

Alkylation of anthracene to 2-isopropylanthracene catalyzed by Lewis acid ionic liquids

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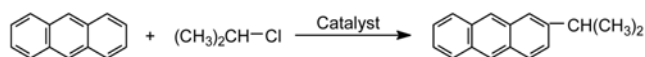
Abstract—Alkylation of anthracene with 2-chloropropane to 2-isopropylanthracene catalyzed by various Lewis acidic ionic liquids (ILs), such as [Emim]Cl-AlCl₃, [Emim]Cl-FeCl₃, [Emim]Cl-ZnCl₂, [Bmim]Cl-AlCl₃, and [Omim]Cl-AlCl₃ ([Emim]⁺=1-ethyl-3-methylimidazolium cation, [Bmim]⁺=1-butyl-3-methylimidazolium cation, [Omim]⁺=1-octyl-3-methylimidazolium cation), was investigated. [Emim]Cl-AlCl₃ ionic liquid was found to be the most active catalyst in the alkylation. The yield of 2-isopropylanthracene was up to 74.5% and the selectivity of 2-isopropylanthracene was up to 82.9%. The [Emim]Cl-AlCl₃ ionic liquid catalyst showed good catalytic activity after running for 6 times. Ease of product separation and the recycling performance of the ionic liquid catalyst is expected to contribute to the development of clean and environmentally friendly strategy for the synthesis of 2-isopropylanthracene.

Key words: Lewis Acidic Ionic Liquid, Alkylation, 2-Isopropylanthracene, Anthracene, 2-Chloropropane

INTRODUCTION

The Friedel-Crafts alkylation products of aromatic compounds are widely used in preparation of anion scours, polyesters, quality plastic, LCD polymers and special chemicals [1-3]. However, the conventional catalysts of the Friedel-Crafts alkylations, such as aluminum trichloride (AlCl₃), hydrofluoric acid (HF) and sulfuric acid (H₂SO₄), are highly corrosive and potentially lethal acids. The spent catalysts are not recoverable and produce environmentally unfriendly effluents. On account of the disadvantages of these catalysts, it is imperative to develop environmentally benign catalysts. Solid acid catalysts involving zeolites [4-7], clays [8], heteropoly acids [9] fluorinated silica-alumina [10], and metal oxide [11] have been widely investigated. The disadvantage of the solid catalysts is that they are easily deactivated because of the accumulation of heavy products in their channels and reactive sites in the catalysts.

In recent years, ionic liquids (ILs) have attracted increasing interest and been successfully used as environmentally benign catalysts and solvents in a variety of catalytic reactions due to their relatively low viscosities, low vapor pressure, high thermal, and chemical stability, etc. [12-16]. Wilkes first reported the Friedel-Crafts reactions of aromatic substrates, such as benzene, toluene, chlorobenzene, and nitrobenzene, in ILs [17]. All of the aromatic substrates were alkylated except nitrobenzene. To date, Friedel-Crafts alkylations [18-20] and acetylations [21,22] of benzene, naphthalene, and their derivatives catalyzed by ILs have been given considerable attention. Acetylations of some polyaromatics, such as naphthalene, pyrene, phenanthrene and anthracene, in ILs were also investigated [23]. But to the best of our knowledge, no alkylation



Scheme 1. Friedel-Crafts alkylation of anthracene to 2-isopropylanthracene.

of anthracene catalyzed by ILs has been reported. In addition, to obtain pure new fine chemical, 2-chloropropane was chosen as alkylating agent for its relative simple structure and high activity. According to structure analysis, the Friedel-Crafts alkylation products of anthracene could be used as new fine chemicals and have broad application prospects.

In the present paper, the catalytic activities of Lewis acidic ILs, such as [Emim]Cl-AlCl₃, [Emim]Cl-FeCl₃, [Emim]Cl-ZnCl₂, [Bmim]Cl-AlCl₃, and [Omim]Cl-AlCl₃, in the alkylation of anthracene with 2-chloropropane to 2-isopropylanthracene (Scheme 1) were investigated under different experimental conditions. The Lewis acidic ILs were easily isolated from the products and effectively recycled.

