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Short communication

Developing effective catalyst system for reductive carbonylation of nitrobenzene based on the diversity of ionic liquids

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Abstract

Based on the diversity of ionic liquids, i.e. tunable structure and physicochemical properties, a series of functional ionic liquids and palladium complexes were investigated, and a highly effective catalyst system, Pd(phen)Cl_2-BAcImPF_6 ionic liquid (phen = 1,10-phenanthroline; BAcIm = 1-butyl-3-acetic acid-imidazolium), was developed for the reductive carbonylation of nitrobenzene to give the corresponding carbamate with higher than 90% of conversion and selectivity at 150 °C and 6 MPa carbon monoxide. The high catalytic performance is attributed to the acidic function of the BAcImPF_6 ionic liquid and the interaction between Pd(phen)Cl_2 and the ionic liquid to form the catalytically active palladium complex $Pd(phen)_2(PF_6)_2$.

Keywords: Nitrobenzene; Carbon monoxide; Carbonylation; Ionic liquids; Palladium complex

1. Introduction

In the last 20 years, there have been numerous attempts to produce carbamates, which could be intermediates for producing isocyanates through non-phosgene methods [1–8]. One of the most convenient approaches has been the catalytically reductive carbonylation of nitro compounds with carbon monoxide in the presence of alcohol using group VIII transition metals or their compounds as catalysts [2–4,6]. Till today, palladium complexes have been regarded as the most effective catalysts. Large amounts of liquid acid co-catalysts, such as HCl and H_3PO_4, etc., which volatility and toxicity usually cause serious environment problems, are needed in order to achieve good results. Therefore, development of an environmentally benign co-catalyst system for the reductive carbonylation of nitro-containing compounds is highly desired.

Ionic liquids are molten salts and usually composed of organic cations and inorganic anions. They have received much attention due to their thermal stability, negligible vapor pressure, peculiar ion environment and diversity [9–16]. Recently, it has been reported that ionic liquids could be effective reaction media or co-catalysts for the oxidative carbonylation of aniline to yield the corresponding carbamate, which offered a new way for developing a highly efficient and environmentally friendly carbonylation process [17,18]. However, problems such as the formation of water as byproduct, which may cause anions hydrolysis, the potential explosion of the $CO + O_2$ mixture gas and the high price of aniline because it was derived from hydrogenation of nitrobenzene are difficult to overcome. On the other hand, the use of ionic liquids as promoters in the reductive carbonylation of nitro-containing compounds has been scarcely dealt with, although the diversity and non-volatility of ionic liquids may offer good opportunities to find a proper and environment benign ionic liquid-mediated noble-metal complex catalyst system.

We wish to report that a catalyst system composed of the proper palladium complex and ionic liquid could be very effective for the formation of ethyl phenyl carbamate by reductive carbonylation of nitrobenzene in the presence of ethanol as illustrated in Scheme 1.

2. Experimental

2.1. Compounds and materials

The ionic liquids and palladium complexes Pd(phen)Cl_2 (phen = 1,10-phenanthroline), $Pd(phen)_2(BF_4)_2$ and $Pd(phen)_2$

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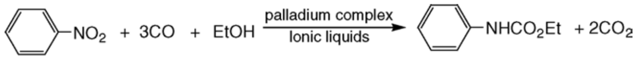


Scheme 1. Reductive carbonylation of nitrobenzene to ethyl phenyl carbamate over an ionic liquid-Pd complex catalyst.

Table 1
Results of the carbonylation of nitrobenzene with palladium complex-ionic liquids

Entry	Catalyst	Ionic liquids	Conversion (%)	Selectivity (%)
1	$Pd(OAc)_2$	–	37	56
2	$PdCl_2$	–	50	67
3	$(NH_4)_2PdCl_4$	–	19	26
4	$Pd(phen)Cl_2$	–	67	81
5	$Pd(phen)_2(BF_4)_2$	–	85	77
6	$Pd(phen)_2(PF_6)_2$	–	78	91
7	$Pd(phen)Cl_2$	$BMImBF_4$	85	92
8	$Pd(phen)Cl_2$	BMImBr	43	52
9	$Pd(phen)Cl_2$	BMImCl	34	32
10	$Pd(phen)Cl_2$	$BMImPF_6$	90	95
11	$Pd(phen)Cl_2$	$EMImPF_6$	91	87
12	$Pd(phen)Cl_2$	$HMImPF_6$	66	92
13	$Pd(phen)Cl_2$	$DMImPF_6$	59	81

$(PF_6)_2$ were synthesized according to previously published methods [19–22] with slight modifications. $PdCl_2$, $Pd(OAc)_2$, $(NH_4)_2PdCl_4$ and phenanthroline were of AR grade. The ionic liquids indicated in Scheme 2 were used in this work.

