH₃/*p*-CNB and CuI/*p*-CNB of 21 and 0.1, respectively. A possible reaction mechanism was proposed, in which NH₃ was not only a substrate but also a ligand to coordinate with CuI and formed a watersoluble Cu complex, and then it started the catalytic cycle. The influence of reaction variables such as NH₃ concentration, CuI concentration, temperature and time on the *p*-CNB conversion and the *p*-NAN selectivity water-soluble and so the aqueous phase including the catalyst and NH₃ can be easily separated and reused for the subsequent reaction runs. The green and sustainable system is effective for the conversion of diverse halonitrobenzenes to nitroanilines.

1. Introduction

Aromatic primary amines are important building blocks for the preparation of large variety of organic and inorganic chemicals [1]. Over the last decades, impressive progress has been made in the direct C-N bond formation; more straightforward approach for the amination of aryl halides with amine compounds is the copper- [2-12], palladium-[13,14], and nickel- [15–17] catalyzed coupling reaction. While, by comparison, the direct C-N bond formation between aryl halides and ammonia (NH₃) is an attracting method to produce aromatic primary amines, due to the facts that NH3 is one of the most abundant, less expensive and easy-to-handle nitrogen sources [18,19]. The reaction can be catalyzed effectively by copper [20-23], palladium [24] and nickel [15] catalysts, among which efforts have been given to find and tailor active catalysts using lower-cost copper species. When copper salts or oxides were used as catalysts, ligands such as organonitrogen compounds [22,25-31], diones [20], N²,N²-diisopropyloxalyldihydrazide [32] and oxalyldihydrazide were required to be mixed with

diones [33,34], oxascorbic acid and the salts [35,36] were added in order to promote their catalytic activity. However, some ligands are expensive and difficult to be separated from organic solvents under usual conditions. Recently, some achievements have been obtained for the amination catalyzed by Cu catalysts without ligands; for example, CuI catalyze the amination of aryl halides (-Br and -I) with aqueous NH₃ solution and CuBr, CuI and Cu(acac)₂ the amination of heteroaryl bromides with gaseous NH_3 in the presence of K_3PO_4 in DMF [37,38]. Furthermore, CuI/Fe₂O₃ could catalyze the amination of aryl iodides with NH₃ in the presence of NaOH in ethanol [39], Cu₂O catalyze the amination of bromonaphthyridines with NH₃ in ethylene glycol/glyme without additional inorganic bases [40], and CuI catalyze the amination of aryl halides (-Br and -I) with NH3 in polyethylene glycol with or without additional inorganic bases [23,41]. As reported in the literature, the amination of aryl halides with NH₃ could be catalyzed by Cu salts or its oxides smoothly in the absence of ligands. For these reactions, however, some additives and large amounts of organic solvents were used, which are unpractical for its application (product isolation,

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catalyst recovery). More recently, it was reported that CuO-CeO₂ nanocomposite could catalyze the amination of aryl halides (-Br and -I) with NH₃ aqueous solution in the presence of Cs_2CO_3 ; it is a heterogeneous system but the stability of the CuO-CeO₂ catalysts is not good with a serious decrease in activity during recycling [21]. Thus, for the amination reactions of aryl halides, a challenge still remains open for the researcher to develop an efficient and clean catalytic system.