EXPERIMENTAL

1. Materials

1-ethyl-3-methylimidazolium chloride ([Emim]Cl) was purchased from Institute of Chemistry & Chemical Engineering, Hebei Normal University and used without further purification. Anthracene (98%) was recrystallized from ethanol and AlCl₃ was sublimated before being used. All other chemicals used in this study were commercially available and were used without further purification.

2. Preparation of Ionic Liquids

1-butyl-3-methylimidazolium chloride ([Bmim]Cl) and 1-octyl-3-methylimidazolium chloride ([Omim]Cl) were synthesized according to the procedures reported by Huddleston et al. [24]. All the alu-

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Table 1. The catalytic activities of the Lewis acidic ILs and metal halides in the alkylation of anthracene to 2-isopropylanthracene

Entry	Catalyst and molar fraction of metal halide	Catalyst loading ^a	Ratio of reactants ^b	Temperature (°C)	Time (h)	Yield ^c (%)	Selectivity ^c (%)
1	AlCl ₃	3.5	2 : 1	60	7	52.3	55.0
2	FeCl ₃	3.5	2 : 1	35	7	1.3	11.5
3	ZnCl ₂	3.5	2 : 1	35	7	0	0
4	[Emim]Cl-AlCl ₃ 0.67	4	1.5 : 1	30	4	74.5	82.9
5	[Emim]Cl-FeCl ₃ 0.67	4	1.5 : 1	30	4	5.2	25.8
6	[Emim]Cl-ZnCl ₂ 0.67	4	1.5 : 1	30	4	0	0
7	[Bmim]Cl-AlCl ₃ 0.67	4	1.5 : 1	30	4	69.2	77.1
8	[Omim]Cl-AlCl ₃ 0.67	4	1.5 : 1	30	4	60.5	63.9

^aThe molar ratio of catalyst to anthracene

^bThe molar ratio of 2-isopropylanthracene to anthracene

^cThe yield and selectivity were determined by GC

minum ionic liquids (Al-IL) were synthesized by using the method reported in the literature [25], and all the iron ionic liquids (Fe-IL) or Zinc ionic liquids (Zn-IL) were synthesized according to the synthesis procedures of Al-IL, but AlCl₃ was replaced by FeCl₃ and ZnCl₂, respectively.

3. Alkylation of Anthracene with 2-Chloropropane

Given amounts of anthracene (0.36 g, 2 mmol) and 2-chloropropane (0.24 g, 3 mmol) were put into a 100 mL three-neck flask equipped with a stirrer, a reflux condenser with a drying pipe and a thermometer. Then an appropriate amount of catalyst and solvent was added dropwise to the flask in 10 min with stirring. The alkylation reaction was typically carried out for 2-6 h at the desired temperature and ambient atmosphere with vigorous stirring. Then, the reaction mixtures were cooled to room temperature. The mixtures included two liquid phases (organic phase and ionic liquid phase); ionic liquid could be reused after extracting the organic phase with ether. The yields and the selectivity of the desired product were obtained through GC analysis in the organic phase. The crude desired product in the organic phase was washed with distilled water and petroleum ether, respectively, then recrystallized from methanol to give pure product as yellow solid. Qualitative and quantitative analysis was conducted with GC/MS (HP 6890), ¹H NMR (BRUKER 600), and FT-IR (Nexus 470), respectively.

