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Catalysis Today 93–95 (2004) 301–305

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Alkylation of diphenyl oxide with α-dodecene catalyzed by ionic liquids

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Abstract

The use of ionic liquids of the type 1-butyl-3-methylimidazolium aluminium chloride ([bmim]Cl/$AlCl_3$) as catalyst for the synthesis of monododecyl diphenyl oxides has been demonstrated. By using acetonitrile as an IR spectroscopic probe, the Lewis acidity–activity correlation for the ionic liquid catalysts in the alkylation reaction has been studied. A comparative study of the ionic liquids catalyzed system and the traditional $AlCl_3$ system has been carried out and the effects of varying reaction time, temperature, the relative amount and acid strength of the ionic liquids, as well as the molar ratio of diphenyl oxide to α-dodecene have been explored. The yield of the target product with [bmim]Cl/$AlCl_3$ ionic liquids as catalyst for the alkylation of the diphenyl oxide with α-dodecene is much higher than that observed using $AlCl_3$ as catalyst. Furthermore, use of ionic liquids leads to a significant simplification in product isolation, and the system can be regarded as environmentally benign. The maximum yield of the monododecyl diphenyl oxides is about 90% when [bmim]Cl/$AlCl_3$ ionic liquids are used as catalyst under mild reaction conditions. The highest yield is obtained at a reaction temperature of 80 °C with a molar ratio of diphenyl oxide to α-dodecene of 7 and α-dodecene to ionic liquid molar ratio of 2. The potential for reuse of the acidic ionic liquids has been investigated. The main cause of deactivation of the acidic ionic liquid was found to be the leaching of the active catalytic species $Al_2Cl_7^-$ as a result of the interaction between the acidic ionic liquid and diphenyl oxide.

Keywords: Ionic liquids; Lewis acidity; IR spectroscopy; Alkylation reaction; Diphenyl oxide; α-Dodecene

1. Introduction

Ionic liquids (ILs) are low melting point salts that represent an exciting new class of Lewis acidic materials [1–3]. ILs have been employed as solvents or catalysts in many catalytic processes [4–7]. In particular, ILs based on imidazolium cations and chloroaluminate anions, such as 1-butyl-3-methylimidazolium aluminium chloride ([bmim]Cl/$AlCl_3$), have attracted growing interest in the last few years [8,9]. Friedel-Crafts alkylation is a commercially important reaction [10] for which the conventional catalysts are HF, H_2SO_4 or $AlCl_3$, all of which give rise to serious environmental problems. In recent years, ILs such as [bmim]Cl/$AlCl_3$ have been used in place of these acids as catalysts for alkylation reactions [10–14]. In such cases, the ILs act not only as catalyst but also as the solvent for the reaction. The main advantages are greatly enhanced reaction rate, as well as higher conversion and selectivity [15–18]. At the same time, the product can be easily separated from the acidic catalyst.

The alkylation of benzene with long chain alkenes or halogenated alkanes to produce linear alkylbenzenes (LAB) is one example of a commercially important Friedel-Crafts alkylation reaction. The traditional catalyst is HF or $AlCl_3$ with a catalyst/olefin molar ratio of 5–20. Acidic ILs have also been used as catalyst in ratios as low as 0.004 with very high conversion [19].

Monoalkyl diphenyl oxides (typically with alkyl chains of 12 C-atoms) are raw materials for the production of alkyldiphenyl oxide disulfonates, an important class of surfactants marketed by Dow Chemical Company under the trade name Dowfax® [20]. The company originally employed $AlCl_3$ as alkylation catalyst giving a conversion of about 80% [21] but in 1992, switched to fluorocarbon sulfonic acid polymers (FSA) as catalyst and obtained conversions of 80–90% [22]. In this

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doi:10.1016/j.cattod.2004.06.135

work, 1-butyl-3-methylimidazolium aluminium dichloride ([bmim]Cl/$AlCl_3$) ILs have been used to catalyze the alkylation of diphenyl oxide with α-dodecene. Acetonitrile has been used as an IR spectroscopic probe to determine the Lewis acidity of the ILs and thus correlate the Lewis acidity with the catalytic activity of the ILs in the alkylation reaction. The effects of varying reaction conditions on the synthesis of monododecyl diphenyl oxide catalyzed by [bmim]Cl/$AlCl_3$ ILs have been extensively studied. The potential for reuse of the acidic ionic liquids has been investigated.