In this work, we report a new efficient and green protocol for the amination of halonitrobenzenes with aqueous NH₃ solution catalyzed by CuI without additional ligands, inorganic bases, and organic solvent. p-Nitroaniline (p-NAN) is one of the aromatic primary amines and an important synthetic building block in the synthesis of antioxidants, pharmaceuticals, gum inhibitors, poultry medicines, and corrosion inhibitors [1]. p-NAN can be produced via the partial hydrogenation of pdinitrobenzene [42] or the amination of *p*-halonitrobenzene [21,23,25-28,35-37,43-45]. The partial hydrogenation of *p*-dinitrobenzene to p-NAN is difficult to control because p-NAN is easily further hydrogenated to p-phenylenediamine at the later stage of reaction [42]. Relatively, the amination of p-halonitrobenzene to p-NAN is easy to operate. Compared with the amination of p-bromo- and piodo-nitrobenzene with NH₃, the amination of p-CNB is much more difficult. It is reported that *p*-bromonitrobenzene is aminated with NH₃ to p-NAN in H₂O/NMP over Cu₂O at 80 °C, with a p-NAN yield of 86% in 15 h, a lower p-NAN yield of 79% was obtained at 110 °C with microwave irradiation for 15 h in the amination of p-CNB [44]. Herein, the present authors have investigated the effectiveness (activity, selectivity, recyclability) of transition metal halides among others for the amination of p-CNB with NH3 into p-NAN in water in the absence of any ligand, inorganic base and organic solvent. It should be noted that, with the most effective catalyst of CuI, a high *p*-CNB conversion of > 97% and a high *p*-NAN selectivity of > 99% were achieved at 200 °C in 6.5 h. The reaction mixture was examined by UV/Vis spectroscopy and a possible reaction mechanism was proposed. Furthermore, the product is solid and insoluble in water at room temperature and, hence, the aqueous phase including Cu catalyst and NH3 is easily separated and recycled. A green and recyclable Cu-based catalyst system has been developed for the synthesis of p-NAN via the amination of p-CNB in aqueous NH₃ solution. The catalyst system can effectively catalyze the amination of other different functionalized halonitrobenzene substrates as well.

2. Experimental

2.1. Amination reactions

In a typical experiment, p-CNB (1 g, 6.35 mmol), CuI (0.635 mmol), commercial 25% aqueous NH₃ solution (10 mL, NH₃/p-CNB molar ratio 21/1) were loaded into a 50 mL stainless steel reactor and sealed. The material of the autoclave used is AISI 316 L, for which the composition is Cr 16–18%, Ni 10–14%, Mo 2–3%, Mn \leq 2%, Si \leq 1%, C \leq 0.03%, $S \le 0.03\%$, $P \le 0.045\%$, and the other part is Fe. After being heated to 200 °C, the reaction was conducted while stirring with a magnetic stirrer (1200 rpm). The pressure of the vapor phase (NH₃ and H₂O) was about 3 MPa at the reaction temperature. After stirring for 1 h, the reactor was cooled to room temperature and the reaction mixture was separated by centrifugation. The solid substrate and product were dissolved in ethanol and analyzed by a gas chromatograph (Shimadzu GC-2010) equipped with a capillary column (Rtx-5 capillary column: 30 m $\times 0.25 \text{ mm} \times 0.25 \mu \text{m}$, carrier: N₂) and a flame ionization detector (FID) and gas chromatograph-mass spectrometer (GC-MS, Agilent 5890, HP-5). o-Xylene was used as an internal standard for quantitative analysis. The liquid phase was also analyzed by gas chromatograph and no p-CNB or p-NAN were detected. The carbon balance was near 99% and trace amount of other unidentified byproducts were observed.

2.2. Catalyst recycling test

The catalyst, CuI, is soluble in aqueous NH₃ solution and the substrate (*p*-CNB) and product (*p*-NAN) are insoluble solids in the media at room temperature. So, the liquid phase can be separated from the solid materials by centrifugation and then reused for next reaction runs. However, a small volume of aqueous phase (ca. 0.5 mL) was missed by the separation procedures. So, required amounts of fresh 25% NH₃ solution and CuI were added to the separated solution for the loss of these species to prepare the same aqueous solution (10 mL), as used in the first run, containing NH₃ and CuI in the same concentrations; under ordinary conditions, 0.5 mL of 25% NH₃ aqueous solution and 0.032 mmol of CuI were added. Fresh *p*-CNB (1 g) was added into the reactor for the next run.

