

CuCl₂ and PdCl₂ catalysts for oxidative carbonylation of aniline with methanol

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Abstract

Synthesis of methyl-*N*-phenyl carbamate from the oxidative carbonylation of aniline with methanol has been studied over CuCl₂-NaI, PdCl₂-NaI, PdCl₂-CuCl₂-NaI, and PdCl₂-CuCl₂-HCl in an autoclave at 373/438 K and 0.13/3.79 MPa. Carbamate yields decreased in the order: CuCl₂-NaI > PdCl₂-NaI > PdCl₂-CuCl₂-NaI > PdCl₂-CuCl₂-HCl at 438 K and 3.79 MPa. Product distribution profiles showed that carbamate yield increased with reaction time and leveled off at 43.5% over CuCl₂-NaI after 1 h of batch reaction at 438 K and 3.79 MPa. The low cost and high activity of CuCl₂-NaI could provide a novel and cost-effective process for carbamate synthesis.

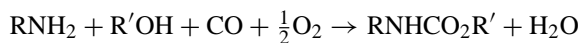
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Keywords: Oxidative carbonylation; Aniline; CuCl₂-NaI; Carbamate synthesis; Methyl-*N*-phenyl carbamate

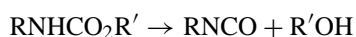
1. Introduction

Oxidative carbonylation of aniline with methanol produces carbamate in the presence of noble metal catalysts [1–12]. The reaction provides an environmentally benign pathway for the synthesis of isocyanate via the thermal decomposition of carbamate [2–12].

Oxidative carbonylation at 443–453 K:



Thermal decomposition of carbamate to isocyanate at 493–513 K:



where R and R' are either alkyl or phenyl group.

Since the thermal decomposition of carbamate to isocyanate is a highly selective and facile step, most research has been focused on the development of effective catalysts for oxidative carbonylation. Table 1 compares various catalysts for oxidative carbonylation of aniline with methanol/ethanol. Rh/C-LiI gave a 96.7% carbamate yield at 443–453 K and 4.8 MPa for 2 h [8]; PdCl₂-CuCl₂-HCl gave a 99% carbamate yield at 298 K and 0.1 MPa for overnight [6]. The major drawback of these catalytic processes is the use of expensive noble metal catalysts. To further improve the economic feasibility of the carbamate synthesis process, there is a need to develop a low-cost catalyst for the reaction at mild conditions.

Pd/C and PdCl₂-CuCl₂ catalysts exhibited activities for not only oxidative carbonylation but also CO oxidation [13–15]. It has been shown that PdCl₂-CuCl₂ and CuCl₂ are highly active for CO oxidation at 300 K in the presence of H₂O [13,16]. The unique oxidation activity of PdCl₂-CuCl₂ catalyst has long been

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Table 1
Catalysts for oxidative carbonylation of aniline

| Catalyst | Reaction conditions | | | Yield (%) | Reference | |
|---|---|-----------------|----------------|-----------|-----------|-----------|
| | Reactants ratio | Temperature (K) | Pressure (MPa) | | | Time (h) |
| PdCl ₂ -CuCl ₂ -HCl | Methanol/aniline = 148; PdCl ₂ , 1.0 mmol; CuCl ₂ , 2.0 mmol; HCl, 0.1 ml | 298 | 0.1 | Overnight | 99 | [6] |
| Pd/C-NaI | Ethanol/aniline = 27.7; CO/O ₂ = 8.6; Pd, 1.5 mg; NaI, 45 mg | 443–453 | 6.7 | 2 | 91.0 | [7] |
| Rh/C-LiI | Ethanol/aniline = 29.7; CO/O ₂ = 14; catalyst, 0.04 g; LiI, 0.873 mg | 443 | 4.8 | 2 | 96.7 | [8] |
| Pd/ZSM-5-NaI | Methanol/methylamine = 2468; CO/O ₂ = 13; Pd catalyst concentration, 2.35 μmol/ml; NaI concentration, 2.30 μmol/ml | 443 | 6.2 | 6 | 47.0 | |
| PdCl ₂ (PPh ₃) ₂ -NaI | | | | 6 | 69.8 | [9] |
| PdI ₂ | | | | 2 | 69.5 | |
| PVP-PdCl ₂ | Ethanol/aniline = 257; CO/O ₂ = 10; Pd catalyst 0.04 mmol; base (NaOAc), 2 mmol; NaI/Pd = 1 | 338 | 0.1 | 20 | 42.3 | |
| PVP-PdCl ₂ -2MnCl ₂ | | | | | 83.3 | [10] |
| PdCl ₂ -2MnCl ₂ | | | | | 50.0 | |
| SeO ₂ -Rb ₂ CO ₃ | Methanol/aniline = 61.7; CO/O ₂ = 4; toluene as solvent | 393 | 6.8 | 2 | 75.5 | [11] |
| Pd black-NaI | Ethanol/aniline = 17.13; CO/O ₂ = 13.3; catalyst, 0.5 mg; basic substance, 1 mmol; NaI or CsI, 5 mmol; I ₂ , 1 mmol | 433 | 8.4 | 1 | 62 | |
| Ru black-CsI | | | | | 44 | [12] |
| IrCl ₃ -I ₂ | | | | | 33 | |
| CuCl ₂ -NaI | Methanol/aniline = 13.5; CO/O ₂ = 10; catalysts, 2 mmol; NaI, 1 mmol | 438 | 3.79 | 1 | 43.5 | This work |