2. Experimental

[bmim]Cl/$AlCl_3$ ILs were prepared as previously described [23].

2.1. Alkylation reactions

The alkylation experiments were carried out in a three-neck flask reactor equipped with a magnetic stirring bar. In a typical reaction, diphenyl oxide (0.28 mol) was initially added to a three-neck flask and stirred vigorously at 80 °C under dry N_2. A mixture of ILs (0.02 mol) and α-dodecene (0.04 mol) was subsequently added dropwise. After a given reaction time, the upper layer containing unreacted diphenyl oxide and the reaction products was separated from the ILs phase by decantation. The reaction time, temperature, the amount and acidic strength of ILs and molar ratio of diphenyl oxide to α-dodecene were varied. The target product of the alkylation reaction is a mixture of *para*- and *ortho*-monododecyl diphenyl oxide. The byproducts are mainly didodecyl diphenyl oxides.

The alkylation reaction was carried out under the same conditions with $AlCl_3$ as catalyst. The amount of $AlCl_3$ was equal to that of the ILs used in the above experiments. Experiments were carried out at 80 °C with a molar ratio of diphenyl oxide to α-dodecene of 7. The reaction time was 40 min. It was found that the upper layer had to be washed many times with deionized water when $AlCl_3$ was used as the catalyst. Large amounts of HCl were released during this procedure.

2.2. Acidity determination

Acetonitrile was refluxed over, and distilled from, P_2O_5. All IR samples were prepared by mixing acetonitrile and ILs in a given volume ratio, and then spreading as liquid films on KBr windows. The spectra were recorded on a Bruker Vector 22 Fourier transform infrared spectrophotometer at room temperature.

2.3. Analysis and characterization

The amount of H_2O in the raw materials was analyzed by RIPP (Research Institute of Petroleum Processing, in china). The amount of H_2O in the diphenyl oxide and α-dodecene as supplied was found to be 100–150 ppm. The composition of the upper organic layer was analyzed by HPLC using an Agilent HPLC1100 system. Elemental analysis was carried out by X-ray fluorescence (XRF) using an S4 Explorer instrument (Bruker). ^1H NMR measurements were carried out using a Mercury 200 MHz NMR spectrometer (Varian).

3. Results and discussion

3.1. Comparison of [bmim]Cl/$AlCl_3$ ILs and $AlCl_3$ systems

As shown in Table 1, alkylation of diphenyl oxide with α-dodecene with ILs as catalyst gives a much higher yield of monododecyl diphenyl oxide than that observed with $AlCl_3$ as catalyst. Even small quantities of ILs result in high yields of the target product.

In discussing the relative performance of catalyst systems the physical nature of the catalyst must be considered. In systems where solid catalysts with limited solubility in the reaction media are used and generally insoluble, often crystalline, intermediate complexes are formed, lattice energies have a significant influence. In addition, solvation energies play an important role in determining the relative reactivity of Friedel-Crafts systems and influence the selectivity of these systems to a considerable degree [24]. The reactivity of a liquid phase catalyst such as ILs should be higher than that of a solid catalyst such as $AlCl_3$.