2.3. Characterization

UV–vis absorption spectra of various liquid reaction mixtures were recorded on a UV–vis spectrometer (PE Lambda 35) under ambient conditions. In a typical measurement, a mixture of 6.35 mmol *p*-CNB, 0.635 mmol CuI and 10 mL aqueous NH_3 solution was kept at a temperature of 200 °C for a certain period of time, cooled to room temperature and centrifuged. The liquid phase was separated and diluted to 500 times with water and then subjected to UV–vis measurement. Electrospray ionization-mass spectrometer (ESI-MS, Acquity UPLC & Quattro Premier XE) was used to examine possible Cu species in the reaction mixture. The solid substrate and product dissolved in ethanol phase and the aqueous ammonia phase were measured respectively.

3. Results and discussion

3.1. Catalyst screening

Transition metal salts were used as catalysts for the amination of *p*-CNB with aqueous NH_3 solution in the absence of ligand and inorganic base. The obtained results are listed in Table 1. Among Cu salts examined (entries 1–9), CuI, CuCl and CuBr₂ showed the best catalytic performance in the conversion of *p*-CNB (> 40%) and selectivity to *p*-NAN (> 98%) (entries 1, 3, 4). Cu(acac)₂ was also active but the

Table 1

Amination of p-CNB to p-NAN over various catalysts.

O ₂ N C1 Catalyst Aqueous NH ₃ solution O ₂ N O ₂ N						
Entry	Catalyst	Conversion of <i>p</i> -CNB (%)	Selectivity to p -NAN (%) ^a			
1	CuI	42.5	99.6			
2	CuBr	37.8	99.3			
3	CuCl	43.0	99.3			
4	CuBr ₂	40.3	98.7			
5	CuCl ₂ ·2H ₂ O	25.3	99.0			
6	$Cu(acac)_2$	41.2	82.8			
7	CuSO ₄ ·5H ₂ O	31.8	99.4			
8	Cu(OAc)2·H2O	25.6	99.2			
9	Cu(NO ₃) ₂ ·3H ₂ O	23.4	99.4			
10	MnCl ₂ ·4H ₂ O	22.5	97.8			
11	FeCl ₃ ·6H ₂ O	43.8	99.7			
12	FeCl ₂ ·4H ₂ O	24.6	93.7			
13	CoCl ₂ ·6H ₂ O	30.2	96.2			
14	NiCl ₂ ·6H ₂ O	18.3	98.6			
15	ZnCl ₂	19.7	99.3			
16 ^b	CuI	31.1	99.0			
17	-	17.5	98.6			

Reaction conditions: p-CNB 1 g (6.35 mmol), 25% aqueous $\rm NH_3$ solution 10 mL, $\rm NH_3$ /p-CNB molar ratio 21/1, catalyst 0.635 mmol, 200 °C, 1 h.

^a Selectivity to *p*-NAN, others are unidentified by-products.

^b CuI 0.318 mmol.