manifested in the commercial Wacker process for oxidation of ethylene to acetaldehyde at 300 K [17,18]. The fact that CuCl₂ alone is active for the oxidation of CO to CO₂ reflects its capability of activating CO and O₂ under mild conditions. This interesting property of CuCl₂ has led us to investigate its catalytic activity for the oxidative carbonylation of aniline with methanol.

The objectives of this study are to determine the activity/selectivity of CuCl₂-NaI for the oxidative carbonylation of aniline with methanol and to compare its activity/selectivity with those of PdCl₂-NaI, PdCl₂-CuCl₂-NaI, and PdCl₂-CuCl₂-HCl

at 373/438 K and 0.13/3.79 MPa. Product distribution was determined as a function of time to unravel the kinetic behavior of the product formation. NaI was selected as a promoter because of its effectiveness in promoting carbamate formation on the Pd/C and Pd(PPh₃)₂ catalysts [7,9]. The carbamate yield was found to decrease in the order: CuCl₂-NaI > PdCl₂-NaI > PdCl₂-CuCl₂-NaI > PdCl₂-CuCl₂-HCl at 438 K and 3.79 MPa. The low cost and high activity of CuCl₂-NaI may provide a cost-effective and environmentally benign route for the synthesis of isocyanate via carbamate [19].

2. Experimental

2.1. Materials

Palladium(II) chloride, copper(II) chloride, and sodium iodide were purchased from Sigma Chemicals Co. Methanol (HPLC grade), aniline (Certified ACS), and hydrochloric acid (Certified ACS Plus) were purchased from Fisher Scientific. All compounds were used without further treatment. Oxygen (4.3 ultra high purity grade) and carbon monoxide (99.0%) were obtained from Praxair.

2.2. Oxidative carbonylation

The batch oxidative carbonylation reaction was carried out in a 500-cm³ autoclave with a glass liner (Pressure Products Industries Inc.). The liquid reactant/catalyst mixture consisted of 2.96 mol methanol, 0.22 mol aniline, 2.0 mmol CuCl₂·2H₂O and/or 1.0 mmol PdCl₂, and 1.0 mmol NaI (the molar ratio of methanol:aniline: CuCl₂/NaI = 1483/110/1/0.5). This specific reaction mixture was prepared by mixing 120 cm³ methanol and 20 cm³ aniline with 0.34 g CuCl₂·2H₂O and/or 0.18 g PdCl₂. The high molar ratio of methanol to aniline is used because methanol serves as not only a reactant but also an excellent solvent for the reaction [8,20–22]. The autoclave was first charged with the reactants and catalyst mixture and then the headspace above the reactant/catalyst mixture was purged with O₂. The reaction was initiated by pressurizing the reactor with CO and O₂ (CO/O₂ (molar ratio) = 10/1) to the specified reaction pressure and increasing the temperature to 373 or 438 K. The low O₂ concentration was used to limit the total oxidation of methanol/reaction products and to move the reactant composition away from the explosion limit. The starting time (i.e. $t = 0$) as shown in Figs. 1–5 is the time when CO and O₂ were introduced into the reactor. It typically takes less than 20 min to bring the reaction condition to the desired temperature and pressure.

