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Introduction

Aromatic ketones can be used in the synthesis of spices, dyes, pharmaceuticals and agrochemicals,¹⁻⁵ which were important fine chemical and pharmaceutical intermediates. Friedel-Crafts acylation was one of the important reactions of synthetic aromatic ketones,^{2,6-8} which was widely used because of its simple reaction and high selectivity. The acylation reactants were generally acyl halides or anhydrides that were introduced through electrophilic substitution reactions in aromatic rings to produce aromatic ketones. Traditional catalysts mainly include Lewis acids⁹⁻¹¹ (such as anhydrous ZnCl₂, A1Cl₃, FeCl₃, etc.) or Brønsted acids^{5,11} (such as concentrated sulfuric acid, hydrochloric acid, etc.). However, traditional catalysts easily cause side reactions that were highly corrosive to equipment and cannot be easily recycled. The large amount of industrial wastewater produced in the reaction process easily causes environmental pollution. Therefore, the study found solid acid catalysts such as zeolite molecular sieves,^{2,12-15}

p-Toluenesulfonic acid functionalized imidazole ionic liquids encapsulated into bismuth SBA-16 as high-efficiency catalysts for Friedel–Crafts acylation reaction[†]

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Bismuth SBA-16 catalyst was synthesized by the hydrothermal method. Four kinds of *p*-toluenesulfonic acid functionalized imidazole ionic liquids were prepared by a two-step method and their molecular structures were characterized by ¹H NMR and MS. The post-synthesis impregnation method was used to functionalize the Bi(10)-SBA-16 silicon mesoporous material with the ionic liquids and the obtained materials were characterized by FT-IR, XRD, BET, XPS, and TG. The results show that the volume and pore size of SBA-16 were changed by loading Bi and ionic liquids, while the three-dimensional cubic pore structure of SBA-16 was not destroyed. The composite catalyst was evaluated in Friedel–Crafts acylation of anisole with acetic anhydride. The effects of reaction temperature and the ratio of anisole and acylating agent on the acylation of anisole were investigated by experimental design. The results showed that 1.2ILc@Bi(10)-SBA-16 was used as the catalyst, the conversion of anisole was 85.41% and the yield of aromatic ketone was 69.19% under the conditions of a reaction temperature of 100 °C, a catalyst dosage of 0.5 g, a time period of 4 h and a molar ratio of 1:1.5. After 5 recycling runs, the reduction in the overall ratio of reactant conversion and product yield did not exceed 7.5%, indicating that 1.2ILc@Bi(10)-SBA-16 has good stability.

metal oxides,4,16,17 heteropoly acids,18,19 solid superacids,8,20 ionic liquids,^{21,22} etc. Due to its high thermal stability, good electrical conductivity, and low vapor pressure reverse recovery, ionic liquids have been widely used in organic reactions, such as Friedel-Crafts alkylation, esterification, oxidation, and acetalization,^{21,22} etc. Tran et al.²³ synthesized the imidazole ionic liquid catalyst Bi(OTf)₃/[BMIM]OTf by the microwave radiation method and found that active aromatic hydrocarbons and naphthalene can be benzoylated to obtain aromatic ketones in a short reaction time. Yeung et al.²⁴ synthesized an acidic imidazoline-chloroaluminate ionic liquid that can carry out the Friedel-Crafts acylation at the C-3 position of indole at room temperature. There is no denying that these catalysts are more or less flawed. Therefore, it is necessary to develop a catalyst that is environmentally friendly, has excellent performance, and has high economic benefits.