selectivity was not satisfactory (entry 6). The other Cu salts were selective to the target reaction but the conversion levels were not good (entries 2, 5, 7-9). The difference in the performance among the Cu salts is similar as reported in the literature [37,38]. The anions in Cu salts may affect the nucleophilic coordination of Cu salts to the active species, which will be discussed later. Moreover, among the other transition metal salts such as MnCl₂·4H₂O, FeCl₃·6H₂O, FeCl₂·4H₂O, CoCl₂·6H₂O, NiCl₂·6H₂O, and ZnCl₂ (entries 10-15), FeCl₃·6H₂O exhibited the highest conversion of p-CNB (43.8%) and the highest selectivity to p-NAN (99.7%) (entry 11), which were comparable to those obtained with CuI and CuCl (entries 1, 3). The other metal salts were less effective for the reaction and the p-CNB conversion values were lower than 30% (entries 10, 12–15). With decreasing of CuI loading from 10 to 5 mol.%, the conversion of *p*-CNB decreased from 42.5% to 31.1%, while the selectivity to *p*-NAN changed slightly (entries 1, 16). The conversion of *p*-CNB with no catalyst was only 17.5% (entry 17), much lower than that with CuI catalyst, and so CuI had the high catalytic efficiency for the amination of p-CNB to p-NAN. In contrast to these Cu salts, the other metal chlorides of Mn, Fe, Co, Ni, and Zn changed from water-soluble salts to the corresponding insoluble metal oxides during reaction; namely, they are not stable and isolated from the solid organic product. In addition to its better catalytic performance (entry 1), CuI and the formed Cu species were soluble in aqueous ammonia solution during the reaction, easily separable from the organic solid product of p-NAN, and reusable for the recycling runs. Hence, CuI was chosen as a catalyst for the subsequent work to examine the effects of reaction conditions and the reusability of aqueous phase in which Cu catalyst and NH₃ were soluble. Note a conversion of 17.5% was obtained in the absence of catalyst (entry 17), as above-mentioned, and the same conversion was also observed in a Teflon-lined reactor, indicating no reactor wall effect on the reaction.

3.2. Influence of reaction conditions

Using the most active copper catalyst (CuI), some variables were studied. Table 2 shows the influence of temperature over conversion and selectivity values (entries 1–4). Under the conditions used, the conversion increased from 13.3% at 180 °C to 87.6% at 230 °C and the high *p*-NAN selectivity of > 99% remained unchanged at these temperatures. The amount of NH₃ was observed to affect the amination of *p*-CNB (Table 2). When NH₃/*p*-CNB molar ratio was raised from 10.5 to 26.25 (entries 2, 5–7), the *p*-CNB conversion increased from 9.2% to 58.1% and the *p*-NAN selectivity reached to 99.6% at a NH₃/*p*-CNB molar ratio of 21. The present amination reaction took place in a liquid - liquid biphasic mixture including aqueous (NH₃, CuI) and organic (*p*-CNB) phases, in which the catalytic reactions should occur at interfacial layer, as detailed later. With increasing of bulk NH₃ concentration, the NH₃ concentration at the interfacial layer may increase and promote the rate of amination.

The influence of reaction time on the amination of *p*-CNB with aqueous NH_3 solution at a NH_3/p -CNB molar ratio of 21/1 was



Fig. 1. Influence of reaction time on the amination of *p*-CNB. Reaction conditions: *p*-CNB 1 g (6.35 mmol), 25% aqueous NH_3 10 mL, NH_3/p -CNB molar ratio 21/1, CuI 0.635 mmol, 200 °C.



Fig. 2. Plot of $\ln[1/(1-x_t)]$ against reaction time for the data in Fig. 1. x_t is conversion at a reaction time *t*. The four data can be correlated by a straight line going through the origin, y = 0.5600x - 0.0024 with a correlation coefficient, R = 0.99996.

investigated at 200 °C. The results obtained are shown in Figs. 1 and 2. The *p*-CNB conversion increased smoothly with time, the *p*-NAN selectivity was close to 100% at the initial stage of reaction and the high selectivity remained unchanged at higher conversion levels (Fig. 1). Fig. 2 shows that the amination of *p*-CNB follows a pseudo first order reaction kinetics with respect to the concentration of *p*-CNB. The phase behavior of reaction mixture is illustrated in Scheme 1. The CuI catalyst can be soluble in aqueous NH₃ solution but the solid substrate of *p*-CNB is insoluble at room temperature. At reaction temperature of 200 °C, *p*-CNB melts but it is insoluble in aqueous NH₃ solution; so, the reaction occurs at the aqueous - organic *p*-CNB two-phase interface. The pressure of the vapor phase (NH₃, H₂O) was initially ca. 3 MPa and the pressure slightly changed during reaction. The desired product of *p*-NAN is

