

Alkylation of benzene and dichloromethane to diphenylmethane with acidic ionic liquids

Xijin Cai^a, Shuhan Cui^a, Liping Qu^b, Dandan Yuan^a, Bin Lu^a, Qinghai Cai^{a,*}

^a Department of Chemistry, Harbin Normal University, No. 50 Hexing Road, Nangang District, Harbin 150080, PR China

^b Heilongjiang Radio and TV University, No. 50 Hexing Road, Nangang District, Harbin 150080, PR China

Received 25 October 2006; received in revised form 26 October 2007; accepted 26 October 2007

Available online 4 November 2007

Abstract

Liquid-phase alkylation of benzene and dichloromethane as alkylating agent to diphenylmethane with acidic ionic liquids such as $\text{Et}_3\text{NHCl-AlCl}_3$, $\text{Et}_3\text{NHCl-FeCl}_3$, $\text{Et}_3\text{NHCl-ZnCl}_2$, $\text{Et}_3\text{NHCl-CuCl}_2$, $\text{Et}_3\text{NHCl-SnCl}_2$ and $\text{Et}_3\text{NHCl-SnCl}_4$ was investigated. The results showed that $\text{Et}_3\text{NHCl-AlCl}_3$ proved to be superior catalytic activity to other five ionic liquids with the conversion of 83.8% and the selectivity of 86.3% at a moderate temperature. Meanwhile, the influence of reaction conditions on the reaction, the reaction kinetics and the usability of the catalyst were explored.

© 2007 Elsevier B.V. All rights reserved.

Keywords: Diphenylmethane; Benzene; Dichloromethane; Ionic liquid; Alkylation

1. Introduction

Diphenylmethane (DPM) is a valuable chemical in spice production and an important intermediate in pharmaceuticals and insecticides [1,2]. Commercially, DPM has been synthesized by Friedel–Crafts alkylation of benzyl chloride and benzene in the presence of homogeneous acid catalysts such as AlCl_3 , FeCl_3 or H_2SO_4 [3]. These homogeneous catalysts suffer from the inherent problems of corrosiveness, non-reusability, environmental hazard and waste control after the reaction. To overcome this unfavorable situation, great efforts have been made to replace these materials with environmentally benign solid catalysts, but the activities of these solid acids are reported to be insufficient. There is, therefore, still a need to develop a new catalytic system and/or an easy-clean technology more suitable for the synthesis of DPM and its derivatives.

Alkylation of benzene with dichloromethane (DCM) to DPM is an economic alternative method as compared with

that of benzene with benzyl chloride, since the raw materials are cheaper. It has already been reported that the synthesis of DPM was carried out by gas-phase alkylation of benzene and DCM over zeolite ZSM-5 catalyst, giving 30.7% of conversion and 28.4% of yield at the reaction temperature of 230 °C [4]. This process has some disadvantages, such as high reaction temperature, low activity of the catalyst and yield of the target product, as well as the unknown lifetime of the catalyst. However, the catalytic reaction of benzene with DCM to form DPM catalyzed by metal-chloride ionic liquids in liquid phase under mild conditions has not been reported.

Here, we wish to report the liquid-phase synthesis of DPM from benzene and DCM catalyzed by metal chloride-based ionic liquids such as $\text{Et}_3\text{NHCl-AlCl}_3$, $\text{Et}_3\text{NHCl-FeCl}_3$, $\text{Et}_3\text{NHCl-ZnCl}_2$, $\text{Et}_3\text{NHCl-CuCl}_2$, $\text{Et}_3\text{NHCl-SnCl}_2$, $\text{Et}_3\text{NHCl-SnCl}_4$ that are cheaper than the dialkylimidazolium ionic liquids for the first time. As compared with the reported works in the literatures, this process possesses more advantages, such as low cost of the raw materials and energy waste due to low reaction temperature, high activity of the catalyst and yield of the product and the

* Corresponding author. Tel./fax: +86 451 88060580.

E-mail address: qinghaic@yahoo.com.cn (Q. Cai).

reusability of the catalyst, etc. which is among the most important targets pursued in catalytic and green chemistry.

2. Experimental

2.1. Preparation of ionic liquids

All the ionic liquids such as $\text{Et}_3\text{NHCl-AlCl}_3$, $\text{Et}_3\text{NHCl-FeCl}_3$, $\text{Et}_3\text{NHCl-ZnCl}_2$, $\text{Et}_3\text{NHCl-CuCl}_2$, $\text{Et}_3\text{NHCl-SnCl}_2$ and $\text{Et}_3\text{NHCl-SnCl}_4$ used in this case were prepared by the reported procedure [5]. The liquid-phase alkylation reaction of benzene and DCM with the ionic liquids as catalysts was performed in a glass reactor, fitted with a reflux condenser and magnetic stirrer. In a typical run, 15 ml (0.17 mol) of benzene after dehydrated with anhydrous calcium chloride and appropriate amounts of DCM were added in the reactor, followed by charging 1–3 g ($2.67\text{--}8.01 \times 10^{-3}$ mol) of new-made catalysts in the reactor with constant stirring. The reactor was heated to desired temperature in an oil bath by an electric heater, while the reaction was carried out at the temperatures. After several hours, the reaction mixture was cooled down to room temperature and was centrifugated to separate the catalyst from the reaction mixture. The liquid samples were analyzed by GC with a flame ionization detector, 30 m \times 0.25 mm 5% phenyl methylsilicone capillary column and nitrogen as carrier gas. Reference substances and GC-MS (GC 6890-MS 5973N) was used for the identification of the products.