Supported molecular sieves are a type of composite catalyst that load active components on zeolite molecular sieves,^{25–31} which can not only reduce the amounts of active components added but also maintain the characteristics of zeolite molecular sieves. Because of its low dosage, high activity and recyclability, it has high research value and application prospects.^{32–35} Recently, introducing metal or other acid functional groups into pore structures to change the properties of

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molecular sieves has become a research hotspot. Madadi et al.³⁶ prepared the Co/SBA-16 catalyst by chelating the metal complex impregnation method and applying it to the limonene aerobic epoxidation reaction, which showed high activity and stable conversion and selectivity in repeatability tests. Dai et al.³⁷ synthesized Zr-SBA-15 mesoporous molecular sieves with different Si/Zr molar ratios by the hydrothermal method and synthesized several Brønsted-Lewis acidic ionic liquid Zr-SBA-15/[mim-ps]Cl-ZnCl₂ catalysts by the impregnation method, exhibiting excellent catalytic performance in the esterification reaction of acetic acid with n-BuOH, BnOH and Naxol. However, the amount of reaction catalyst was large and the cost of using Zr salt was high. Zhang et al.³⁸ studied the esterification of oleic acid and short chain alcohol catalyzed by an acidic ionic liquid composite catalyst supported on Fe-SBA-15. The results showed that due to the synergistic effect of the Lewis and Brønsted acid centers, the catalyst exhibits high catalytic activity in esterification reactions. However, during the preparation of Fe-SBA-15, the valence state of the Fe element was unstable and the reaction conditions were harsh. Therefore, the introduction of ionic liquids into mesoporous molecular sieves or metal-doped molecular sieves can make the catalyst have excellent catalytic activity. In recent years, low-cost non-toxic bismuth compounds have been used as environmentally friendly mild Lewis acid catalyst systems in the synthesis by green chemistry.³⁹ Moreover, to the best of our knowledge, there are fewer research reports on doping bismuth into SBA-16.

p-Toluenesulfonic acid was widely used in the synthesis of medicines, pesticides, stabilizers of polymerization and catalysts for organic synthesis (ester, *etc.*), and is a strong acid slightly weaker than sulfuric acid. In this study, a Bi-doped SBA-16 mesoporous molecular sieve (Bi(*x*)-SBA-16 (x = 5, 10, and 15)) was prepared for the first time by *in situ* synthesis and four imidazole ionic liquids acidified with *p*-toluenesulfonic acid were loaded onto the mesoporous molecular sieve. Above, four composite catalysts with strong acid properties were obtained. They were applied to the acylation reaction of anisole with acetic anhydride. The effects of reaction time,

reaction temperature, catalyst dosage and the molar ratio of reactants on acylation were studied systematically.

Results and discussion

SXRD and WXRD analysis

Fig. 1 displays the small angle X-ray diffraction patterns of the carrier Bi(x)-SBA-16 (x = 5, 10, and 15) and the composite material loaded with the ionic liquids (1.2ILs@Bi(x)-SBA-16 (x = 5, 10, and 15)). As shown in Fig. 1a, the diffraction peaks of SBA-16 at 0.89°, 1.5° and 1.75° were defined as (110), (200) and (211), respectively, which were similar to that reported in the literature,⁴⁰ indicating that the synthesized mesoporous molecular sieves have ordered a three-dimensional cubic channel system. According to the Bragg diffraction equation: $n\lambda = 2d_{110}\sin\theta$, $d_{110} = 10.57$ nm was calculated, due to $a_0 = 2d_{110}/\sqrt{3}$, the cell parameter $a_0 = 12.20$ nm was further calculated (*n* represents the diffraction order, θ represents the angle between the incoming ray and the sub-ray, d represents the crystal plane spacing, and λ represents the wavelength).⁴¹ The above diffraction peaks still exist in the SXRD patterns of Bi(x)-SBA-16 (x = 5, 10, and 15), which was little different compared to those of SBA-16, indicating that the incorporation of Bi and increasing Bi dosage does not affect the mesoporous ordering of SBA-16. As can be seen from Fig. 1b, the peak strength of the composite catalyst decreased significantly when four ionic liquids were introduced into Bi(x)-SBA-16 (x = 5, 10, and 15) mesoporous materials, although it had a mesoporous structure. This may be due to the ionic liquids occupy the pore structure. The position of the diffraction peak of the (110) crystal plane shifts. Combined with the BET pore size distribution, it was speculated that the introduction of ILs may lead to the collapse of the pore channels of the molecular sieve and then lead to the increase of the pore size.⁴²

The wide-angle XRD patterns of Bi(10)-SBA-16 and 1.2ILs@Bi(10)-SBA-16 composite catalysts are shown in Fig. S1.† All samples showed a broad peak in the range of 10° to 25°, which was attributed to amorphous silica. No pure



Fig. 1 The SAXD patterns of (a) Bi(x)-SBA-16 (x = 5, 10, and 15) and (b) 1.2ILs@Bi(x)-SBA-16 (x = 5, 10, and 15) (the mass ratio of ILs to Bi(x)-SBA-16 (x = 5, 10, and 15) was 1.2).