Two cubic centimeters of the reactant/product/catalyst mixture was sampled periodically during the reaction. The samples were analyzed by a Hewlett-Packard 5890A gas chromatograph (GC) equipped with a 6' × 1/8", 12% SE-30 packed column (Supelco Inc.) and a Nicolet Magna 550 Series II in-

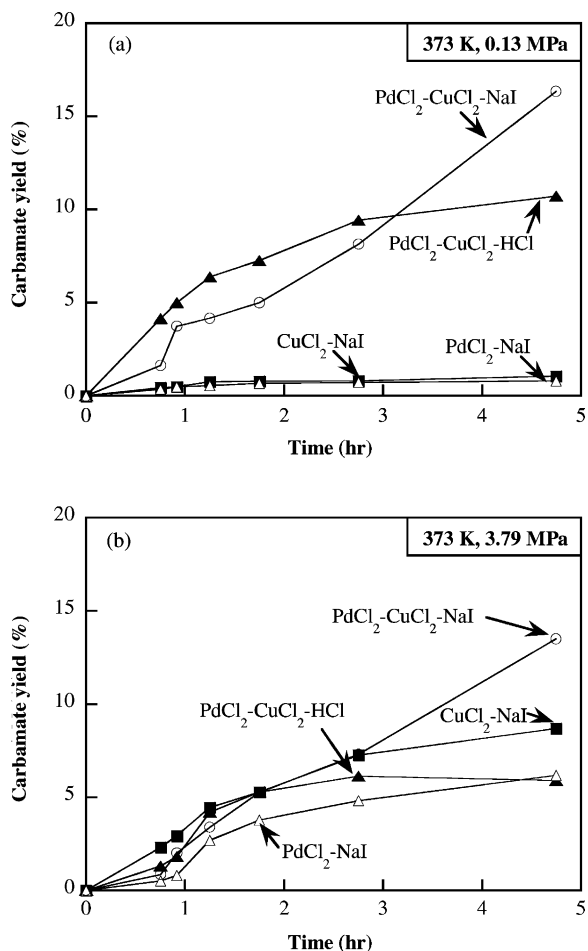


Fig. 1. Carbamate yield vs. reaction time over four catalysts at 373 K: (a) 0.13 MPa and (b) 3.79 MPa.

frared (IR) spectrometer equipped with a deuterated tri-glycine sulfate (DTGS) detector. The GC response factor for the specific species was determined from the slope of a calibration curve, which is a plot of the peak area versus the number of moles of reagent injected into the GC. GC analysis allows accurate quantification of the number of moles of reactants and products in the samples. The aniline conversion is defined as the ratio of the moles of aniline consumed to the initial moles of aniline. The product yield is defined as the ratio of the moles of the specific product to the initial moles of aniline.

The transmission IR spectra of the samples were collected with an IR cell composed of two CaF₂

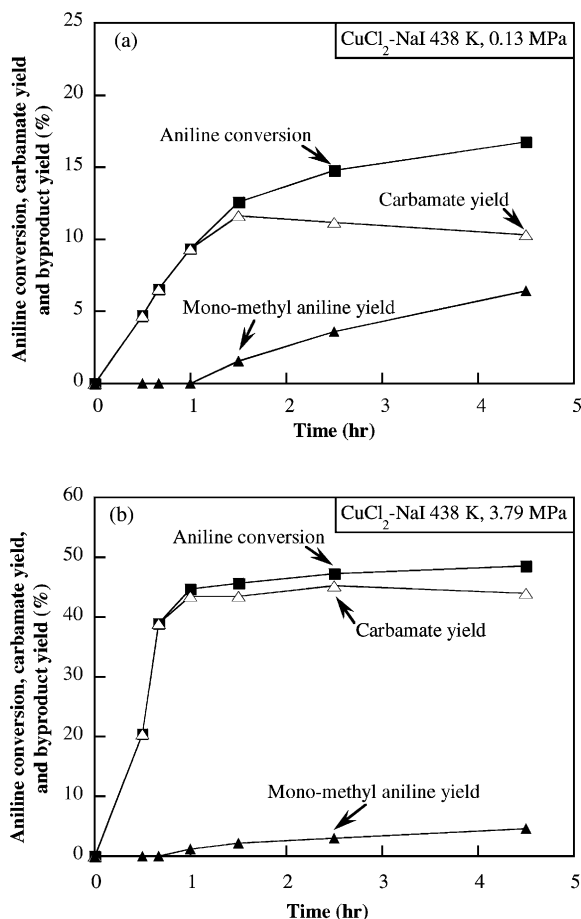


Fig. 2. Aniline conversion, carbamate yield, and byproduct yields (%) vs. reaction time over CuCl₂-NaI at 438 K: (a) 0.13 MPa and (b) 3.79 MPa.