Table 2		
T (1	<i>c</i>	1 3 77 7

Influence of temperature and NH ₃ /p-CNE	molar ratio on the amination	of <i>p</i> -CNB to <i>p</i> -NAN.
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Entry	T (ºC)	Volume of aqueous $\rm NH_3$ solution (mL)	Total volume of aqueous phase (mL)	NH ₃ /p-CNB molar ratio	Conv. (%)	Sel. (%)
1	180	10	10	21	13.3	100
2	200	10	10	21	42.5	99.6
3	220	10	10	21	75.5	99.7
4	230	10	10	21	87.6	99.4
5	200	5	10	10.5	9.2	98.4
6	200	7.5	10	15.75	27.0	99.0
7	200	12.5	12.5	26.25	58.1	99.5

Reaction conditions: p-CNB 1 g (6.35 mmol), CuI 0.635 mmol, 1 h.



Scheme 1. Reaction, separation, and recycling processes for the amination of *p*-CNB with aqueous NH₃ solution catalyzed by CuI. Condition: *p*-CNB 1 g (6.35 mmol), 25% aqueous NH₃ 10 mL, NH₃/*p*-CNB molar ratio 21/1, CuI 0.635 mmol. R.T.: room temperature.

Fable 3	
Comparison of the catalytic performance for the amination of <i>p</i> -CNB among the present catalytic system with other ones.	

Catalyst	Solvent	Base/Ligand	NH ₃ /p-CNB molar ratio	T (°C)	Time (h)	Yield (%)	Ref.
Cu ₂ O	H ₂ O/NMP	-/-	10	110 ^a	15	79	[44]
CuO	H ₂ O/TBAB	$K_3PO_4/L1$	13	120	24	46	[33]
CuSO ₄ ·5H ₂ O	H ₂ O/DMSO/glycerol	$K_2CO_3/L2$	29.6	100	8	69	[36]
CuI	H ₂ O	-/L3	21.45	100	36	74	[35]
CuI	H ₂ O	-/L4	28.6	120	24	< 5	[27]
CuI	H ₂ O	-/-	21	200	6.5	97	This work

L1: oxalyldihydrazide and hexane-2,5-dione, L2: L-ascorbic acid sodium salt, L3: ascorbic acid, L4: 1,4-bis(2-hydroxy-3,5-di-tert-butylbenzyl) piperazine. ^a Microwave irradiation (110 °C, 150 W).

completely soluble in aqueous NH_3 solution at 200 °C, but, after reaction and cooling, it becomes insoluble and precipitates as a needle-like solid. The Cu active species is soluble in aqueous NH_3 solution. Thus, the reaction occurs at the interfacial layer of the aqueous - organic *p*-CNB liquid-liquid two phases, the volume of organic phase decreases with the conversion (the consumption of *p*-CNB), resulting in the decrease of area of the interfacial layer and thus in the rate of amination, which apparently obeys the first order kinetics (Fig. 2). The present amination is not a homogeneous reaction and so detailed reaction kinetics analysis should be made by considering several variables featuring multiphase reactions.

Fig. 1 shows that the conversion of *p*-CNB reaches 97.2% in 6.5 h, the selectivity to *p*-NAN was > 99.5% at any conversion level, and the yield of *p*-NAN reaches 97%. These results are comparable to the best results in the partial hydrogenation of *p*-dinitrobenzene [42] and the amination of *p*-bromo- and *p*-iodo-nitrobenzene substrates [21,23,25–28,35,37,43], but it is much better than the results in the amination of *p*-CNB in literature (Table 3) [35,36,44,45]. For example, in the amination of *p*-CNB with aqueous NH₃ solution, a yield of 79% of *p*-NAN was obtained over Cu₂O in H₂O/NMP at 110 °C in 15 h under microwave irradiation [44], and a *p*-NAN yield of 69% was observed with CuSO₄·5H₂O catalyst in the presence of L-ascorbic acid sodium salt and K₂CO₃ in a mixed solvent of DMSO and glycerol at 100 °C in 8 h [36],Therefore, the present catalytic system is efficient and green for the amination of *p*-CNB, in which water was used as solvent and any other additives were not required.