 Bi_2O_3 phase was found in the wide-angle XRD spectrum, which indicates that the bismuth oxide can be well dispersed on the surface of the silica and cannot be detected by the wide-angle XRD spectrum.^{43,44} The high dispersibility of bismuth on the surface of silica makes the active center close to the reactant molecules during the reaction. The nature of this intermetallic compound will be determined later by XPS characterization.

N2 adsorption-desorption analysis

The N₂ adsorption-desorption isotherms of SBA-16, Bi(x)-SBA-16 (x = 5, 10, and 15) and 1.2ILs@Bi(10)-SBA-16 are shown in Fig. 2. According to IUPAC, all samples show typical type IV adsorption isotherms and have H2 type hysteresis loops, demonstrating that SBA-16 is a mesoporous material with a uniform pore size distribution, and that the introduc-

tion of Bi atom has no significant effect on the uniform pore structure of the carrier. After loading the ionic liquids, the composite catalyst exhibits the same physical properties as the carrier.

Table 1 summarizes the corresponding textural properties of all the samples, including specific surface area, average pore size and pore volume. The results show that the specific surface area, average pore size and pore volume of Bi(*x*)-SBA-16 (x = 5, 10, and 15) decreased with increasing Bi dosage. As shown in Table 1, ILc@Bi(10)-SBA-16 has the lowest specific surface area among ILs@Bi(10)-SBA-16. According to the literature,^{45,46} upon comparing the density of imidazole cation salts with different substituents, the density has a linear relationship with the length of the *N*-alkyl chain on the imidazole cation. As the organic cation becomes larger, the density of the ionic liquid becomes smaller. Compared to Bi(10)-



Fig. 2 N2 adsorption-desorption isotherms and pore size distribution of (a and b) Bi(x)-SBA-16 (x = 5, 10, and 15), (c and d) 1.2ILs@Bi(x)-SBA-16 (x = 5, 10, and 15).

Table 1 The textural properties of Bi(x)-SBA-16 (x = 5, 10, and 15) and 1.2ILs@Bi(x)-SBA-16 (x = 5, 10, and 15)

Catalyst	Surface area (BET) $[m^2 g^{-1}]$	Total pore volume [cm ³ g ⁻¹]	Pore size (BJH ads) [nm]
SBA-16	884	0.714	2.722
Bi(5)-SBA-16	852	0.691	3.170
Bi(10)-SBA-16	838	0.553	3.048
Bi(15)-SBA-16	829	0.462	2.845
1.2ILa@Bi(10)-SBA-16	353	0.228	3.499
1.2ILb@Bi(10)-SBA-16	329	0.263	3.917
1.2ILc@Bi(10)-SBA-16	256	0.279	3.853
1.2ILd@Bi(10)-SBA-16	392	0.281	3.686

SBA-16, the immobilization of ionic liquids greatly reduced the specific surface area of the composite catalyst but the average pore size was relatively increased. This may be due to the fact that the ionic liquids blocked the microporous channel (in Fig. S2,†) The pore size of Bi(10)-SBA-16 is 0.6988 nm and the pore volume is 0.08037 cm³ g⁻¹. After loaded with ionic liquids, the pore size was 0.7522 nm and the pore volume was 0.02503 cm³ g⁻¹ due to the blockage of micropores, making the overall pore size of Bi(*x*)-SBA-16 (*x* = 5, 10, and 15) larger, which further indicates that the ionic liquid has been successfully loaded on the carrier.^{35,37}