windows. IR analysis showed that the product mixture gave characteristic bands of carbamate at 1717–1737 and 1540 cm⁻¹. The former is due to the C=O stretching vibration and the latter is due to the N–H bending vibration in carbamate, respectively. The final reactant/product mixture was also analyzed by a Gemini 300 ¹³C nuclear magnetic resonance (NMR) spectrometer using CDCl₃ as a solvent. The ¹³C NMR spectrum of the product sample gave a carbamate's C=O peak at 154.5 ppm. Both IR and NMR results confirm the formation of methyl-*N*-phenyl carbamate over the four catalysts (i.e. CuCl₂-NaI, PdCl₂-NaI, PdCl₂-CuCl₂-NaI, and PdCl₂-CuCl₂-HCl).

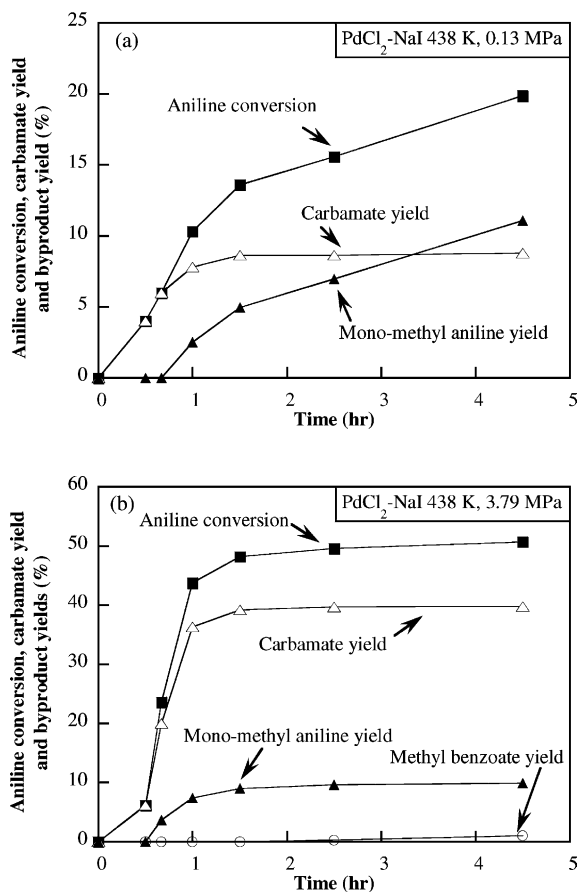


Fig. 3. Aniline conversion, carbamate yield, and byproduct yields (%) vs. reaction time over PdCl₂-NaI at 438 K: (a) 0.13 MPa and (b) 3.79 MPa.

3. Results and discussion

Fig. 1(a) and (b) show the yield profiles of methyl-*N*-phenyl carbamate over CuCl₂-NaI, PdCl₂-NaI, PdCl₂-CuCl₂-NaI, and PdCl₂-CuCl₂-HCl at 373 K and 0.13/3.79 MPa, respectively. The carbamate yields increased with reaction time. Carbamate and CO₂ were the only products produced at 373 K and 0.13 MPa. The activity of the catalysts for carbamate synthesis decreased in the order: PdCl₂-CuCl₂-NaI > PdCl₂-CuCl₂-HCl > CuCl₂-NaI > PdCl₂-NaI. Increasing reaction pressure from 0.13 to 3.79 MPa over CuCl₂-NaI and PdCl₂-NaI catalysts led to a significant increase in the formation rate of carbamate with 100% selectivity. Surprisingly, reaction