The mechanism of the alkylation reaction involves intermediate carbenium ions. For [bmim]Cl/$AlCl_3$ ILs, the actual catalytic species is generally accepted to be $Al_2Cl_7^-$ when the apparent mole fraction of the metal halides, X, is 0.6 [11]. The Lewis acidity of $Al_2Cl_7^-$ is weaker than that of $AlCl_3$. Side reactions (including dealkylation and dialkylation) will be favored by high acid strength of the catalyst [25]. The high polarity and electrostatic field of ILs may stabilize the carbenium ion intermediates and inhibit side reactions and thus the reaction selectivity can be improved by using ILs as catalyst. In addition, use of ILs as catalyst significantly simplifies product isolation, and the process can be regarded as environmentally benign.

3.2. Determination of the acidity of ionic liquids

The Lewis acidic strength of [bmim]Cl/$AlCl_3$ ILs can be adjusted by varying the mole fraction of $AlCl_3$, X. We use acetonitrile as an IR probe to determine the acidity of ILs. As shown in Fig. 1 and Table 2, pure acetonitrile shows two

Table 1
A comparison of ILs and $AlCl_3$ as the catalyst for the alkylation of diphenyl oxide with α-dodecene

Catalyst	ILs	$AlCl_3$
Yield of target product (%)	89.8	77.8

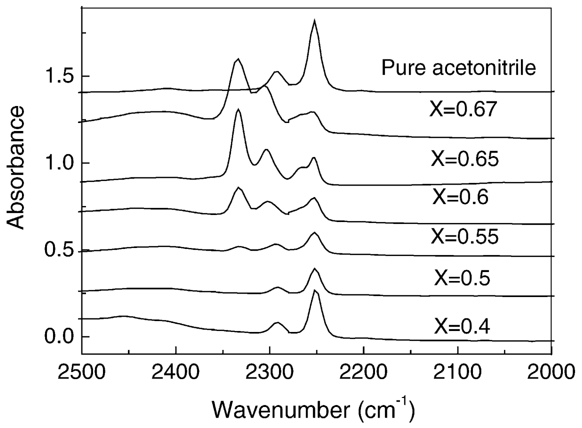

Fig. 1. IR spectra of mixtures of acetonitrile with ionic liquids.

Table 2
Position of IR bands in mixtures of acetonitrile and [bmim]Cl/$AlCl_3$ ionic liquids

Mole fraction of $AlCl_3$ (X)		Wavenumber of bands (cm^{-1})	
Pure acetonitrile		2292	2252
X = 0.40		2290	2251
X = 0.50		2291	2252
X = 0.55	2330	2292	2252
X = 0.60	2332	2302	2252
X = 0.65	2333	2303	2252
X = 0.67	2335	2304	2252

characteristic ν_{CN} stretching vibrations at 2292 and 2252 cm^{-1}. When acetonitrile is mixed with ILs with $X \leq 0.5$, no change in ν_{CN} stretching frequencies is observed (Fig. 1 and Table 2). This indicates that there is no interaction between these relatively weakly acidic ILs and acetonitrile, a weak Lewis base. In contrast, when $X > 0.5$, a third band appears at around 2330 cm^{-1} and a monotonic blue shift of this band as well as the band around 2290 cm^{-1} is observed with increasing X (see Table 2). The band at around 2330 cm^{-1} is indicative of Lewis acid–base interaction between the ILs and acetonitrile. These results indicate that the Lewis acidic strength of ILs can be estimated by using acetonitrile as IR probe molecule.

3.3. *Effects of varying reaction conditions on the alkylation reaction*

3.3.1. *Reaction time*

The effects of varying the reaction time on the alkylation reaction have been studied (see Fig. 2). The reaction was carried out at 80 °C with a diphenyl oxide to α-dodecene molar ratio of 7, and a α-dodecene to ILs (X = 0.6) molar ratio of 2. The results show that the yield of monododecyl diphenyl oxide reaches 80% within the first 40 min even though only small quantities of ILs are employed. The yield of product does not increase significantly when the reaction time is extended to 4 h. We propose that the high catalytic efficiency of the ILs results from both the presence of $Al_2Cl_7^-$ ions as the catalytic species and the high polarity and electrostatic field of the ILs. A reaction time of 40 min is used in subsequent studies.

