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Fe₃O₄@SiO₂ supported aza-crown ether complex cation ionic liquids: preparation and applications in organic reactions†

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A series of aza-crown ether ionic liquids supported on magnetic Fe₃O₄@SiO₂ core–shell particles were designed, synthesized and characterized by elemental analysis, TEM, TG and FT-IR. These new aza-crown ether complex cation ionic liquids were utilized as heterogeneous acidic catalysts in Friedel–Crafts alkylation and Hantzsch reaction in good yields under convenient reaction conditions. Moreover, these magnetic particle supported IL catalysts could be readily recovered by an external magnet and reused five times without obvious loss of activity.

Introduction

Ionic liquids composed entirely of ions have received much attention since they can be functionalized to be catalysts in light of their specific properties and various purposes.[1–3] Although thousands of ILs have been fabricated over the past decades, they commonly consisted of quaternary ammonium, *N,N'*-dialkylimidazolium and *N*-alkylpyridinium cations.[4,5] Differing from these traditional ionic liquids, a series of novel crown ether complex cation ionic liquids were defined and applied to different organic reactions in 2011.[6] Recently, a range of aza-crown ether complex cation ionic liquids, Brønsted and Lewis acidic aza-crown ether complex cation ionic liquids have been reported.[7–9] Those ionic liquids have been utilized in different organic reactions, such as Henry, Michael addition, Biginelli, and Mannich reaction *etc.* Nonetheless they couldn't be recycled conveniently as homogeneous catalysts. By transforming from a homogeneous catalyst to a heterogeneous catalyst, they could be immobilized to overcome this issue.[10]

In accordance with the principles of green chemistry, the researches on the area of separable, reusable, non-toxic, low-cost, and insoluble catalysts have become more and more important in chemistry. Design and preparation of more efficient and stable catalysts has been a main goal for chemists in organic synthesis based on environmental and economic consideration.[11–13] Ionic liquids are these kinds of catalysts

possessing green and environmentally benign features. Recently, the immobilization of structurally well-devised ionic liquids has been proven to be an effective approach to solve the problems of catalyst leaching and product extracting from ionic liquids.[14,15] Moreover, the magnetic nanoparticles (MNPs) as excellent supporters for ionic liquids have been well investigated because of their easy synthesis and functionalization, high surface area and facile separation under a magnetic field instead of traditional supporters.[16] Although unmodified MNPs have these advantages, they aggregate into large clusters in terms of their anisotropic dipolar attraction leading to deleterious effect on their properties. A suitable protection of silica layers can be coated onto the surfaces of nanoparticles to prevent their aggregation.[17,18] For instance, *N*-methyl-imidazolium chloride ionic liquids are bonded by covalently immobilizing onto the surfaces of SiO₂ by reaction of alkoxysilyl groups with hydroxyl groups of the surfaces.[19,20]

According to the understanding aforementioned, we have fabricated a series of magnetically separable aza-crown ether complex cation ionic liquids. In this work, the crown ether ionic liquids were also immobilized onto the interfaces of magnetic core–shell particles Fe₃O₄@SiO₂ by forming C–N bond between the nitrogen atom of the aza-crown ether and the carbon atom of carriers. Comparing with homogeneous acid catalysts, such as H₂SO₄, HF, and H₃PO₄, generally used by chemists in industrial catalytic processes, these new heterogeneous catalysts exhibited a good acidity and could be separated from the final products without a requirement of neutralization.

Indoles and their derivatives are known as an important class of heterocyclic compounds in pharmaceutical as well as synthetic chemistry.[21–24] The most ubiquitous alkaloids are based on the indole moiety. Particularly bisindolylmethanes (BIMs) are widely existed in various natural products and exhibit a wide range of biological activities including anticancer activity against several cancer cell lines.[25,26] Bisindolylmethanes

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have been commonly prepared by reactions of indoles with various aldehydes or ketones in the presence of either Brønsted or Lewis acids.[27–29] Herein, the supported aza-crown ether complex cation ionic liquid containing [HSO_4^-] was applied to the Friedel–Crafts alkylation reaction as a good heterogenous catalyst.

Classical Hantzsch reaction provides a convenient method to approach 1,4-dihydropyrimidines (1,4-DHPs) as scaffold in useful drugs[30,31] from 1,3-dicarbonyl compounds, aldehydes and ammonia in acetic acid at room temperature or in alcohols under refluxing for a long time.[32,33] However, these methodologies still suffer from some drawbacks.[34–37] In this context, the heterogeneous catalysts of supported aza-crown ether complex cation ionic liquid containing counter anion of [BF_4^-] can smoothly initiate this traditional reaction.