FT-IR analysis

The FT-IR spectra of all samples are illustrated in Fig. 3. As shown in Fig. 3a, the absorption peak of SBA-16 at 463 cm⁻¹ was the bending vibration peak of Si-O-Si bonds. The characteristic peaks at 805 cm⁻¹ and 1087 cm⁻¹ correspond to the symmetrical stretching vibrations and asymmetric stretching vibrations of the silicon-oxygen tetrahedron, respectively. The absorption band around 3464 cm⁻¹ corresponds to Si-OH on the surface of the molecular sieve. Compared to SBA-16, the infrared spectrum of Bi(10)-SBA-16 has undergone significant changes. The decrease in the characteristic peak intensity at 805 cm⁻¹ may be due to the formation of the Si-O-Bi bonds.⁴⁷ The absorption peak near 953 cm⁻¹ was considered as the stretching vibration of Si-OH. In the metal loaded sample, the peak was designated as the stretching vibration of the surface hydroxyl group (Si-OH) disturbed by the nearby metal species. It can also be observed from Fig. 3b that there were absorption peaks at 563 cm⁻¹ and 667 cm⁻¹ for 1.2ILs@Bi(10)-SBA-16, indicating the existence of sulfonate and hydrogen sulfonate. The para-vibration band peak of the benzene ring was at 814 cm^{-1} , which can identify *p*-toluenesulfonate. The peak at 1464 cm⁻¹ was ascribed to the vibration band of the benzene ring framework. The absorption peaks around 1539 cm⁻¹, 1657 cm⁻¹ and 3672 cm⁻¹ were caused by the stretching vibrations of C=N, C=C and C-H on the imidazole ring, respectively.48 The absorption vibration peaks of the ionic liquid and functional groups of Bi(10)-SBA-16 were observed

on the spectra of the composite catalyst, which proved that the ionic liquid was successfully compounded with the support.

SEM analysis

SEM was used to observe the particle size and particle morphology of the synthesized sample. As shown in Fig. 4b, Bi (10)-SBA-16 was composed of the aggregated nanoparticles with a size range of 30-60 nm. Similar to SBA-16 (in Fig. 4a), Bi(10)-SBA-16 has the characteristics of a spherical shape, and the particle size was relatively uniform and the surface was smooth. After the ionic liquids were encapsulated (in Fig. 4c (1.2ILa@Bi(10)-SBA-16), Fig. 4d (1.2ILb@Bi(10)-SBA-16), Fig. 4e (1.2ILc@Bi(10)-SBA- 16) and Fig. 4f (1.2ILd@Bi(10)-SBA-16)), the surface of the carrier became rough, floccus and particulate matter appeared and the morphology became irregular. However, the overall morphology and size did not change significantly, indicating that the ionic liquid has been encapsulated on the carrier. In addition, the existence and dispersion of Bi ions in Bi(10)-SBA-16 samples were studied by EDS. Fig. S3[†] shows the EDS spectra of all samples, verifying the existence of the Bi element.

TEM analysis

Fig. 5 illustrates the TEM images of SBA-16 and the composites with bismuth doped and loaded ionic liquids. Fig. 5b–f show the TEM images of SBA-16, 1.2ILa@Bi(10)-SBA-16, 1.2ILb@Bi(10)-SBA-16, 1.2ILc@Bi(10)-SBA-16 and 1.2ILd@Bi(10)-SBA-16 perpendicular to the pore axis. Upon combining with the small angle XRD and BET data, it is proved that the SBA-16 and Bi(10)-SBA-16 materials have good ordering. When compared with the carrier, the pore size of the composite catalyst obtained by loading the ionic liquid was decreased, indicating that the ionic liquid was well encapsulated in the cage structure of Bi(10)-SBA-16.

XPS analysis

Fig. 6a demonstrates X-ray photoelectron spectroscopy of SBA-16, Bi(10)-SBA-16 and 1.2ILa@Bi(10)-SBA-16. The binding energy, which can be obtained by using a curve fitting



Fig. 3 The FT-IR spectra of (a) SBA-16, Bi(10)-SBA-16 and (b) 1.2ILs@Bi(10)-SBA-16.