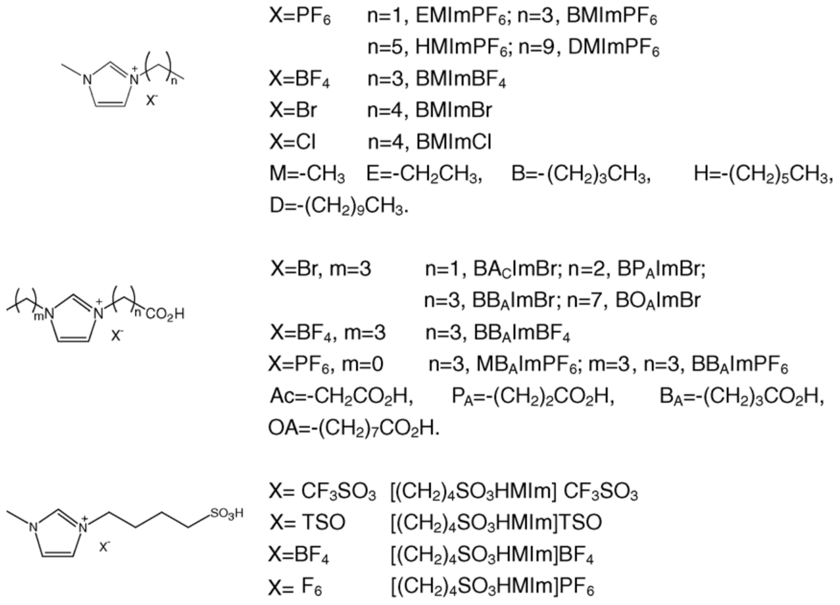
The characterizations of ionic liquids and palladium complexes were conducted with elementary analysis (Elementar Vario EL), NMR (Varian Inova 400) and FTIR (Nicolet Nodule 5700).

2.2. Reaction procedure

All reactions were conducted in a 90 ml autoclave with a glass tube inside equipped with magnetic stirring. In each reaction, 0.017 mmol Pd complex catalyst, 10 mg phenanthroline, 30 mg ionic liquid, 0.5 ml nitrobenzene, 5 ml ethanol and 6.0 MPa of carbon monoxide (purity 99.99%) were successively introduced without any additional organic solvent. The reaction proceeded at 150 °C for 3 h. When the conversion and selectivity were high enough, pale yellow solid methyl phenyl carbamate could be deposited after addition of 10 ml H_2O and it could be obtained by simple filtration. Qualitative analyses were conducted with a HP 6890/5973 GC–MS. The conversion of nitrobenzene was measured with an Agilent 6820 GC equipped with a FID detector using an external standard method, and the selectivities were calculated according to the chromatographic peak areas of the resulting products given by the GC chemstation.

3. Results and discussion

The ionic liquids based on dialkyl imidazolium with BF_4^- and PF_6^- anions as co-catalyst were explored. The results were shown in Table 1. The catalytic activities of $PdCl_2$, $Pd(OAc)_2$ and $(NH_4)_2PdCl_4$ were examined and poor to moderate conversions (19–50%) and selectivities (26–67%) were obtained (Entries 1–3). The main byproduct was azoxybenzene and trace amounts of aniline, phenyl isocyanate, nitroso benzene and azobenzene (<0.5% in total) were also detected in the reaction mixtures. In order to further improve the catalytic activity, $Pd(phen)Cl_2$, $Pd(phen)_2(BF_4)_2$ and $Pd(phen)_2(PF_6)_2$ were tested in the reductive carbonylation of nitrobenzene because the introduction of phenanthroline could improve the catalytic activity of palladium complexes in carbonylation reactions. As expected, much higher conversion of nitrobenzene (67–85%) and good selectivity to ethyl phenyl carbamate (77–91%) were achieved although they were not high enough (Entries 4–6). $Pd(phen)Cl_2$ was selected as the catalyst to explore the effect of ionic liquids as co-catalyst on the reductive carbonylation reaction. The results showed that the addition of ionic liquids as co-catalysts effectively promoted the conversion of nitroben-



Scheme 2. Ionic liquids synthesized and used in the experiments.