Experimental

General

All reagents were obtained from commercial resources and used without further purification. Elemental analyses were carried out on a Carioel elemental analyzer. FT-IR spectra were recorded on a Nicolet Fourier-transform infrared spectrometer (NEXUS 670) using a KBr pallet in the range of 400–4000 cm^{-1}. TEM images were photographed on a field emission transmission electron microscope (Tecnai-G2-F30). Thermal gravimetric (TG) analyses were measured on a Linseis STA PT 1600 thermoanalyzer. The analyses were carried out in N_2 atmosphere from room temperature to 800 °C with a heating rate of 10 °C min^{-1}. The synthetic route for the magnetic core–shell particle supported aza-crown ether complex cation ionic liquids was illustrated in Scheme 1.

Preparation of catalysts

Synthesis of Fe_3O_4 particles. The magnetic particles of Fe_3O_4 were prepared through a solvothermal reaction.[11] Briefly, 2.70 g of $FeCl_3 \cdot 6H_2O$ and 7.20 g of sodium acetate were dissolved in 100 mL of ethylene glycol under magnetic stirring. The obtained homogeneous yellow solution was transferred to a Teflon-lined stainless-steel autoclave and sealed to heat at 200 °C for 8 h. After completion, the autoclave was cooled down to room temperature. The obtained black magnetite particles were washed with ethanol for 6 times, and then dried in vacuum at 60 °C for 12 h.

Synthesis of $Fe_3O_4@SiO_2$ microspheres. Typically, 200 mg of the prepared Fe_3O_4 MNPs were dispersed in a mixture of 320 mL of ethanol and 80 mL of distilled water by ultrasonication for 15 min. After adding 12 mL of ammonia solution (25%) to the mixture under continuous mechanical stirring, 1.2 mL of tetraethyl orthosilicate (TEOS) was added dropwise. The reaction was then allowed to proceed at 40 °C for 3 h. The solid products were collected using an external magnetic bar, rinsed with water and ethanol, dried in a vacuum drying oven at 60 °C for 6 h.[38]

γ-Chloropropyltrimethoxysilane supported on $Fe_3O_4@SiO_2$. After dispersing $Fe_3O_4@SiO_2$ and γ-chloropropyltrimethoxysilane (weight ratio 1 : 1) into dehydrated toluene, the mixture was refluxed for 48 h under argon. When the reaction was completion, toluene was removed from mixture by a distillation under reduced pressure, and the excess γ-chloropropyltrimethoxy-silane was removed by washing with anhydrous ethanol several times. The modified magnetic particles were then dried in vacuum at 60 °C for 12 h.

Aza-18-crown-6 immobilized on $Fe_3O_4@SiO_2$. 1.00 g obtained product 3, 0.848 g (8 mmol) anhydrous Na_2CO_3 and 13 mg (0.08 mmol) KI were added in sequence to a toluene solution of 0.21 g (0.8 mmol) aza-18-crown-6. The resulting mixture was refluxed for 24 h under argon.[39] After cooling to room temperature, the catalysts were separated from the liquid phase by an external magnetic bar. The solid products were isolated by evaporating the solvent under reduce pressure, washed with water, anhydrous ethanol and dichloromethane several times, and then dried in vacuum at 60 °C for 12 h.

Aza-crown ether complex cation ionic liquids on $Fe_3O_4@SiO_2$. To a solution of 4 (1.00 g, 0.45 mmol), 10 mL H_2O, 10 mL THF, 78 mg $KHSO_4$ (0.45 mmol), and 0.45 mL H_2SO_4 (1 mol L^{-1}) were added in sequence. The obtained solution was then stirred for 24 h at room temperature. The excess THF and water was evaporated under reduced pressure. The desired product 5a was obtained by drying at 80 °C under vacuum for 12 h.
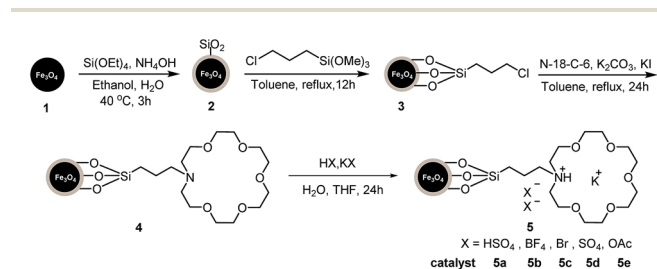
The synthesis methods of other magnetic particle supported aza-crown ether complex cation ionic liquids (5b–5e) are very similar to magnetic particle supported aza-crown ether complex cation ionic liquid 5a.