Fig. 3. The recycling of CuI in the amination of *p*-CNB. Reaction conditions: *p*-CNB 1 g, 25% aqueous NH₃ 10 ml, NH₃/*p*-CNB molar ratio 21/1, catalyst 10 mol%, 200 $^{\circ}$ C, 4 h.

3.3. Catalyst system recycling test

The desired product of *p*-NAN is completely soluble in aqueous NH_3 solution at a reaction temperature but, after reaction and cooling, it becomes insoluble and precipitates as a needle-like solid (Scheme 1). The Cu active species is soluble in aqueous NH_3 solution. Thus, the aqueous solution including soluble Cu catalyst and NH_3 can be easily separated from solid *p*-NAN via simple centrifugation. Since some



Scheme 2. A possible catalytic cycle for Cu-catalyzed amination of p-CNB with NH_3 in water.

volume (ca. 0.5 mL) of the aqueous solution was missed by the separation, certain amounts of aqueous NH_3 solution and CuI were added to the separated aqueous phase to prepare a 10 mL aqueous solution including the same contents of NH_3 and CuI as used in the first run and this solution was used for next reaction run. The results of so repeated reactions are given in Fig. 3, showing no obvious changes in the conversion of *p*-CNB and in the selectivity to *p*-NAN for 5 runs. Namely, the present aqueous catalyst system is recyclable. Moreover, the addition of 25.4 mmol NH_4Cl (the quadruple of the amount of *p*-CNB) into the system had no effect on the conversion of *p*-CNB (86.6%) and the selectivity to *p*-NAN (99.7%), and the conversion of *p*-CNB and the selectivity to *p*-NAN did not change on the generation and accumulation of NH_4Cl in the recycling experiment, indicating no significant effect of the accumulation of NH_4Cl on the present amination reaction.

3.4. Possible catalytic mechanisms

On the basis of Cu-catalyzed coupling mechanisms as proposed in previous studies [46,47], a possible catalytic cycle for the CuI - catalyzed amination of *p*-CNB with aqueous NH₃ solution without ligand, inorganic base, and organic solvent is proposed in Scheme 2. Initially, CuI is complexed with NH₃·H₂O to form a [Cu(NH₃)₂]OH (complex 1), in which NH₃ can act as a ligand. The neutral [Cu(NH₃)₂]OH complex should be the active Cu species rather than the CuI salt according to the previous results [47,48]. Then, the ligand exchange, oxidative addition, deprotonation, and reductive elimination occurred and the final product of p-NAN was formed. At the end of a catalytic cycle, CuCl is formed and used for the next catalytic cycle. The deprotonation via H₂O is more kinetically likely to occur than that via HCl and so no strong inorganic base is needed for the amination reaction [47]. The differences in the catalytic performance among the Cu salts observed (Table 1) are similar as reported in the literature [37,38], and the different anions in the Cu salts may affect the nucleophilic coordination of Cu salts to the active species (Scheme 2).

To obtain more information about the present amination reaction, UV/Vis spectroscopy was used to examine various liquid mixtures (Fig. 4). CuI was insoluble in H_2O and the substrate of *p*-CNB was insoluble in aqueous NH₃ solution, so no obvious absorbance peaks were seen for samples a–c. The product of *p*-NAN was slightly soluble in aqueous NH₃ (solubility < 0.1%) at room temperature, the absorbance band was apparent at 381 nm for sample d. When aqueous NH₃ solution was added to CuI, it became momentarily soluble and the solution was blue and transparent; the absorbance bands appeared at 225 and 273 nm for sample e, indicating NH₃ acted as a ligand and complexed with CuI easily to form complex 1 (Scheme 2). With the introduction of