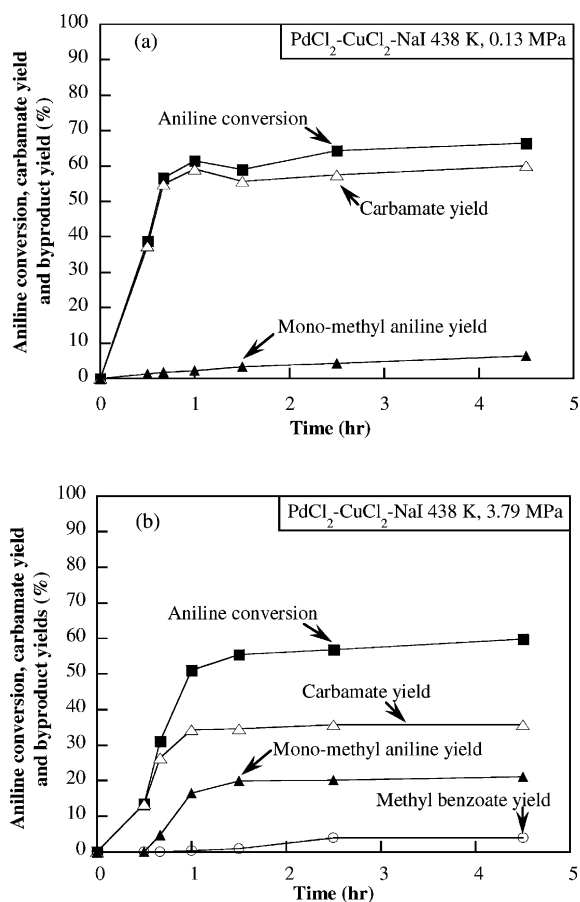


Fig. 4. Aniline conversion, carbamate yield, and byproduct yields (%) vs. reaction time over PdCl₂-CuCl₂-NaI at 438 K: (a) 0.13 MPa and (b) 3.79 MPa.

pressure had little effect on the carbamate formation rate over PdCl₂-CuCl₂-NaI and PdCl₂-CuCl₂-HCl catalysts. Increasing reaction pressure caused the formation of a minor byproduct, monomethylaniline, over PdCl₂-CuCl₂-HCl (Table 3). The control experiment, which used methyl-*N*-phenyl carbamate as a starting reactant, showed that monomethylaniline was not a product resulting from the reaction of methyl-*N*-phenyl carbamate with other reagents under reaction conditions. It has been reported that monomethylaniline can be produced from the reaction of aniline with methanol in the presence of a Lewis acid [23,24]. Monomethylaniline may be a direct byproduct of the oxidative carbonylation of aniline with methanol.

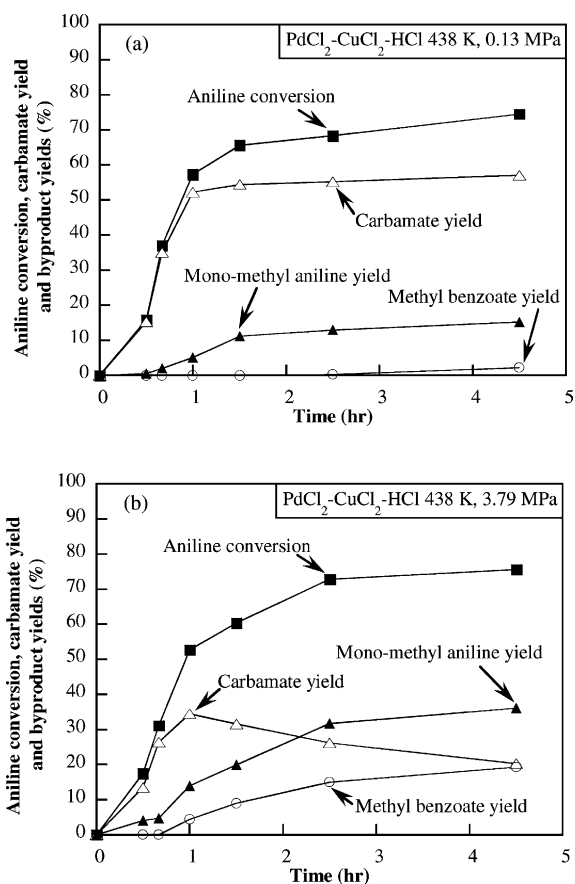


Fig. 5. Aniline conversion, carbamate yield, and byproduct yields (%) vs. reaction time over PdCl₂-CuCl₂-HCl at 438 K: (a) 0.13 MPa and (b) 3.79 MPa.

Fig. 2(a) and (b) show the profiles of aniline conversion, carbamate yield, and monomethylaniline yield over CuCl₂-NaI at 438 K and 0.13/3.79 MPa, respectively. At 438 K and 0.13 MPa, carbamate yield increased with reaction time and leveled off at 1 h at which the formation of monomethylaniline began. The plateau in the carbamate yield is due to the depletion of O₂, a limiting reactant. Increasing reaction pressure from 0.13 to 3.79 MPa increased the carbamate yield and its formation rate. To our knowledge, this is the first report on the activity of CuCl₂-NaI for the synthesis of methyl-*N*-phenyl carbamate from the oxidative carbonylation of aniline with methanol.