General procedure for the synthesis of bisindolylmethanes

Aldehyde (1.00 mmol), indole (2.00 mmol, 0.2343 g) and catalyst 5a (0.1 mmol, 0.2222 g) were added in 2 mL solvent. The mixture was stirred at 30 °C for appropriate time. The reaction was monitored by TLC. After completion, catalyst 5a was separated by an external magnet from reaction mixture, washed with 3 × 5 mL CH_2Cl_2. After evaporating solvent, the residue was then purified by a flash column chromatography (eluent: petroleum ether/ethyl acetate) yielding target product. To examine the reusability of catalyst, the recovered 5a was dried at 60 °C in a vacuum dry oven for the next cycle.

General procedure for the Hantzsch reaction

Aldehyde (1 mmol), ethyl acetoacetate (3 mmol, 0.38 mL), ammonium acetate (1 mmol, 0.0771 g) and catalyst 5b (0.1 mmol, 0.2222 g) were added to ethanol (2 mL) and heated to

Scheme 1 Synthetic route for the magnetic core−shell particle supported aza-crown ether complex cation ionic liquids.

reflux for 2 h. The reaction was monitored by TLC. The mixture was cooled down to room temperature when aldehyde was disappeared. Catalyst **5b** was recovered by an external magnet. The solvent was evaporated under reduced pressure to yield the crude product, which was then purified by flash column chromatography (eluent: petroleum ether/ethyl acetate). To examine the reusability of catalyst, the recovered catalyst **5b** was dried at 60 °C in vacuum for the next cycle.

Results and discussion

The magnetic nano-particles Fe_3O_4 (**1**), SiO_2 coated core–shell particles $Fe_3O_4@SiO_2$ (**2**), silane modified particles (**3**), aza-crown ether functionalized particles (**4**) and magnetic core–shell particle supported aza-crown ether metal complex ionic liquids (**5**) were successfully fabricated step by step (*vide infra* Scheme 1). The TEM of catalyst **5a** are illustrated in Fig. 1 and verify the core–shell structure of particles. The related mapping pictures demonstrate that the distributions of C, N, O, S, Si, and Fe elements are well arranged (Fig. 2). The crystal faces (111) and (311) of Fe_3O_4 can be seen in the HRTEM picture (Fig. S8†). The elemental analyses of particles **3**, **4** and catalyst **5a** are summarized in Table 1. The percentage of 3.96% carbon and 0.85% hydrogen clearly indicate that silanes are successfully hybridized onto particles **3**. The percentage of 0.64% nitrogen in particles **4** shows that the aza-crown ethers are introduced in the particles *via* a covalent bond of C–N. The percentage of 2.85% sulfur in catalyst **5a** demonstrates that equivalent moles

Table 1 The elemental analyses of nanoparticle **3**, **4**, **5a**

| Entry | Substance | Elemental analyses (%) | | | | Organic component (mmol g^{-1}) |
		S	N	C	H	
1	**3**	—	—	3.96	0.85	1.10
2	**4**	—	0.63	12.53	2.22	0.45
3	**5a**	2.84	0.62	12.45	2.15	0.44
4	**5a**	2.55	0.61	12.76	2.19	0.40^a

^{a} Catalyst **5a** after five times reuse in Friedel–Crafts alkylation.

of H_2SO_4 and chelates $KHSO_4$ are really penetrated into the aza-crown ether skeleton, in which, the loading is 0.44 mmol of aza-crown ether complex cation ionic liquids on per gram magnetic supporters of $Fe_3O_4@SiO_2$.