3.3.2. *Acidic strength of the ionic liquids*

The effects of varying the acidic strength of the ILs on the alkylation reaction have been studied (see Fig. 3). The reaction was carried out at 80 °C with a diphenyl oxide to α-dodecene molar ratio of 7, and a α-dodecene to ILs molar ratio of 2. Weakly acidic ILs with $X \leq 0.55$ do not exhibit any catalytic activity in the alkylation reaction. The maximum product yield is obtained when X = 0.6. ILs with very strong Lewis acidity (e.g. X = 0.67) give lower yields of the target product because increasing amounts of byproducts (such as polyalkyldiphenyl oxides) are formed when X exceeds 0.6. These results indicate that ILs with intermediate Lewis acidity are preferred as catalysts for the alkylation reaction.

3.3.3. *Amount of ionic liquids*

The effects of varying the relative amount of the ILs on the alkylation reaction have been explored (see Fig. 3). The results indicate that the maximum yield of target product is

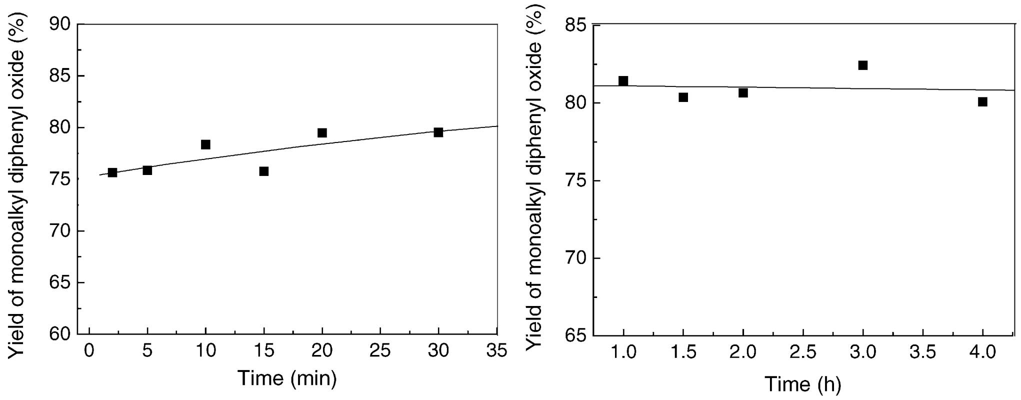

Fig. 2. Effects of reaction time on the alkylation reaction.

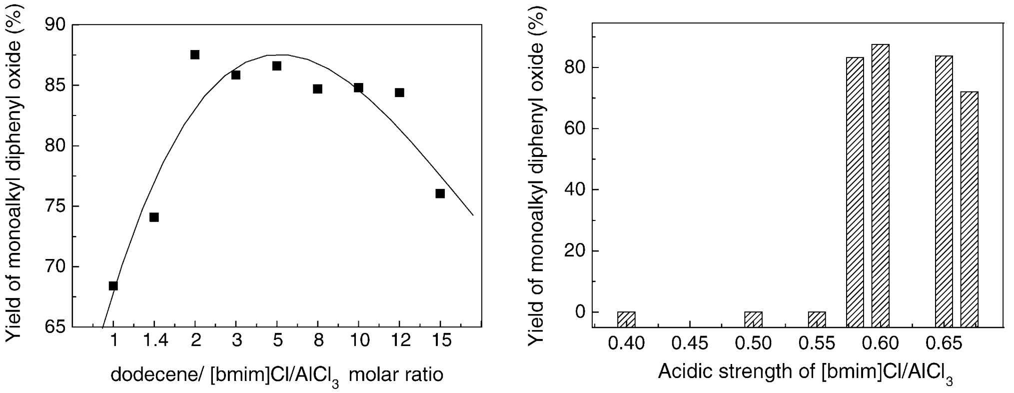

Fig. 3. Effects of amount and acidic strength of ILs on the alkylation reaction.

obtained when the α-dodecene to ILs molar ratio is in the range 2–3. An excess of ILs may result in an increase of acidity in the system promoting undesirable side-reactions and reduced yield of target product.