Fig. 3(a) and (b) show that PdCl₂-NaI exhibits the similar product formation profile as CuCl₂-NaI in

Table 2

Carbamate yield, aniline conversion and byproduct yields of final solution over four catalysts at 0.13 MPa

| T (K) | Catalyst | Aniline conversion (%) | Carbamate yield (%) | Monomethylaniline yield (%) | Methyl benzoate yield (%) | TOF ^a (h ⁻¹) |
|-------|---|------------------------|---------------------|-----------------------------|---------------------------|-------------------------------------|
| 373 | PdCl ₂ -CuCl ₂ -HCl | 10.7 | 10.7 | 0 | 0 | 4.0 |
| | PdCl ₂ -CuCl ₂ -NaI | 16.3 | 16.3 | 0 | 0 | 3.0 |
| | PdCl ₂ -NaI | 0.8 | 0.8 | 0 | 0 | 1.2 |
| | CuCl ₂ -NaI | 1.1 | 1.1 | 0 | 0 | 0.7 |
| | PdCl ₂ | 0 | 0 | 0 | 0 | – |
| 438 | PdCl ₂ -CuCl ₂ -HCl | 74.4 | 57.0 | 15.2 | 2.2 | 42.0 |
| | PdCl ₂ -CuCl ₂ -NaI | 66.4 | 60.1 | 6.4 | 0 | 45.1 |
| | PdCl ₂ -NaI | 19.9 | 8.8 | 11.1 | 0 | 22.7 |
| | CuCl ₂ -NaI | 16.8 | 10.3 | 6.4 | 0 | 10.3 |
| | PdCl ₂ | 0 | 0 | 0 | 0 | – |

Conditions: aniline (0.22 mol); methanol (2.96 mol); CuCl₂·2H₂O (2.0 mmol) and/or PdCl₂ (1.0 mmol); NaI (1.0 mmol) or HCl (0.1 ml); CO:O₂ (10:1); reaction time (4 h).

^a Initial TOF for aniline conversion (the number of aniline molecule reacted per hour per metal atom) determined from the slope of the aniline conversion at $t = 0$ as shown in Figs. 1–5.

Fig. 2(a) and (b). Comparison of the slope of aniline conversion and carbamate yield curves shows that the rate of carbamate formation over PdCl₂-NaI is higher than that over CuCl₂-NaI. Fig. 4(a) and (b) show the profiles of aniline conversion, carbamate yield, and byproduct (i.e. monomethylaniline and methyl benzoate) yields over PdCl₂-CuCl₂-NaI at 438 K and 0.13/3.79 MPa, respectively. Carbamate yield leveled off at 60% within 1 h of the reaction at 0.13 MPa and 438 K. Increasing the reaction pressure from 0.13 to 3.79 MPa caused a decrease in carbamate yield and an increase in the formation of byproducts. Similar prod-

uct yield profiles were observed for PdCl₂-CuCl₂-HCl in Fig. 5(a) and (b).

Tables 2 and 3 summarize the aniline conversion as well as monomethylaniline, methyl benzoate, and carbamate yields after 4.5 h of the batch reaction. Both tables present the initial TOF for aniline conversion which is determined from the slope of the aniline conversion curve at $t = 0$ as shown in Figs. 1–5. TOF decreased in the order: PdCl₂-CuCl₂-NaI > PdCl₂-CuCl₂-HCl > PdCl₂-NaI > CuCl₂-NaI at 438 K and 0.13 MPa; and PdCl₂-NaI > CuCl₂-NaI > PdCl₂-CuCl₂-HCl > PdCl₂-CuCl₂-NaI at 438 K

Table 3

Carbamate yield, aniline conversion, and byproduct yields of final solution over four catalysts at 3.79 MPa

| T (K) | Catalyst | Aniline conversion (%) | Carbamate yield (%) | Monomethylaniline yield (%) | Methyl benzoate yield (%) | TOF ^a (h ⁻¹) |
|-------|---|------------------------|---------------------|-----------------------------|---------------------------|-------------------------------------|
| 373 | PdCl ₂ -CuCl ₂ -HCl | 7.6 | 5.9 | 1.7 | 0 | 4.2 |
| | PdCl ₂ -CuCl ₂ -NaI | 13.5 | 13.5 | 0 | 0 | 3.4 |
| | PdCl ₂ -NaI | 6.2 | 6.2 | 0 | 0 | 4.8 |
| | CuCl ₂ -NaI | 8.7 | 8.7 | 0 | 0 | 3.9 |
| | PdCl ₂ | 0 | 0 | 0 | 0 | – |
| 438 | PdCl ₂ -CuCl ₂ -HCl | 75.6 | 20.3 | 36.1 | 19.2 | 38.6 |
| | PdCl ₂ -CuCl ₂ -NaI | 59.8 | 35.7 | 20.2 | 4.0 | 37.5 |
| | PdCl ₂ -NaI | 50.7 | 39.8 | 9.9 | 1.1 | 96.3 |
| | CuCl ₂ -NaI | 48.6 | 44.0 | 4.6 | 0 | 49.1 |
| | PdCl ₂ | 0 | 0 | 0 | 0 | – |