In Fig. S1,† IR band around 570 and 475 cm^{-1} are attributed to characteristic vibrations of Fe–O bands in all samples. When SiO_2 particles are coated to Fe_3O_4 particles producing core–shell particles of $Fe_3O_4@SiO_2\cdot$**2**, a very strong band around 1100 cm^{-1} and a wide weak band of 3430 cm^{-1} should be assigned to the stretching vibration of Si–O–Si and Si–OH bonds, respectively. The peak at 2957 cm^{-1} significantly belongs to stretching vibrations of C–H in alkyl group of **3**. When the aza-crown ether is combined with organic silane in particles **4**, and **5a**, the S=O stretching vibrations[40] is close to the Si–O field at 1000–1150 cm^{-1} leading to a slight change of the peak. The peak at 619 cm^{-1} in fingerprint region of **5a** is attributed to the bending vibration of S=O bonds. A new medium band in the range of 1635 cm^{-1} should be the combination peak of 587 and 1105 cm^{-1} in catalyst **5a**.

The thermal properties of the catalysts **5a** and **5b** are determined by TG analyses and the results are illustrated in Fig. S1 and S2.† Generally, the decomposition points of catalysts are up
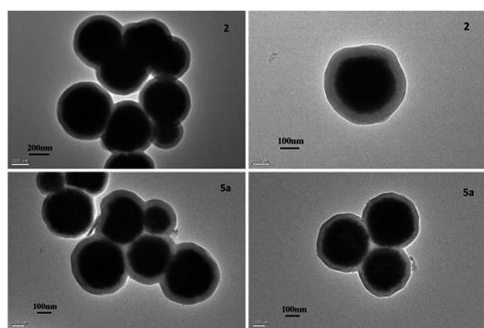

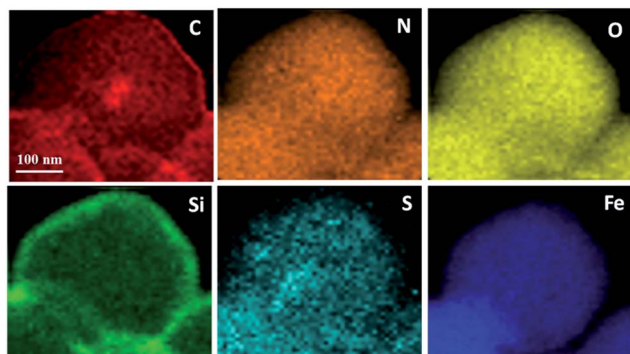**Fig. 1** TEM of $Fe_3O_4@SiO_2$ (**2**) and catalyst **5a**.

Fig. 2 The mapping of **5a**.

Table 2 Screening of catalysts in the reaction of benzaldehyde and indole^a

Entry	Catalyst	Solvent	Yield^b (%)
1	**5a**	CH_3OH	92
2	**5a**	CH_2Cl_2	82
3	**5a**	C_2H_5OH	86
4	**5a**	CH_3CN	89
5	**5b**	CH_3OH	Trace
6	**5c**	CH_3OH	10
7	**5d**	CH_3OH	26
8	**5e**	CH_3OH	41
9	$Fe_3O_4@SiO_2$	CH_3OH	NA

^{a} Reaction conditions: indole 2.0 mmol, benzaldehyde 1.0 mmol, catalyst **5a** 0.1 mmol, solvent 2 mL, 30 °C, 1.5 h. ^{b} Isolated yield.
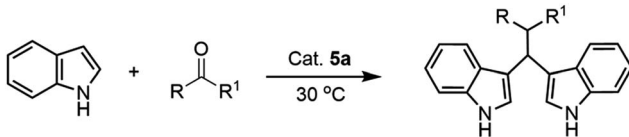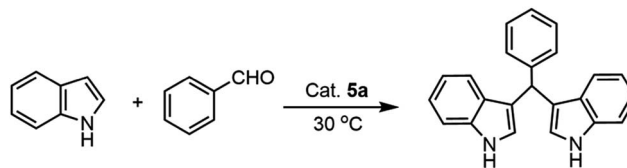
Table 3 Reaction of aldehydes with indole over catalyst **5a**[a]

| Entry	R	R1	Time/h	Yield[b] (%)
1	2-NO$_2$C$_6$H$_4$	H	1	90
2	3-NO$_2$C$_6$H$_4$	H	1	92
3	4-NO$_2$C$_6$H$_4$	H	1	95
4	3-ClC$_6$H$_4$	H	1	92
5	4-ClC$_6$H$_4$	H	1	93
6	4-BrC$_6$H$_4$	H	1	95
7	2-CH$_3$OC$_6$H$_4$	H	1	91
8	3-CH$_3$OC$_6$H$_4$	H	1	95
9	4-CH$_3$C$_6$H$_4$	H	1	93
10	4-OHC$_6$H$_4$	H	0.5	96
11	CH$_3$CH$_2$CH$_2$	H	3	88
12	CH$_3$(CH$_2$)$_4$CH$_2$	H	3	89
13	R + R1: CH$_2$(CH$_2$)$_3$CH$_2$		3	85
14	C$_6$H$_5$	CH$_3$	3	81