The spectral data for the desired product 2-isopropylanthracene: GC/MS, *m/z* (%): 220 (M⁺, 92.1), 205 (100), 178 (26.3), 165 (7.5), 101 (15.2); ¹H NMR (600 MHz, CDCl₃): δ: 1.38 (q, 6H, J=7.2 Hz), 3.10 (t, 1H, J=7.2 Hz), 7.43 (t, 4H, J=7.2 Hz), 7.77 (s, 1H), 7.98 (m, 4H, J=9.6 Hz); FT-IR (KBr), cm⁻¹: 3049 (Ar-H), 2955-2864 (C-H), 1379 (CH₃), 1379, 2823, 1452 (CH), 1628 (C=C).

RESULTS AND DISCUSSION

1. Effect of Lewis Acidic ILs

The yields and the selectivity of the alkylation of anthracene with 2-chloropropane catalyzed by three metal halides and five Lewis

acidic ILs containing 1-alkyl-3-methylimidazolium chloride and different metal halides are listed in Table 1. When the reaction was catalyzed by the metal halides, CS₂ was used as a solvent.

The experimental results show that Lewis acidic ILs containing AlCl₃ and FeCl₃ had better catalytic activities than those of the corresponding metal halides catalysts in the alkylation of anthracene to 2-isopropylanthracene while Zn-IL had no catalytic activity. Among all the investigated catalysts, [Emim]Cl-AlCl₃ IL exhibited the best catalytic activity with a yield of 74.5% and a selectivity of 82.9% for 2-isopropylanthracene (Entry 4). On the other hand, among three metal halides, AlCl₃ had the highest catalytic activity in the alkylation of anthracene to 2-isopropylanthracene, while FeCl₃ showed poor catalytic activity and ZnCl₂ had no activity (Entry 1-3). The catalytic activity order of the metal halides is consistent with that of their Lewis acidic strengths. Although AlCl₃ showed good catalytic activity in the alkylation of anthracene to 2-isopropylanthracene, the procedure suffered from severe problems, such as horrible corrosion and pollution, uneasy product purification, and impossible catalyst recycle. While Lewis acidic ILs were used as the catalysts, the product isolation and purification was quite easier and the alkylation was free of any volatile organic solvent since the ILs play a dual role of catalyst and solvent.

While the ILs prepared with same [Emim]⁺ cation and different anions, such as [Emim]Cl-AlCl₃, [Emim]Cl-FeCl₃, and [Emim]Cl-ZnCl₂, were used as the catalysts, the yields and the selectivity of 2-isopropylanthracene were 74.5%, 82.9%, 5.2%, 25.8%, and 0%, 0%. The predominant anionic species of [Emim]Cl-AlCl₃, [Emim]Cl-FeCl₃, and [Emim]Cl-ZnCl₂ with a molar fraction of metal halides of 0.67 are Al₂Cl₇⁻, Fe₂Cl₇⁻ and ZnCl₃⁻, respectively, and the Lewis acidic strength of those anions decreases in the order of Al₂Cl₇⁻ > Fe₂Cl₇⁻ > ZnCl₃⁻ [26]. Therefore, it is reasonable to conclude that the increasing of the anion's Lewis acidic strength increases the catalytic activity of the resultant Lewis acidic IL.

When the ILs were prepared with the same metal halide (AlCl₃) and different alkyl groups, such as [Emim]Cl-AlCl₃, [Bmim]Cl-

AlCl_3 , and $[\text{Omim}]\text{Cl}-\text{AlCl}_3$, the catalytic activity decreased with the chain length of N-substituted alkyl of imidazole cations (Entry 4, 7, 8). According to the carbenium mechanism of Friedel-Crafts alkylation reaction [27], Friedel-Crafts alkylation reaction is significantly influenced by the concentration and stability of the intermediate carbenium ions, and the high molecular polarizability of the reaction medium greatly facilitates the generation of carbenium ions [28]. It was reported that the polarizability of the ILs decreased with increasing the alkyl length because the longer alkyl groups can provide a more hydrophobic (hence non-polar) environment than the smaller ones can [29]. Therefore, the molecular polarizability of the used ILs should be in the order of $[\text{Emim}]\text{Cl}-\text{AlCl}_3 > [\text{Bmim}]\text{Cl}-\text{AlCl}_3 > [\text{Omim}]\text{Cl}-\text{AlCl}_3$, resulting in a decrease in their alkylation activity with increasing alkyl length. Furthermore, the imidazolium ion itself shows a weak Lewis acid [30] and the Lewis acidic strength decreased with increasing the alkyl length [31]. This is probably another reason why the catalytic activity decreases with increasing alkyl length of the imidazolium cations.