Conditions: aniline (0.22 mol); methanol (2.96 mol); CuCl₂·2H₂O (2.0 mmol) and/or PdCl₂ (1.0 mmol); NaI (1.0 mmol) or HCl (0.1 ml); CO:O₂ (10:1); reaction time (4 h).

^a Initial TOF for aniline conversion (the number of aniline molecules reacted per hour per metal atom) determined from the slope of the aniline conversion at $t = 0$ as shown in Figs. 1–5.

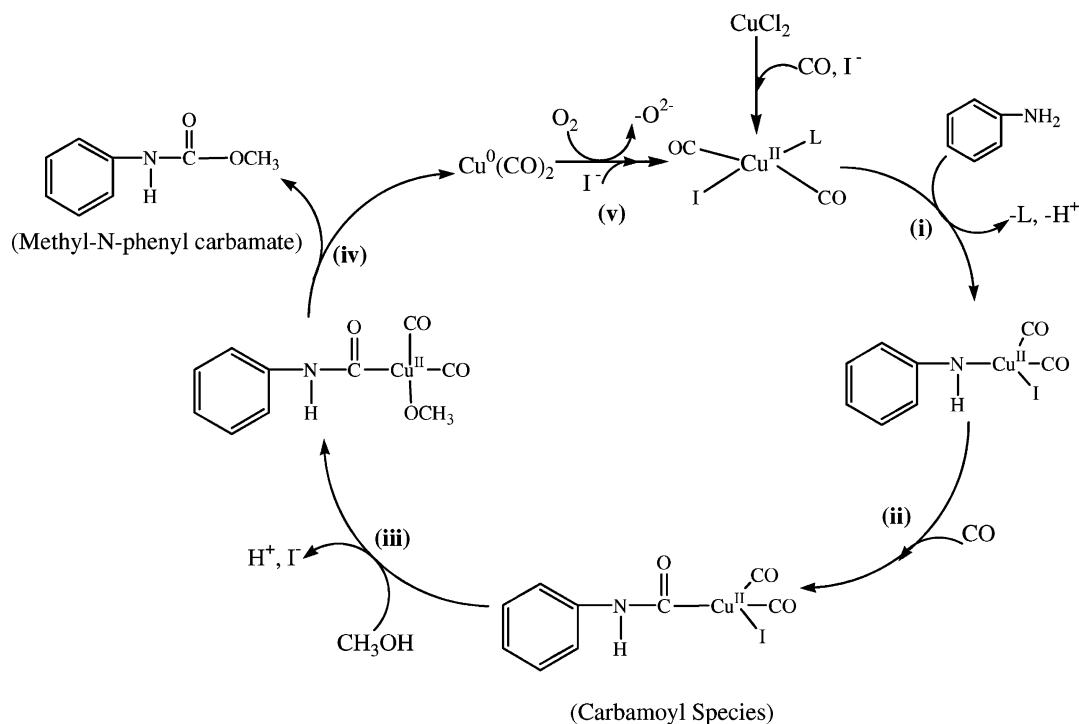


Fig. 6. Proposed reaction scheme for the synthesis of the carbamate from the oxidative carbonylation of aniline with methanol over $\text{CuCl}_2\text{-NaI}$.

and 3.79 MPa. The single metal ($\text{PdCl}_2\text{-NaI}$ and $\text{CuCl}_2\text{-NaI}$) and bimetallic ($\text{PdCl}_2\text{-CuCl}_2\text{-NaI/-HCl}$) catalysts differ significantly in their dependence of TOF on reaction pressure. Increasing reaction pressure resulted in an increase in carbamate yield over $\text{CuCl}_2\text{-NaI}$ and $\text{PdCl}_2\text{-NaI}$, but a decrease in carbamate yield over $\text{PdCl}_2\text{-CuCl}_2\text{-NaI/-HCl}$ catalysts. The latter is due to the formation of byproducts including monomethylaniline and methyl benzoate.