[a] Reaction conditions: indole 2.0 mmol, substrate 1.0 mmol, catalyst **5a** 0.1 mmol, methanol 2 mL, r.t. [b] Isolated yield.

to 235 °C shown their good stability. The 14% weight losses of catalysts appeared between 230 °C and 400 °C is assigned to the decomposition of aza-18-C-6 component.

In our previous studies, we have reported the use of an acidic Brønsted ionic liquids aza-[18-C-6KH][HSO$_4$]$_2$ as an homogeneous catalyst for the synthesis of bis-indolylmethanes in good to excellent yields.[8] In this work, aza-crown ether complex cation ionic liquids are immobilized on the surfaces of Fe$_3$O$_4$@SiO$_2$ particles as heterogeneous catalysts for the synthesis of bis-indolylmethanes. The results are summarized in Table 2. Initially, the catalyst **5a–e** are demonstrates various activities in this Friedel–Crafts alkylation reaction, in which, **5a** with a Brønsted anion of HSO$_4^-$ reveals the better activity than **5b–e** (Table 2 entries 1–4 vs. 5–8). In contrast, a blank reaction is carried out using a silica coated magnetic particles Fe$_3$O$_4$@SiO$_2$ as catalyst and showing no activity in the absence of aza-crown ether complex cation ionic liquids (Table 2, entry 9). In addition, different solvents are also screened (Table 2, entries 1–4), which the methanol is evidently the optimal solvent. As comparison, the traditional imidazole cation ionic liquid can only achieved a Friedel–Crafts alkylation reaction in 31% yield.[41]

Under the optimized reaction conditions, this Friedel–Crafts alkylation reaction is then extended to different substrates (Table 3). It can be seen that excellent yields are obtained from a variety of aldehydes. Obviously, both the electron-withdrawing groups and the electron-donating groups of aromatic aldehydes have no negative effects on this reaction (Table 3, entries 1–10). Aliphatic aldehydes and ketones can also take place this reaction under mild conditions in good yields (Table 3, entries 11–14).

A plausible mechanism for this Friedel–Crafts alkylation reaction in the presence of supported ILs is proposed and is
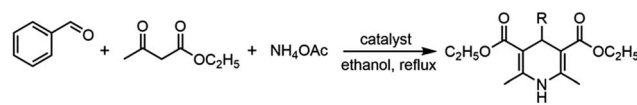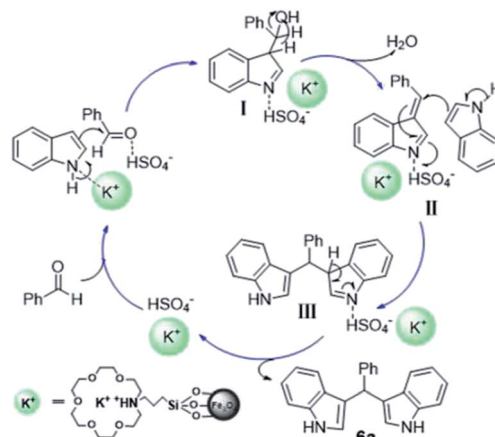

Scheme 2 Proposed mechanism for Friedel–Crafts alkylation catalysed by IL.

similar to our previous report[9] (Scheme 2). First, the carbonyl group of the aldehyde is activated by the anion [HSO$_4$]$^-$ and attacked by a molecule of indole to generate intermediate I. After the loss of H$_2$O to afford intermediate II, it is attacked by another molecule of indole to afford intermediate III. The bis(indolyl)methane 6 is finally formed with the leaving of cation [18C-6K]$^+$. Meanwhile, the catalyst of ionic liquid [18-C-6K][HSO$_4$] is regenerated for the next catalytic cycle.