2. Effects of Experimental Parameters on the Catalytic Activity of $[\text{Emim}]\text{Cl}-\text{AlCl}_3$ Catalyst

$[\text{Emim}]\text{Cl}-\text{AlCl}_3$ exhibited the most excellent catalytic performance with satisfactory yield and selectivity of the desired product (entry 4, Table 1). Therefore, we chose $[\text{Emim}]\text{Cl}-\text{AlCl}_3$ as the high effective catalyst to further investigate the effects of experimental parameters on the catalytic alkylation reaction and the recycling performance of the catalyst.

2-1. Effect of the Molar Fraction of AlCl_3 in Ionic Liquid

The Lewis acidity of chloroaluminate-based ILs can be varied over a wide range by manipulating the relative amounts of organic base and AlCl_3 [32]. The molar fraction of AlCl_3 in IL (N) less than 0.5 affords basic, $N=0.5$ gives neutral, and those greater than 0.5 afford acidic ILs [21]. The catalytic activities of ILs with different N values are listed in Table 2. It was found that no reaction occurred in the basic as well as the neutral ILs (Entries 1, 2, $N \leq 0.5$), as expected. When the N value was in the range of 0.60-0.75, the yield and selectivity of 2-isopropylanthracene had maximum values. The optimum composition of $[\text{Emim}]\text{Cl}-\text{AlCl}_3$ IL catalyst was $N=0.67$ (i.e., $n(\text{AlCl}_3) : n([\text{Emim}]\text{Cl}) = 2 : 1$, Entry 4). In the basic IL, the predominant anionic species are $[\text{AlCl}_4]^-$ and Cl^- . In acidic IL, $[\text{Al}_2\text{Cl}_7]^-$ predominates and its concentration in the liquid is a function of the mole fraction of AlCl_3 . In highly acidic IL, larger aluminum chlo-

Table 2. Effects of the molar fraction of AlCl_3 in ILs on the alkylation of anthracene to 2-isopropylanthracene

Entry	N	$n(\text{AlCl}_3) : n([\text{Emim}]\text{Cl})$	Yield ^a (%)	Selectivity ^a (%)
1	0.33	0.5 : 1	0	0
2	0.50	1 : 1	0	0
3	0.60	1.5 : 1	61.8	68.3
4	0.67	2 : 1	74.5	82.9
5	0.71	2.5 : 1	68.3	70.9
6	0.75	3 : 1	57.3	65.3

Reaction conditions: $n_{\text{rea}} = 1.5 : 1$, $n([\text{Emim}]\text{Cl}-\text{AlCl}_3) : n(\text{anthracene}) = 4 : 1$, $T = 30^\circ\text{C}$, $t = 4$ h