zene and the selectivity to ethyl phenyl carbamate (Entries 7–13). The best results were achieved over the Pd(phen)Cl_2/BMImPF_6 ionic liquid catalyst system, in which the conversion reached 90% with >95% selectivity to ethyl phenyl carbamate. Good result was also obtained in the presence of the BMImBF_4 ionic liquid with 85% conversion and 92% selectivity. Therefore, the anions in dialkyl ionic liquids have a strong impact on the catalytic activity of the palladium complex and the following sequence was observed, $PF_6^- > BF_4^- > Br^- > Cl^-$. The presence of large amounts of Br^- and Cl^- anions caused partial deactivation of the palladium complex. The substituted alkyl group of the imidazolium side chain also affected the catalytic activity to a certain extent. Along with the increasing number of carbon atoms of the alkyl group (from 2 to 10), the conversion of nitrobenzene decreased from 91 to 59%, although the selectivity was only varied slightly (Entries 10–13).

A series of relatively novel acid functional ionic liquids were also investigated in the reductive carbonylation of nitrobenzene because acids were usually effective co-catalysts for this reaction (see Table 2). In comparison with the results in Table 1, the incorporation of a carboxyl group in the side chain of the imidazolium cation could effectively improve the selectivity of the carbonylation reaction. The selectivity to ethyl phenyl carbamate reached 98.8, 97.9 and 96% with conversions of 85, 94 and 94.5% when using BA_CImBF_4, BA_CImPF_6 and MB_AImPF_6 as co-catalysts, respectively, (Table 2, Entries 1–3). These results were better than those obtained in the presence of BMImBF_4 and BMImPF_6 ionic liquids. At the same time, substitution of BF_4^- and PF_6^- anions in functional ionic liquids with Br^-, and especially with Cl^-, also led to the decrease of the conversion and selectivity (Table 2, Entries 4 and 5), which was quite similar to those using ordinary dialkyl ionic liquids as co-catalysts. Using carboxyl-functionalized ionic liquids with longer side chains, BP_AImBr, BP_AImBr and BO_AImBr, as co-catalysts, gave poor results for the reductive carbonylation of nitrobenzene, both the conversions and selectivities decreased with the increasing of the numbers of the carbon atoms (Table 2, Entries 6–8). Sulfonic acid group functionalized ionic liquids, the most popular acid functional ionic liquids with strong acid strength, were also tested in the carbonylation reaction. However, less good results in comparison with the carboxyl-functionalized ionic liquids were obtained (Table 2, Entries 9–12).

Table 2
Effect of acid functional ionic liquids on the carbonylation of nitrobenzene

Entry	Ionic liquids	Conversion (%)	Selectivity (%)
1	BA_CImBF_4	89	98.8
2	BA_CImPF_6	94	97.9
3	MB_CImPF_6	94.5	96
4	BA_CImBr	58.2	89.8
5	BA_CImCl	43	58
6	BP_AImBr	50.8	82
7	BB_AImBr	48	71
8	BO_AImBr	28	63
9	$[(CH_2)_4SO_3HMIm]CF_3SO_3$	79.5	47
10	$[(CH_2)_4SO_3HMIm]$TSO	80	89
11	$[(CH_2)_4SO_3HMIm]BF_4$	88	64
12	$[(CH_2)_4SO_3HMIm]PF_6$	79	93

In comparison with the results obtained using ordinary dialkyl ionic liquids, carboxyl and sulfonic acid-functionalized ionic liquids as co-catalysts, the following conclusions could be obtained: (1) the best results were achieved in the presence of an ionic liquid containing a carboxyl group and BF_4^-, PF_6^- anions; (2) the selection of the co-catalyst should not only be based on acid strength and (3) imidazolium ions with a shorter side chain, i.e. 2–4 carbon atoms, which are more hydrophilic and possessed appropriate coordination effects on the metal complex, promoted the conversion of nitrobenzene to ethyl phenyl carbamate more effectively. Although the catalytic activity using acid-functionalized ionic liquid as co-catalysts were lower (TOF ~ 150 mol/(mol h)) than that the reported most active catalyst system for reductive carbonylation of nitrobenzene (TOF ~ 6000 mol/(mol h)) [4], it offered us a new choice for this process because the volatile and toxic phosphorus acids could be avoided.

