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Efficient synthesis of benzaldehyde by direct carbonylation of benzene in ionic liquids

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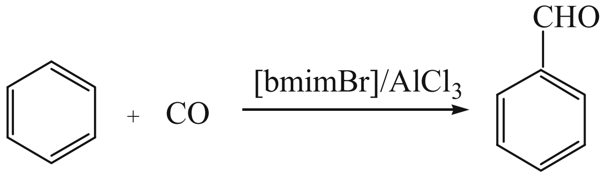
The direct carbonylation of benzene to benzaldehyde, for the first time, was achieved in the presence of chloroaluminate ionic liquids, with relatively high yield (up to 91%) and selectivity (ca. 96%). Under this reaction conditions diphenylmethane was the only by-product. The reuse of the ionic liquids was also studied.

KEY WORDS: benzene; carbonylation; benzaldehyde; ionic liquids.

1. Introduction

Selective carbonylation of benzene to benzaldehyde has attracted much interest because it is difficult to achieve and the selectivity is hard to be controlled. In the literature two types of catalyst system have been reported, one utilized the strong acids such as HF–SbF_5 [1] and liquid superacids [2,3], typified for electrophilic attack on the C–H bond; the other applied Ir(CO)($Ph_2CH_2PPh_2$) [4], RhCl(CO)$(PPh_3)_2$ [5] and RhCl(CO)$(PMe_3)_2$ [6,7], which are found to be efficient catalysts for selective carbonylation of benzene to benzaldehyde using irradiation via oxidative addition of the metal center of the complex. We have previously reported that the synthesis of benzaldehyde was achieved via selective carbonylation of benzene under two different catalyst systems, i.e. $Co(OAc)_2/CCl_3COOH/K_2S_2O_8/$pyridine [8] and $Co(OAc)_2/CCl_3COOH/O_2/$pyridine [9]. Particularly in the latter case, oxygen, instead of $K_2S_2O_8$, was used as the oxidant, which was environmentally benign and economic. However under the above two catalyst systems, the yields of benzaldehyde (37–38%) were fairly poor, the selectivity (ca. 80%) was not high, and several by-products, such as phenol, benzoic acid and chlorobenzene were formed.

Recently, ionic liquids have attracted much attention as conversion agents and alternative solvents for chemical transformations [10–12]. Chloroaluminate ionic liquids have been reported as effective catalysts for many reactions, such as for the direct carbonylation of toluene to tolualdehyde [13–16]. In the present study, direct carbonylation of benzene to benzaldehyde was achieved in the presence of chloroaluminate ionic liquids, the general type *N*-methyl imidazole based cation/$AlCl_3$, with relatively high yield (up to 91%) and selectivity (ca. 96%). Meanwhile diphenylmethane was the only by-product under the reaction conditions. The carbonylation reaction is shown in scheme 1



2. Experimental

2.1. Materials

Benzene (Shanghai Chemical Reagent Company) was dried with 4A molecular sieves. *N*-methylimidazole, 1-chlorobutane, and 1-bromobutane were purchased from Shanghai Chemical Reagent Company and used after distillation. Anhydrous aluminum chloride ($AlCl_3$) was purchased from Shanghai Mei Xing Chemical Reagent Company and used as received. CO was obtained from Shanghai Gas Company and used without further purification.

The ionic liquids [bmim]Cl/$AlCl_3$ and [bmim]Br/$AlCl_3$ were prepared according to literature [10].

2.2. Catalytic performance

The reaction was conducted in a stainless-steel autoclave (250 mL) equipped with a stirrer, a purging valve and a thermocouple. A mixture of benzene (0.167 mol) and acidic ionic liquid [bmimBr]/$AlCl_3$ (0.091 mol) was added into the autoclave. Then the mixture was heated

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to 70 °C under 40 kg cm^{-2} of carbon monoxide by stirring. After 17 h the reaction mixture was cooled down to room temperature, hydrolyzed by ice water followed by a step of extract with ethyl ether, and then analyzed by G.C. (HP-1102; capillary column: OV-101 30 m×0.25 mm×0.33 μm flame ionization detector) and identified by using GC-MS (HP-5973).