^aThe yield and selectivity were determined by GC

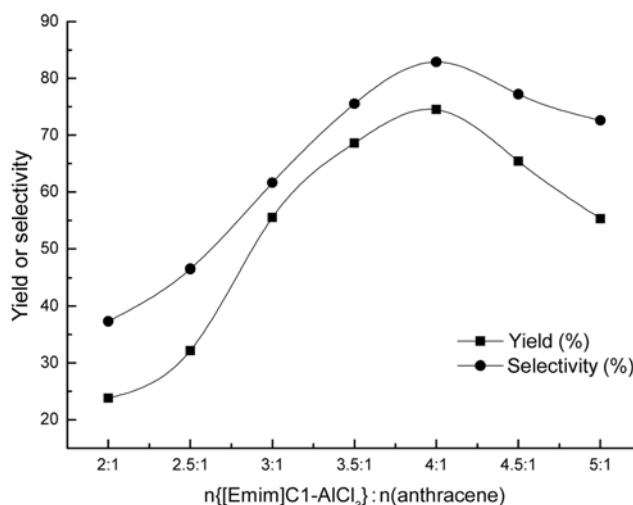


Fig. 1. Effect of molar ratio $[\text{Emim}]\text{Cl}-\text{AlCl}_3$ to anthracene on the alkylation of anthracene to 2-isopropylanthracene.

$N=0.67$, $n_{\text{rea}}=1.5 : 1$, $T=30^\circ\text{C}$, $t=4$ h

ride adducts, e.g., $[\text{Al}_3\text{Cl}_{10}]^-$ ion were formed at a high N level [33-35]. The results evidently reveal that the Al_2Cl_7^- species are the active sites in the alkylation reaction

2-2. Effect of Molar Ratio of Ionic Liquid to Anthracene

The effect of the molar ratio of $[\text{Emim}]\text{Cl}-\text{AlCl}_3$ to anthracene on the yield and selectivity of 2-isopropylanthracene were tested and the results are shown in Fig. 1. The yield and selectivity of 2-isopropylanthracene increased when the molar ratio of $[\text{Emim}]\text{Cl}-\text{AlCl}_3$ to anthracene increased from 2 : 1 to 4 : 1, then decreased as further increasing the molar ratio of $[\text{Emim}]\text{Cl}-\text{AlCl}_3$ to anthracene, and this may be due to other single-alkylations, two-alkylations, and multi-alkylations of anthracene resulting from the strong activity of abundance $[\text{Emim}]\text{Cl}-\text{AlCl}_3$. The maximum yield and the selectivity were 74.5% and 82.9%, respectively, when $n([\text{Emim}]\text{Cl}-$

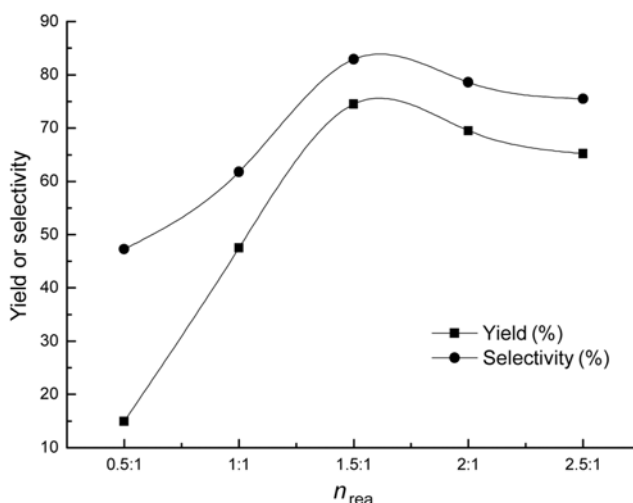


Fig. 2. Effects of molar ratio of reactants on the alkylation of anthracene to 2-isopropylanthracene.

$N=0.67$, $n([\text{Emim}]\text{Cl}-\text{AlCl}_3) : n(\text{anthracene}) = 4 : 1$, $T=30^\circ\text{C}$, $t=4$ h