3.3.4. Reaction temperature

Fig. 4 shows the effect of varying the temperature on the alkylation reaction. The maximum yield of target product is obtained with a temperature of about 80 °C. The reaction rate is very slow at lower temperatures but since alkylation is an exothermic reaction, higher reaction temperatures are undesirable. A temperature of 80 °C represents an adequate compromise between thermodynamic and kinetic factors.

3.3.5. Molar ratio of diphenyl oxide to α-dodecene

The effect of varying the molar ratio of diphenyl oxide to α-dodecene on the reaction is shown in Fig. 4. The reaction was carried out at 80 °C with a α-dodecene to ILs ($X = 0.6$) molar ratio of 2. Increasing the molar ratio of diphenyl oxide to α-dodecene from 2 to 7 leads to an increase in the yield of the target product because an excess of diphenyl oxide inhibits production of polyalkylated byproducts. The relative amount of ILs decreases with increasing amount of diphenyl oxide however and a larger excess of diphenyl oxide results in reduced product yields. Thus the maximum yield of the target product is obtained when the molar ratio of diphenyl oxide to α-dodecene is about 7.

3.4. Reuse of ionic liquids

The potential for reuse of the ILs in the alkylation reaction has been studied. Fig. 5 shows the FT-IR spectra of mixtures of the reused [bmim]Cl/AlCl$_3$ ILs and acetonitrile (A) and the activities of the reused ILs in the alkylation reaction (B). The experiments were carried out at 80 °C with a diphenyl oxide to α-dodecene molar ratio of 7, and a α-dodecene to ILs ($X = 0.6$) molar ratio of 2. The notation R*n* indicates that the ILs have been used *n* times. As shown in Fig. 5 (A), the intensity of the IR band at 2333 cm^{-1}, indicative of the presence of Lewis acid–base interaction between ILs and acetonitrile, decreases rapidly as n increases and is almost absent in the spectra of R3 and R4. As shown in Fig. 5 (B), whilst there is slight decrease in activity of the ILs from R0 to R2, in contrast R3 and R4 have negligible activity. This demonstrates that the activity of ILs in the alkylation decreases when their Lewis acidity becomes weaker. The mass of the ILs layer increased by

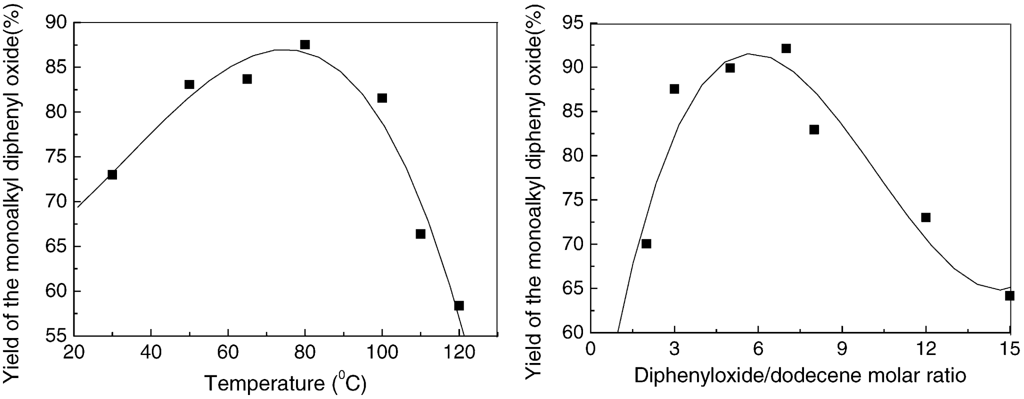

Fig. 4. Effects of temperature and diphenyl oxide/dodecene molar ratio on the reaction.