As a continuation studies of the application of crown ether complex cation IL in organic reactions, we report in this article a novel and efficient synthesis of dihydropyridines by a classical Hantzsch reaction using supported aza-crown ether complex cation ionic liquids as catalysts under mild conditions. After screening different catalysts (Table 4, entries 1–5), the catalysts **5a** and **5b** shown better catalytic activities than other catalysts because that **5a** is acidic and able to activate the carbonyl group; BF$_4^-$ in **5b** has more affinity with ammonium group than the others. As comparison, the blank experiment was carried out and gave 48% yield in the present of carriers Fe$_3$O$_4$@SiO$_2$ (Table 4, entry 6). When the ratio of benzaldehyde (BA) : ethyl acetoacetate (EAAT) : ammonium acetate (AAT) was 1 : 3 : 1, the
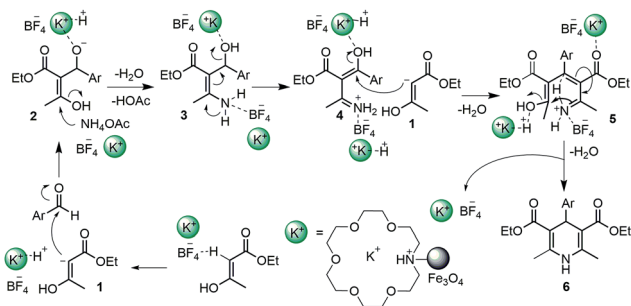
Table 4 Screening of catalysts in Hantzsch reaction[a]

Entry	Catalyst	Yield[b] (%)
1	**5a**	83
2	**5b**	92
3	**5c**	58
4	**5d**	65
5	**5e**	61
6	Fe$_3$O$_4$@SiO$_2$	48

[a] Reaction conditions: EAAT 3.0 mmol, BA 1.0 mmol, AAT 1.0 mmol, catalyst 0.1 mmol, ethanol 2 mL, reflux, 2 h. [b] Isolated yield.

Scheme 3 Proposed mechanism for the formation of 1,4-DHP compounds.

Fig. 3 Recycling results: **5a** in Friedel–Crafts alkylation (**1**), **5b** in Hantzsch reaction (**2**).

Table 5 Hantzsch reaction over catalyst **5b**[a]

Entry	R	Yield[b] (%)	Entry	R	Yield (%)
1	C_6H_5	92	11	3-$CH_3OC_6H_5$	85
2	C_6H_5	53[c]	12	4-$CH_3OC_6H_4$	82
3	2-$NO_2C_6H_4$	88	13	2,5-$CH_3OC_6H_4$	74
4	3-$NO_2C_6H_4$	95	14	4-HOC_6H_4	80
5	4-$NO_2C_6H_5$	96	15	4-OH-3-$CH_3OC_6H_4$	71
6	4-ClC_6H_4	93	16	Furfural	96
7	2,4-ClC_6H_4	92	17	Picolinaldehyde	72
8	4-BrC_6H_4	90	18	Cinnamaldehyde	94
9	4-$CH_3C_6H_4$	86	19	Citral	88
10	2-$CH_3C_6H_4$	85	20	Butylaldehyde	61

[a] Reaction conditions: BA 1.0 mmol, EAAT 3.0 mmol, AAT 1.0 mmol, catalyst **5b** 0.1 mmol, ethanol 2 mL, reflux, 2 h. [b] Isolated yield. [c] Temperature 40 °C.

highest yield of 92% could be obtained using **5b** as catalyst (Table 4, entry 2).

It can be explained by a proposed mechanism depicted in Scheme 3.[42] Initially, ethyl acetoacetate might be activated by BF_4^- anion to form an enolate anion **1** that attacks benzaldehyde to produce intermediate **2**. Under aid of IL catalyst, ammonium acetate reacts with **2** generating intermediated **3** accompanying with the loss of water and HOAc. The intermediated **3** can be then transformed by **4** that is immediately attacked by **1** to produce intermediate **5**. The target product **6** is then obtained by an intramolecular cyclization of **5** in the presence of ILs. We can see that the excessive amount of ethyl acetoacetate could promote increase of intermediate **2** as well as **5** to enhance better yield.