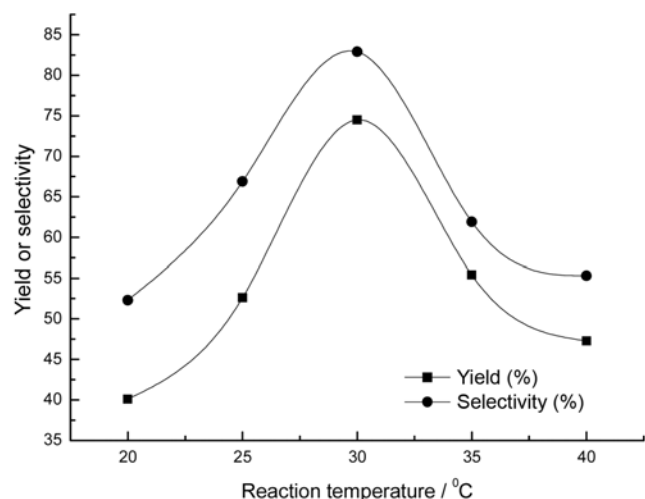


Fig. 3. Effect of reaction temperature on the alkylation of anthracene to 2-isopropylanthracene.

$N=0.67$, $n_{\text{red}}=1.5:1$, $n([\text{Emim}]\text{Cl}-\text{AlCl}_3) : n(\text{anthracene})=4:1$, $t=4$ h

$\text{AlCl}_3) : n(\text{anthracene})=4:1$.

2-3. Effect of Molar Ratio of 2-Chloropropane to Anthracene

Fig. 2 shows the results at various mole ratios of 2-chloropropane to anthracene (n_{red}) from 0.5 : 1 to 2.5 : 1. It was found that the activity was influenced dramatically by the change of n_{red} . The yield and selectivity of 2-isopropylanthracene were significantly improved with increasing the molar ratio 2-chloropropane to anthracene from 0.5 : 1 to 1.5 : 1, then the yield and the selectivity decreased as further increasing the mole ratios from 1.5 : 1 to 2.5 : 1 due to side reactions because of the superfluous alkylation reagent. The molar ratio of 2-chloropropane to anthracene of 1.5 : 1 favors the formation of 2-isopropylanthracene.

2-4. Effects of Reaction Temperature and Reaction Time

The effect of reaction temperature on both yield and selectivity of 2-isopropylanthracene was investigated at reaction temperatures ranging from 20 to 40 °C (Fig. 3). The results show that the yield and selectivity of 2-isopropylanthracene rapidly increased with increasing the reaction temperature from 20 to 30 °C. However, as a result of the exothermic nature of the reaction, an obvious decrease in yield and selectivity of the desired product took place when the reaction temperature was further raised. The suitable reaction temperature was 30 °C.

The effect of reaction time was studied in a range of 2–6 h. The results show that increasing the reaction time from 2 to 4 h caused a noticeable increase in the yield and selectivity of 2-isopropylanthracene; then the yield and the selectivity decreased as further decreasing the reaction time from 4 to 6 (Fig. 4). This is because Friedel-Crafts alkylation is a reversible electrophilic substitution reaction. In the initial stage of the reaction, 9-isopropylanthracene was the predominant product because the 9-position in anthracene has maximum electron cloud density. However, with the prolongation of reaction time, as a result of thermodynamic control of the reaction, 2-isopropylanthracene became the superior product because of its most stable structure. But bis-substituted and polysubstituted alkyanthracenes were also produced while the reaction time was further prolonged. Therefore, the yield and selectivity of 2-isopropyl-

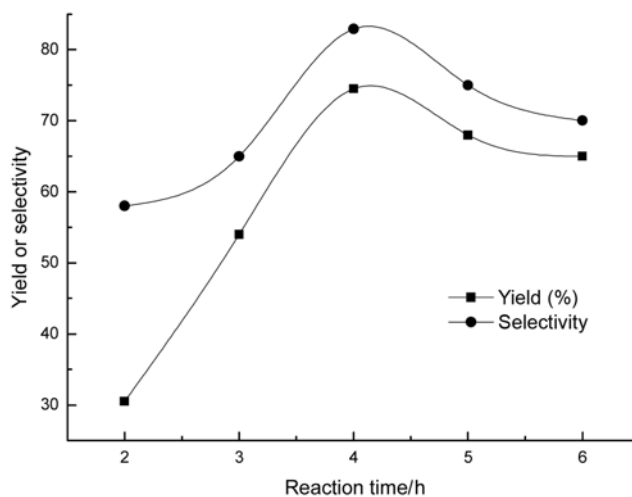


Fig. 4. Effect of reaction time on the alkylation of anthracene to 2-isopropylanthracene.