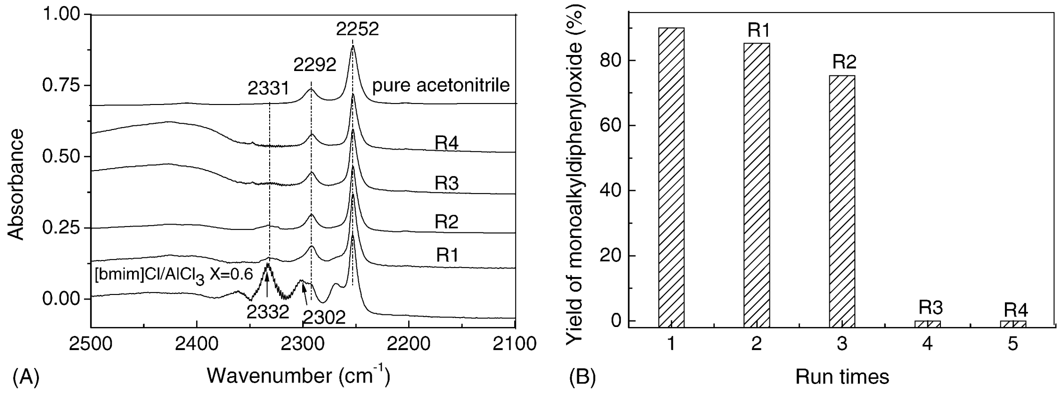

Fig. 5. FT-IR spectra of mixtures of acetonitrile and reused [bmim]Cl/$AlCl_3$ ILs (A) and the activities of the reused ILs in the alkylation reaction (B).

about 30 wt.% after the first alkylation reaction. ^1H NMR spectroscopy indicates that some diphenyl oxide is dissolved in the ILs layer. In addition, elemental analysis (XRF) of the organic layer after reaction shows that some $AlCl_x$ ($x \cong 2.7$) is present.

The reason for deactivation of the ILs could be due to the interaction between the ILs and either water or diphenyl oxide. Rigorous drying of the raw materials [resulting in a molar ratio of $AlCl_3$ in the ILs ($X = 0.6$) to H_2O in the raw materials in the range 28–39 had no effect on the stability of the catalyst however. This suggests that the main reason for the deactivation of the ILs is the interaction with diphenyl oxide, which results in a leaching of the catalytic species $Al_2Cl_7^-$ into the upper organic layer. Elemental analysis (XRF) indicates that around 30% of the initial Al content is leached into upper layer after one alkylation reaction, leading to a rapid loss in activity. Further studies aimed at enhancing the potential for reuse of acidic ILs are underway in this laboratory.

4. Conclusions

Alkylation of diphenyl oxide with α-dodecene is catalyzed by acidic ionic liquids (ILs). The yield of target product is much higher with [bmim]Cl/$AlCl_3$ ILs as catalyst compared with that observed for $AlCl_3$. Catalysis by ILs leads to a considerable simplification in product isolation and the system can be regarded as environmentally benign. Acetonitrile has been used as an IR spectroscopic probe in order to compare the relative Lewis acidic strengths of ILs.

The yield of the monododecyl diphenyl oxides is about 90% when [bmim]Cl/$AlCl_3$ ILs with mole fraction of $AlCl_3$, X, of 0.60 is used as catalyst under mild reaction conditions. The maximum yield is obtained at 80 °C, when the molar ratio of diphenyl oxide to α-dodecene is about 7 and that of α-dodecene to ILs is about 2. The main reason for deactivation of the acidic ILs is the leaching of the actual catalytic species $Al_2Cl_7^-$ as a result of the interaction between the acidic ILs and diphenyl oxide.

Acknowledgement

Financial support from the ‘973’ Program of the Chinese Ministry of Science and Technology under contract number G-2000048002 is gratefully acknowledged.

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