It is worthwhile investigating the role of ionic liquids in the reductive carbonylation of nitrobenzene. According to the mechanisms previously reported, there are two strategies to achieve satisfactory results [23,24]. The first one is the selection of non-coordinating anions, i.e. PF_6^- and BF_4^-. The other one is the presence of acid co-catalysts. Therefore, the reason for the high catalytic activity exhibited in the presence of PF_6^- and BF_4^- containing ionic liquids should first be attributed to the ion exchange between PF_6^-/BF_4^- and Cl^-, i.e. the formation of $Pd(phen)_2(BF_4)_2$ or $Pd(phen)_2(PF_6)_2$. As to the carboxyl-functionalized ionic liquids, the presence of the carboxyl group could effectively promote the ion exchange of ionic liquids with the palladium complex, which may possess a more suitable acid strength than the sulfonic acid-functionalized ionic liquids, therefore a better catalytic performance was achieved. The replacement of PF_6^- and BF_4^- anions in the ionic liquids with Br^- or Cl^- would strengthen the coordination between halogen ions and palladium complex, thus resulting in a poor catalytic performance.

Pd-carbenes, which are usually produced from imidazolium-based compounds and palladium complexes and play an important role in many catalytic processes, are not a catalytic active species in the reductive carbonylation reaction because a basic component is necessary for the deprotonation of –C(2)H of the imidazolium cation [25]. FTIR characterization showed that no changes occurred in comparison with the spectra of the BAcImPF_6 ionic liquid before and after addition of $Pd(OAc)_2$ and Pd(phen)Cl_2 (Fig. 1). This suggested that the interaction between the –C(2)H group of the imidazolium and palladium complexes was very weak, confirming that no Pd-carbene formed from the imidazolium cation and palladium complexes. The ion exchange between the ionic liquid and palladium complex was difficult to detect by FTIR because the anions had negligible effect on the FTIR spectra of the cations.

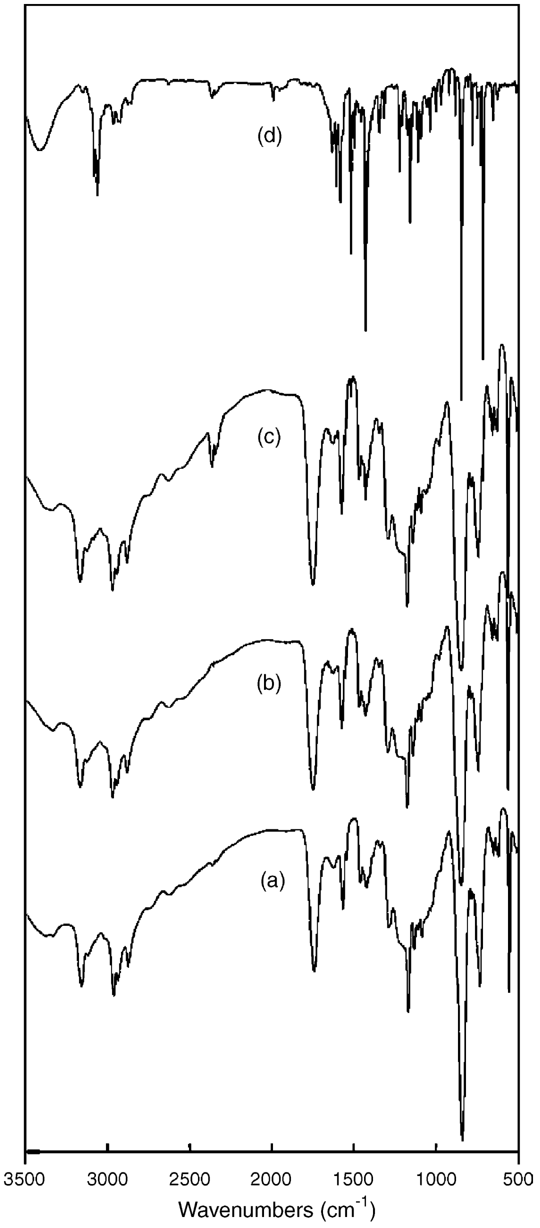


Fig. 1. FTIR spectra of the ionic liquid BAcPF$_6$ (a), Pd(OAc)$_2$/BAcPF$_6$ (b), Pd(phen)Cl$_2$/BAcPF$_6$ (c) and pure Pd(phen)Cl$_2$ (d).

4. Conclusion

An effective Pd(phen)Cl$_2$ complex-BAcImPF$_6$ ionic liquid catalyst system was developed for the reductive carbonylation of nitrobenzene to the corresponding carbamate. The diversity of ionic liquids enabled us to find an optimal co-catalyst towards a specific reaction. The synergism between the palladium complexes and the ionic liquid, and the multi-function possessed by the ionic liquids are the reason for the high catalytic efficiency.

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