Fig. 4. UV–vis spectra of various liquid mixtures. Conditions: (a) 0.635 mmol CuI and 10 mL H_2O was mixed at room temperature (RT) for 0.5 h and the solution was centrifuged. (b) 10 mL NH_3 solution (c, d) 6.35 mmol *p*-CNB or *p*-NAN and 10 mL NH_3 solution were mixed at RT for 0.5 h, followed by centrifugation. (e) 0.635 mmol CuI and 10 mL NH_3 solution was mixed at RT for 0.5 h, (f1) 6.35 mmol, *p*-CNB, 0.635 mmol CuI and 10 mL NH_3 solution were mixed at RT for 0.5 h and the solution was centrifuged, (f2-5) 6.35 mmol *p*-CNB, 0.635 mmol CuI and 10 mL NH_3 solution were mixed at RT for 0.5 h and the solution was kept at 200 °C for 0.5, 2, 4, 6.5 h, respectively, and, after cooling to RT, the solution was centrifuged. All these liquid samples were diluted to 1/500 with H_2O before UV/Vis measurements.

p-CNB into the sample e, the peaks of absorption bands at 225 and 273 nm increased a little for sample f1, suggesting the ligand exchange of *p*-CNB with complex 1 to form complex 2. When the sample f1 was kept at 200 °C for 0.5 h (sample f2), the absorbance band at 225 nm decreased a little; that at 273 nm decreased and shifted to 269 nm, and a new absorption band appeared at 392 nm. The decrease of the absorbance peaks at 225 and 269 nm may be due to the decrease of amount of *p*-CNB by the amination reaction. The new absorption band located at 392 nm may be assignable to the complex 3 and/or 4. With extending reaction time to 4 h (samples f2 - f4), the intensity of the three peaks increased, but decreased with the further extending reaction time to 6.5 h (sample f5), The absorption bands at 225, 269, and 392 nm may also be assigned to the complex 3 and/or 4; when the reaction time was extended to 6.5 h, almost all p-CNB was transformed to p-NAN, the amount of complex 3 and/or 4 decreased (the intensity of the absorption bands at 225, 269, and 392 nm decreased). Complexes 3 and 4 were confirmed to exist during the reaction as their derivatives dissociated a Cl ion were detected from EMI-MS measurement (Fig. 5).

3.5. Amination of various halonitrobenzenes

The applicability of the most effective catalyst, CuI, and aqueous NH3 solution was further examined with various halonitrobenzene substrates. Table 4 summarizes the results of their amination reaction obtained. Similar to p-CNB (entry 1), excellent conversion and selectivity were observed for o-CNB (entry 2) but the results were not so good for m-CNB (entry 3), showing the steric hindrance of the substituent position, and the same phenomenon was also reported in the literature [35]. The catalyst system was also effective for p-bromo- and p-iodo-nitrobenzenes, and the activities of both substrates were higher than that of p-CNB (entries 3, 4). It has been reported that the reactivity follows the order of iodo- > bromo- > chloro-nitrobenzene in the amination of halonitrobenzenes [21,36,37,44], which may be due to the difference in the atomic radius I > Br > Cl and the easier elimination of C-X (X: I, Br, or Cl) with the bigger atomic radius of X. For p-CNB compounds bearing -NH₂, -COOH and -CN groups at o-position to -Cl, satisfactory results were obtained (entries 6-8). However, the total conversion and the selectivity to the desired corresponding amine compounds were low for p-CNB with -CH₃ (entry 9) and -OCH₃ (entry 10), respectively. The amination reactivity of C-Cl could be increased by the electron-withdrawing groups but decreased by the electron-



Fig. 5. ESI-MS of the aqueous NH₃ phase of the mixture of amination of *p*-CNB. Reaction conditions: *p*-CNB 1 g (6.35 mmol), 25% aqueous NH₃ solution 10 mL, NH₃/*p*-CNB molar ratio 21/1, catalyst 0.635 mmol, 200 °C, 2 h.