To extend the scope of this reaction, a variety of substituted aldehydes were investigated under the optimal conditions. The results are listed in Table 5. It can be seen that the substituted aromatic aldehydes and olefin aldehydes can generate the target products readily (Table 5, entries 1–17). When the temperature was decreased from reflux to 40 °C, the yield deceased obviously due to low activity of benzaldehyde (Table 5, entry 2). The aromatic aldehydes bearing electro-withdrawing group were superior to this reaction than that with electron-donating group (Table 5, entries 3–5 *vs.* 9–15) since the electron-donating group in aldehyde could stabilized intermediate **2**. In contrast, the *n*-butylaldehyde gave the worst yield of 61%.
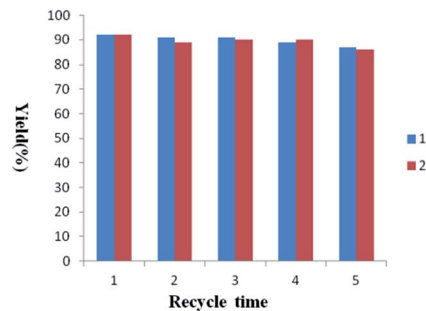
The catalyst recovery was quite simple. Upon completion of the reaction, the solid catalyst was easily recovered by an external magnetic bar. The catalytic activities of recycling catalysts of **5a** and **5b** were both investigated and illustrated in Fig. 3. The yields decreased slightly after five times reuse which could be attributed to the loss of anion that was confirmed by elemental analysis of used catalyst due to washing (Table 1, entry 4). The TEM of used catalyst **5a** manifests that the core–shell structure of nano-particles is stable (Fig. S9†).

Conclusions

In summary, we devised and synthesized a series of aza-crown ether complex cation ionic liquids supported by $Fe_3O_4@SiO_2$. Compared with crown ether complex cation ionic liquids, the new supported ionic liquids have protons enabling the catalytic activity of the cations and can increase effectively the electrophilicity of the carbonyl. Then we investigated their applications in Friedel–Crafts alkylation and Hantzsch reaction. The magnetic core–shell nano-particle $Fe_3O_4@SiO_2$ supported ILs not only achieved good yields in these reactions, but also can be reused for at least five times by magnetic separation conveniently without significant loss of catalytic activity. Further discoveries on the applications of these supported aza-crown ether complex cation ionic liquids are underway in our laboratory.

Acknowledgements

Notes and references

1 H. Li, P. S. Bhadury, B. Song and S. Yang, *RSC Adv.*, 2012, **2**, 12525–12551.

2 H. Olivier-Bourbigou, L. Magna and D. Morvan, *Appl. Catal., A*, 2010, **373**, 1–55.

3 Z. S. Qureshi and K. M. Deshmukh, *Clean Technol. Environ. Policy*, 2014, **16**, 1487–1513.

4 S. Udayakumar, S. W. Park, D. W. Park and B. S. Choi, *Catal. Commun.*, 2008, **9**, 1563–1570.

5 X. X. Zheng, S. Z. Luo, L. Zhang and J. P. Cheng, *Green Chem.*, 2009, **11**, 455–458.

6 Y. Y. Song, H. W. Jing, B. Li and D. S. Bai, *Chem.–Eur. J.*, 2011, **17**, 8731–8738.

7 Y. Y. Song, C. Cheng and H. W. Jing, *Chem.–Eur. J.*, 2014, **20**, 12894–12900.

8 C. Cheng and H. W. Jing, *RSC Adv.*, 2014, **4**, 34325–34331.

9 Y. Liang, J. Wang, C. Cheng and H. Jing, *RSC Adv.*, 2016, **6**, 93546–93550.

10 B. W. Xin and J. C. Hao, *Chem. Soc. Rev.*, 2014, **43**, 7171–7187.

11 A. Q. Wang, X. Liu, Z. X. Su and H. W. Jing, *Catal. Sci. Technol.*, 2014, **4**, 71–80.

12 D. S. Bai, Q. Wang, Y. Y. Song, B. Li and H. W. Jing, *Catal. Commun.*, 2011, **12**, 684–688.

13 H. W. Jing, X. M. Wang, Y. Liu and A. Q. Wang, *Chin. J. Catal.*, 2015, **36**, 244–251.

14 J. H. Ji, P. H. Zeng, S. F. Ji, W. Yang, H. F. Liu and Y. Y. Li, *Catal. Today*, 2010, **158**, 305–309.

15 D. D. Shao, K. K. Xu, X. J. Song, J. H. Hu, W. L. Yang and C. C. Wang, *J. Colloid Interface Sci.*, 2009, **336**, 526–532.