3. Results and discussion

3.1. *Effect of different ionic liquids on reaction performance*

In the present work, the chloroaluminate ionic liquids were *N*-methyl imidazole based cation/$AlCl_3$ ionic liquids, such as [bmim]Br/$AlCl_3$ and [bmim]Cl/$AlCl_3$ etc. The catalytic performances of different ionic liquids were given in table 1. It can be seen from therein that when [bmim]Br was used as the conversion agent (Entry 1), there was nearly no reaction between benzene and CO. The acidity of the ionic liquids depends on the amount of $AlCl_3$ in the mixed *N*-methyl imidazole based cation/$AlCl_3$ system. The more the amount of $AlCl_3$, the higher the acidity and the better catalytic activity of the ionic liquids. Therefore, we can see that when the molar ratio of [bmim]Br/$AlCl_3$ was 1:1 (Entry 2), the ionic liquid was neutral, the conversion of benzene was very poor (ca. 3.0%), and the yield and selectivity of benzaldehyde were 2.5% and 83%, respectively. When increasing the amount of $AlCl_3$, for instance the molar ratio of [bmim]Br/$AlCl_3$ was altered to 1:2 (Entry 3), the ionic liquid was acidic, the conversion of benzene was 84.0%, and the yield and selectivity of benzaldehyde were 80.3% and 95.6%, respectively. When sequentially increasing the amount of $AlCl_3$, the molar ratio of [bmim]Br/$AlCl_3$ was changed to 1:3 (Entry 4), the ionic liquid became more acidic, the conversion of benzene was increased to 94.7%, diphenylmethane was the only by-product, and the yield and selectivity of benzaldehyde were 91.0% and 96.0%, respectively. When [bmim]Cl/$AlCl_3$ (1:2) was used as the conversion agent (Entry 5), the conversion of benzene was slightly lower than [bmim]Br/$AlCl_3$ (1:2). In table 1, it should be noticed that, when $AlCl_3$ was used solely (Entry 6), the conversion of benzene was 44.5%, and the yield and selectivity of benzaldehyde were 42.9% and 96.4%, respectively. It indicates that $AlCl_3$ does play a crucial role in the *N*-methyl imidazole based cation/$AlCl_3$ catalyst system, and with the increase of the amounts of $AlCl_3$, the catalytic performances of ionic liquids will be remarkably improved. In the literatures [17–20], they describe that Brönsted acid HCl plays an important role in the catalyst system, small amount of HCl gas (<1 kg cm^{-2}) can accelerate reaction rate. In the case of the present study, no HCl gas was directly introduced into the reaction system, however, the ionic liquids as the satisfying conversion agents still performed effectively.

Table 1

Effect of different ionic liquids on catalytic performance

Entry	Catalyst	Conversion (%)	Yield (%)	Selectivity (%)
1	[bmim]Br	Trace	Trace	Trace
2	[bmim]Br/$AlCl_3$ (1:1)	3.0	2.5	83.0
3	[bmim] Br/$AlCl_3$ (1:2)	84.0	80.3	95.6
4	[bmim] Br/$AlCl_3$ (1:3)	94.7	91.0	96.0
5	[bmim] Cl/$AlCl_3$ (1:2)	55.1	52.7	95.8
6	$AlCl_3$[a]	44.5	42.9	96.4

Reaction conditions: *n* (benzene): 0.167 mol, *n* (ionic liquid): 0.091 mol, 70 °C, *P*(CO): 40 kg cm^{-2}, 17 h.

[a] *n* (benzene): 0.453 mol, *n* ($AlCl_3$): 0.226 mol.

3.2. *Reuse of ionic liquids*

The recycle of the ionic liquids was also studied as presented in table 2. After reaction, the benzaldehyde is normally present as a complex with the acid catalyst in the system. In this study, a mixing solvent of dichloromethane and ethyl ether was used to compete for the acidic ionic liquids in the system, thereby releasing the bezaldehyde from ionic liquids. A typical procedure for the reuse of ionic liquid was as follows: dichloromethane (40 mL) and ethyl ether (60 mL) were added to reaction mixture (50 mL), and then the mixture was stirred for 0.5 h at room temperature, the upper phase of the mixture rich in the benzaldehyde products was separated from the acidic ionic liquid. The ionic liquid layer was sequentially extracted by ethyl ether (20 mL each time) for two more times, and then the mixing solvent was concentrated, as well as identified by G.C. After extracted for three times, benzaldehyde remained in the acidic ionic liquids was very poor. The ionic liquid phase was filtrated through a 2 cm thickness of Celite, and distilled in vacuum to remove the solvent. Because small amount ($\sim$10 wt%) of $AlCl_3$ was hydrolyzed during the separating process, 10 wt% of the initial amounts of $AlCl_3$ were needed for the supplement in order to reform effective acidic catalyst. It can be seen from table 2 that the ionic liquid was still effective after recycled for four times. But with the increase in reuse times, the color of the ionic liquid gradually became darker, because of containing more impurity.

Table 2

Reuse of the acidic ionic liquid

Reuse	1st run	2nd run	3rd run	4th run	5th run
Yield (%) of benzaldehyde	84.0	81.4	75.8	69.2	60.1

Reaction conditions: *n* (benzene): 0.167 mol, *n* (ionic liquid): 0.091 mol, 70 °C, *P*(CO): 40 kg cm^{-2}, the mole ratio of [bmim]Br and $AlCl_3$ is 1:2.

4. Conclusions

In conclusion, for the first time, we have developed the synthesis of benzaldehyde via direct carbonylation of benzene in the presence of chloroaluminate ionic liquids with relatively high yield and selectivity, particularly in the case of dialkylimidazolium bromide. And the only by-product was diphenylmethane in the present reaction conditions. The ionic liquid was able to be reused with supplementing some fresh $AlCl_3$, about 10 wt% of the initial amounts. Therefore, the direct carbonylation of benzene to benzaldehyde in acidic ionic liquids exhibits a promising practical application.

Acknowledgments

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