$N=0.67$, $n_{\text{red}}=1.5:1$, $n([\text{Emim}]\text{Cl}-\text{AlCl}_3) : n(\text{anthracene})=4:1$, $T=30$ °C

anthracene were decreased after reaction for 4 h.

3. Reusability of $[\text{Emim}]\text{Cl}-\text{AlCl}_3$

As one of the most active Lewis acidic IL catalysts, $[\text{Emim}]-\text{AlCl}_3$ was selected to investigate the possibility of reusability. After reaction, the reaction mixtures became two liquid phases, being organic phase (unreacted reactants and products phase) and the $[\text{Emim}]\text{Cl}-\text{AlCl}_3$ IL phase. $[\text{Emim}]\text{Cl}-\text{AlCl}_3$ was reused after extracting the organic phase with ether and treated under vacuum (0.01 Torr) at 80–100 °C for 30 min. The results of the alkylation catalyzed by the recycled $[\text{Emim}]/\text{AlCl}_3$ are shown in Fig. 5.

After the $[\text{Emim}]\text{Cl}-\text{AlCl}_3$ catalyst ran six times, the yield and selectivity of 2-isopropylanthracene were only slightly lowered as compared to the fresh catalyst. Although the amount of IL used is much higher than the reactants, the result of the recycled use indicates that the actual consumption of $[\text{Emim}]\text{Cl}-\text{AlCl}_3$ in synthe-

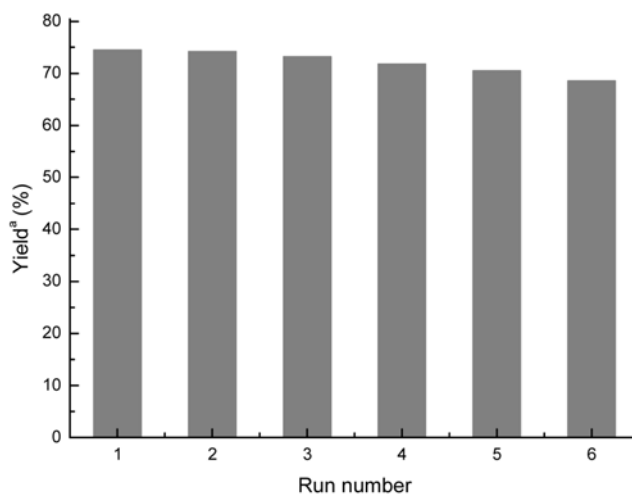


Fig. 5. Catalytic activity of the spent $[\text{Emim}]\text{Cl}-\text{AlCl}_3$ catalyst in synthesis of 2-isopropylanthracene.

$N=0.67$, $n_{\text{red}}=1.5:1$, $n([\text{Emim}]\text{Cl}-\text{AlCl}_3) : n(\text{anthracene})=4:1$, $T=30$ °C, $t=4$ h

sis of 2-isopropylanthracene has relatively less amount. The present study shows that [Emim]Cl-AICl₃, as a recoverable catalyst and solvent, is not only environmentally benign but also economical for alkylation of anthracene to 2-isopropylanthracene.

CONCLUSIONS

We successfully developed an efficient and eco-friendly Friedel-Crafts alkylation route for the synthesis of 2-isopropylanthracene using Lewis acidic IL as both catalyst and solvent under mild conditions. [Emim]Cl-AICl₃ IL exhibited the highest catalytic activity among five used ILs. The product and [Emim]Cl-AICl₃ IL were easily separated. [Emim]Cl-AICl₃ IL showed stable catalytic activity after running 6 times. The use of [Emim]Cl-AICl₃ IL in the alkylation provides a better and practical alternative to the existing procedures.

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