16 Y. H. Deng, D. W. Qi, C. H. Deng, X. M. Zhang and D. Y. Zhao, *J. Am. Chem. Soc.*, 2008, **130**, 28–29.

17 D. W. Kim and D. Y. Chi, *Angew. Chem., Int. Ed.*, 2004, **43**, 483–485.

18 A. Riisager, P. Wasserscheid, R. van Hal and R. Fehrmann, *J. Catal.*, 2003, **219**, 452–455.

19 T. Selvam, A. Machoke and W. Schwieger, *Appl. Catal., A*, 2012, **445–446**, 92–101.

20 L. Zhu, D. Pan, L. Ding, F. Tang, Q. L. Zhang, Q. Liu and S. Z. Yao, *Talanta*, 2010, **80**, 1873–1880.

21 Z. Y. Lu, J. Dai, X. N. Song, G. Wang and W. S. Yang, *Colloids Surf., A*, 2008, **317**, 450–456.

22 T. Sasaki, M. Tada, C. M. Zhong, T. Kume and Y. Iwasawa, *J. Mol. Catal. A: Chem.*, 2008, **279**, 200–209.

23 M. V. Khedkar, T. Sasaki and B. M. Bhanage, *ACS Catal.*, 2013, **3**, 287–293.

24 T. P. Pathak, J. G. Osiak, R. M. Vaden, B. E. Welm and M. S. Sigman, *Tetrahedron*, 2012, **68**, 5203–5208.

25 K. R. M. Naidu, S. I. Khalivulla, S. Rasheed, S. Fakurazi, P. Arulselvan, O. Lasekan and F. Abas, *Int. J. Mol. Sci.*, 2013, **14**, 1843–1853.

26 D. K. Sharma, A. K. Tripathi, R. Sharma, R. Chib, R. U. Rasool, A. Hussain, B. Singh, A. Goswami, I. A. Khan and D. Mukherjee, *Med. Chem. Res.*, 2014, **23**, 1643–1653.

27 T. Abe, S. Nakamura, R. Yanada, T. Choshi, S. Hibino and M. Ishikura, *Org. Lett.*, 2013, **15**, 3622–3625.

28 A. S. Azmi, A. Ahmad, S. Banerjee, V. M. Rangnekar and R. M. Mohammad, *Pharm. Res.*, 2008, **25**, 2117–2124.

29 D. K. Sharma, B. Rah, M. R. Lambu, A. Hussain, S. K. Yousuf, A. K. Tripathi, B. Singh, G. Jamwal, Z. Ahmed, N. Chanauria, A. Nargotra, A. Goswami and D. Mukherjee, *MedChemComm*, 2012, **3**, 1082–1091.

30 M. L. Deb and P. J. Bhuyan, *Tetrahedron Lett.*, 2006, **47**, 1441–1443.

31 C. Velázquez and E. E. Knaus, *Bioorg. Med. Chem.*, 2004, **12**, 3831–3840.

32 S. V. Nadkarni, M. B. Gawande, R. V. Jayaram and J. M. Nagarkar, *Catal. Commun.*, 2008, **9**, 1728–1733.

33 P. R. Singh, D. U. Singh and S. D. Samant, *Synth. Commun.*, 2005, **35**, 2133–2138.

34 Y. L. Chen, K. C. Fang, J. Y. Sheu, S. L. Hsu and C. C. Tzeng, *J. Med. Chem.*, 2001, **44**, 2374–2377.

35 J. P. Wan and Y. Y. Liu, *RSC Adv.*, 2012, **2**, 9763–9777.

36 J. E. Biggs-Houck, A. Younai and J. T. Shaw, *Curr. Opin. Chem. Biol.*, 2010, **14**, 371–382.

37 L. M. Wang, J. Sheng, L. Zhang, J. W. Han, Z. Y. Fan, H. Tian and C. T. Qian, *Tetrahedron*, 2005, **61**, 1539–1543.

38 G. Sabitha, G. S. K. K. Reddy, C. S. Reddy and J. S. Yadav, *Tetrahedron Lett.*, 2003, **44**, 4129–4131.

39 S. Ko, M. N. V. Sastry, C. C. Lin and C. F. Yao, *Tetrahedron Lett.*, 2005, **46**, 5771–5774.

40 C. S. Reddy and M. Raghu, *Chin. Chem. Lett.*, 2008, **19**, 775–779.

41 M. Cai and X. Wang, *Asian J. Chem.*, 2015, **27**(2), 649–653.

42 X. Z. Liang, *Ind. Eng. Chem. Res.*, 2014, **53**, 17325–17332.