The difference in pressure dependence of the oxidative carbonylation activity suggests that the reaction mechanism on $\text{CuCl}_2\text{-NaI}$ and $\text{PdCl}_2\text{-NaI}$ is significantly different from the Wacker type catalysts (i.e. $\text{PdCl}_2\text{-CuCl}_2\text{-HCl/-NaI}$), which involve two Pd/Cu redox cycles [6,25]. Fig. 6 shows the proposed reaction scheme for the synthesis of carbamate from the oxidative carbonylation of aniline with methanol over $\text{CuCl}_2\text{-NaI}$. The starting point of the proposed catalytic cycle is a CO-coordinated Cu species, $\text{Cu}^{\text{II}}(\text{CO})_2\text{IL}$, where L may be CO, I^- or Cl^- . NaI is an effective promoter which may play a key role

in activation of Cu to form an active catalyst [7,25]. The proposed catalytic cycle involves: (i) coordination of aniline with Cu complex through the N atom via a dehydrogenation reaction, (ii) CO insertion, (iii) coordination of methoxy species on carbamoyl complex, (iv) reductive elimination to produce carbamate, and (v) regeneration of catalyst. The proposed catalytic cycle suggests that oxygen plays a role in the regeneration of Cu^{II} via oxidation of $\text{Cu}^0(\text{CO})_2$. The presence of $\text{Cu}^0(\text{CO})_2$ species is supported by an IR band at 2045 cm^{-1} observed in an infrared study of the interaction between CO and $\text{CuCl}_2\text{-NaI}$ [26]. The species has also been observed in CO adsorption studies over Cu/SiO_2 [27]. Oxygen may also participate in oxidative dehydrogenation of aniline to produce coordinated aniline species and oxidative dehydrogenation of methanol to produce a methoxy to coordinate with carbamoyl species. The specific role of oxygen in the reaction sequence still requires further verification.

The observed difference in the activity and selectivity of these four catalysts may be explained by their

abilities to catalyze the individual reaction steps: dehydrogenation, CO insertion reactions, and oxidation. The high TOF of PdCl₂-NaI may be related to its high activity for catalyzing CO insertion. It has long been known that Pd is more active in catalyzing CO insertion than Cu. The high CO insertion activity of Pd has been manifested by its high hydroformylation and carbonylation rates [28]. While Cu is less active in catalyzing CO insertion than Pd, Cu is known to be highly active for the dehydrogenation of methanol to produce a methoxy complex [29,30]. This methoxy complex formation activity may play a significant role in providing a high carbamate yield over CuCl₂-NaI at 438 K and 3.79 MPa. The five-fold increase in TOF for carbamate synthesis from 0.13 to 3.79 MPa over CuCl₂-NaI suggests that high CO pressure is necessary to increase the CO insertion rate to provide a high concentration of carbamoyl species, which may then further react with methoxy complex to give a high carbamate yield. Acceleration of the CO insertion rate at high CO partial pressure has also been observed in hydroformylation over Rh catalysts [31].

The significant high activity of PdCl₂-CuCl₂-HCl/-NaI at 0.13 MPa may be explained by the high Pd activity in catalyzing CO insertion (i.e. step (ii)) coupled with high Cu activity in catalyzing the methoxy-Cu complex formation (i.e. step (iii)). The presence of both Pd and Cu components may allow a synergistic acceleration of the rate of both CO insertion and methanol dehydrogenation, thus enhancing the carbamate formation (i.e. step (iv)). This synergistic effect appears to be suppressed at high reaction pressure where the reaction selectivity shifted from carbamate toward monomethylaniline and methyl benzoate.

4. Conclusion

Methyl-*N*-phenyl carbamate syntheses from oxidative carbonylation of aniline and methanol over CuCl₂-NaI, PdCl₂-NaI, PdCl₂-CuCl₂-NaI, and PdCl₂-CuCl₂-HCl were carried out at 373/438 K and 0.13/3.79 MPa. Carbamate yields decrease in the order: PdCl₂-CuCl₂-NaI > PdCl₂-CuCl₂-HCl > CuCl₂-NaI > PdCl₂-NaI at 438 K and 0.13 MPa; CuCl₂-NaI > PdCl₂-NaI > PdCl₂-CuCl₂-NaI > PdCl₂-CuCl₂-HCl at 438 K and 3.79 MPa. The low cost and high activity of CuCl₂-NaI may provide a

cost-effective and environmentally benign route for the carbamate synthesis.

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