 Table 4

 Amination of halonitrobenzenes to corresponding amines over CuI.

Entry	Substrate	Product	Conv. (%)	Sel. (%)
1	CI CI	NH2	97.2	99.6
2	O ₂ N CI	O ₂ N NH ₂	53.0	86.0
3	CI	NH ₂	100	96.9
4		NH2 NH2	100	96.7
5	O ₂ N Br	NH2	100	99.6
6		NH2	100	95.3
7	O ₂ N ^P VH ₂	O ₂ N ⁻ VH ₂	100	92.1
8	O₂N [™] COOH	O ₂ N ⁻ COOH	100	83.8
9		O ₂ N ⁻ CN	24.1	86.7
10	O ₂ N ⁻ CH ₃	O ₂ N ⁻ CH ₃	100	67.8
11 ^a	O ₂ N OCH ₃	O ₂ N OCH ₃	100	87.2
12	O ₂ N CI		100	72.3
	O ₂ N CI	O ₂ N CI		

Reaction conditions: Substrate, 6.35 mmol, 25% aqueous NH $_3$ 10 mL, NH $_3/$ substrate molar ratio 21/1, CuI 0.635 mmol, 200 °C, 6.5 h. ^a 3 h.

donating groups. It has been reported that the electron-withdrawing groups such as ketone, cyano, nitro, carboxylic ester, acetamino and hydroxy increase the amination activity of iodobenzene [25], but the electron-donating groups of -CH₃ and -OCH₃ has an opposite, negative effect in the amination of iodo- and bromo-benzenes [25,35]. For some reactant, the selectivity to the target amination product was not so high due to the formation of condensation products (entries 2, 8-10). For the amination of a dichoronitro-compound of 3,4-dichoronitrobenzene, p-Cl was first aminated, in which the selectivity to 2-choro-4-nitroaniline was 87.2%. Then, *m*-Cl was further aminated or dechlorinated with the extending reaction time, decreasing the selectivity of 2-choro-4-nitroaniline to 72.3% (entries 11, 12). The amination reactivity of 3,4dichoronitrobenzene was much higher than that of *p*-CNB due to the electro-withdrawing effect of *m*-Cl group (entries 1, 11). It is noted that the present catalytic system is also effective for the amination of other halogenated benzenes such as chlorobenzene, 1-bromo-4-ethylbenzene, and iodobenzene (Table S1).

4. Conclusions

A green direct synthesis of p-NAN from p-CNB can be achieved with an aqueous NH₃ and a Cu (I) catalyst in the absence of any ligand, inorganic base and organic solvent. The most effective catalyst, Cul, gave a p-CNB conversion of 97.2% and a p-NAN selectivity of 99.6% at 200 °C in 6.5 h under conditions that NH₃/p-CNB and CuI/p-CNB molar ratios were 21 and 0.1, respectively. For the amination of p-CNB, the yield to p-NAN (97%) with this catalytic system is much better than those with state-of-the-art catalytic systems (Cu₂O-H₂O/NMP, yield: 79%; CuI-H₂O-ascorbic acid, yield: 74%). In the present reaction, NH₃ is not only a substrate but also a ligand to coordinate with CuI and forms a water-soluble Cu complex that starts the catalytic cycle from p-CNB to p-NAN. At room temperature the Cu catalyst is soluble in water but the desired product of p-NAN obtained is insoluble; therefore, the aqueous phase including Cu catalyst and NH₃ can be easily separated from the solid product and then recyclable for the subsequent reaction runs. This efficient, green and recyclable catalytic reaction system can effectively catalyze the amination of other different functionalized halonitrobenzenes to the corresponding nitroanilines as well, and will attract much attention of researchers in the fields of industrial catalysis and chemical engineering.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.mcat.2019.110462.

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