3. Results and discussion

3.1. Catalytic activities of various ionic liquids

The catalytic activities of various catalysts such as $\text{Et}_3\text{NHCl-AlCl}_3$, $\text{Et}_3\text{NHCl-ZnCl}_2$, $\text{Et}_3\text{NHCl-FeCl}_3$ and $\text{Et}_3\text{NHCl-CuCl}_2$, $\text{Et}_3\text{NHCl-SnCl}_2$, $\text{Et}_3\text{NHCl-SnCl}_4$ in the alkylation of benzene or its derivatives with DCM are depicted in Table 1. Among the ionic liquid catalysts screened, chloroaluminate ionic liquid was found to be surprisingly high activity for DPM synthesis at 80 °C for 3 h, giving 83.8% of DCM conversion and 86.3% of selectivity to DPM (entry 1). Besides the main product DPM, small amount of dibenzylbenzene and a wee mount of toluene

and benzyl chloride were also detected in the reaction mixture, for example, there are 9.9% of dibenzylbenzene, 2.7% of toluene and 1.1% of benzyl chloride as byproducts in the case of entry 1. Whereas, $\text{Et}_3\text{NHCl-ZnCl}_2$ showed extremely low activity with conversion of 4.9% (entry 2) and the other four ionic liquids such as $\text{Et}_3\text{NHCl-FeCl}_3$, $\text{Et}_3\text{NHCl-CuCl}_2$, $\text{Et}_3\text{NHCl-SnCl}_2$ and $\text{Et}_3\text{NHCl-SnCl}_4$ were completely inactive (entries 3–7). The activity difference between them might be explained on the basis of their acidities [6], including Lewis and Brönsted one. The Lewis acidity of metal chloride ionic liquids increases in the order $\text{CuCl} < \text{FeCl}_3 < \text{ZnCl}_2 < \text{AlCl}_3$ [7], which is in accord with activity order of the ionic liquids listed in Table 1. On the other hand, stronger Brönsted acidity of the metal chloride ionic liquids, especially $\text{Et}_3\text{NHCl-AlCl}_3$, is generally generated in the presence of trace water in substrate due to the production of nonsolvated H^+ [6]. As a result, the reaction was effectively accelerated in the presence of the chloroaluminate ionic liquid as catalyst.

When aromatic hydrocarbons such as toluene and xylene were used as alternatives of benzene, the alkylation reactions were also investigated with $\text{Et}_3\text{NHCl-AlCl}_3$ as catalyst. The conversion with toluene as an alternative was found to be 77.8% under the same conditions, as well as 73.6% of selectivity to the corresponding products (entry 8). As for the xylene system, the conversion and selectivity were 52.5% and 55.3%, respectively (entry 9). This lower conversion for this system as compared to that using toluene as reactant may be relative to the steric effect of xylene.

3.2. Influence of catalyst amount on the reaction

Amount of the ionic liquid catalyst used in the reaction system has a great influence on the reaction. When the alkylation of DCM and benzene was carried out with various amount of chloroaluminate ionic liquid from 1.0 to 3.0 g under the same reaction conditions, a maximum value of the conversion and selectivity to DPM were observed at 2.0 g of the catalyst (Fig. 1). An excess amount of the catalyst could result in drop of the conversion and selectivity to DPM due to increase of overall amount of acid in the system, promoting undesirable side-reactions. This phenomenon implies that 2.0 g of catalyst in the catalytic system has enough acid strength and amount to effectively catalyze the alkylation with the conversion of 83.8% and 86.3% of the selectivity to DPM, giving the yield of 72.3%.

3.3. Influence of benzene to DCM molar ratio

Fig. 2 exhibits the effect of benzene/DCM molar ratio on the catalytic performances of chloroaluminate ionic liquid at 80 °C. As can be seen from the figure, the conversions of DCM and the selectivity to DPM were linearly increased in the range of the molar ratio from 5:1 to 8:1. This was due to reaction equilibrium shift to the direction producing the product with benzene concentration rising. However, the conversion dropped as the ratio was changed

Table 1
Catalytic activities of alkylation reaction with various ionic liquids

Entry	Catalysts	Aromatics	Conversion (%)	Selectivity (%)	Yield (%)
1	$\text{Et}_3\text{NHCl-AlCl}_3$	C_6H_6	83.8	86.3	72.3
2	$\text{Et}_3\text{NHCl-ZnCl}_2$	C_6H_6	4.9	100	4.9
3	$\text{Et}_3\text{NHCl-FeCl}_3$	C_6H_6	0		
4	$\text{Et}_3\text{NHCl-CuCl}$	C_6H_6	0		
5	$\text{Et}_3\text{NHCl-CuCl}_2$	C_6H_6	0		
6	$\text{Et}_3\text{NHCl-SnCl}_2$	C_6H_6	0		
7	$\text{Et}_3\text{NHCl-SnCl}_4$	C_6H_6	0		
8	$\text{Et}_3\text{NHCl-AlCl}_3$	$\text{C}_6\text{H}_5\text{CH}_3$	77.8	73.6	57.3
9	$\text{Et}_3\text{NHCl-AlCl}_3$	$\text{C}_6\text{H}_4(\text{CH}_3)_2$	52.5	55.3	29.0

Download English Version:

<https://daneshyari.com/en/article/52122>

Download Persian Version:

<https://daneshyari.com/article/52122>

[Daneshyari.com](https://daneshyari.com)