Fig. 4 The SEM images of (a) SBA-16, (b) Bi(10)-SBA-16, (c) 1.2ILa@Bi(10)-SBA-16, (d) 1.2ILb@Bi(10)-SBA-16, (e) 1.2ILc@Bi(10)-SBA-16, and (f) 1.2ILd@Bi(10)-SBA-16.



Fig. 5 The TEM images of (a) SBA-16, (b) Bi(10)-SBA-16, (c) 1.2ILa@Bi(10)-SBA-16, (d) 1.2ILb@Bi(10)-SBA-16, (e) 1.2ILc@Bi(10)-SBA-16, and (f) 1.2ILd@Bi(10)-SBA-16.

program, and relative strength were used to determine the types and chemical properties of each element. Fig. 6b and c show the high-resolution spectrum of 1.2ILa@Bi(10)-SBA-16. As can be seen from the figure Bi(10)-SBA-16 contains the typical peaks of SBA-16: C_{1s} (284.65 eV), O_{1s} (532.85 eV), Si_{2p} (103.85 eV) and other peaks: $Bi_{4f5/2}$ (159.65 eV) and $Bi_{4f7/2}$ (164.95 eV). The difference between the two peaks of Bi_{4f} was about 5.3 eV, which corresponds to the binding energy of Bi^{3+} . It was inferred that Bi exists in the form of Bi_2O_3 . C_{1s} may be caused by air and instrument pollution. The spectrum of

1.2ILa@Bi(10)-SBA-16 characterizes $N_{\rm 1s}$ (401.51 eV) and $S_{\rm 2p}$ (167.81 eV) and the peak value of $C_{\rm 1s}$ (284.65 eV) became stronger when compared to that of Bi(10)-SBA-16, which was supposed to be caused by the introduction of ionic liquids.

¹H NMR analysis

The ¹H NMR (400 MHz, D₂O, ppm, δ) spectrum (see the ESI, Fig. S4[†]) of the four kinds of ILs were shown as follows:

ILa: 8.39(s, 1H), 7.55–7.52(m, 2H), 7.23–7.18(t, J = 20 Hz, 4H), 3.72(s, 3H), 2.23(s, 4H).



Fig. 6 XPS spectra of samples: (a) the XPS full survey spectra of SBA-16, Bi(10)-SBA-16 and 1.2ILa@Bi(10)-SBA-16 and (b and c) Bi_{4f} , S_{2p} and N_{1s} of 1.2ILa@Bi(10)-SBA-16.

ILb: 8.48(s, 1H), 7.55–7.53(m, 2H), 7.27–7.19(m, 4H), 3.99–3.96(t, J = 12 Hz, 2H), 3.70(s, 3H), 2.24(s, 4H), 1.69–1.61 (m, 2H), 1.19–1.10(m, 2H), 0.79–0.75(t, J = 16 Hz, 3H).

ILc: 8.52(s, 1H), 7.52–7.49(d, J = 12 Hz, 2H), 7.31–7.30(t, J = 4 Hz, 1H), 7.24–7.23(t, J = 4 Hz, 1H), 7.18–7.16(d, J = 8 Hz, 2H), 4.16–4.13(t, J = 12 Hz, 2H), 3.69(s, 3H), 2.76–2.72(m, 2H), 2.20 (s, 4H), 2.16–2.09(m, 2H).

ILd: 8.55(s, 1H), 7.54-7.53(m, 2H), 7.32-7.31(t, J = 8 Hz, 1H), 7.26-7.25(t, J = 4 Hz, 1H), 7.22-7.20(d, J = 8 Hz, 2H), 4.08-4.04 (t, J = 16 Hz, 2H), 3.72(s, 3H), 2.81-2.77(m, 3H), 2.24(s, 4H), 1.89-1.81(m, 3H), 1.63-1.55(m, 3H).

MS analysis

Fig. S3a–d† (see the ESI, Fig. S3†) shows the positive and negative ion peaks of the electrospray mass spectra of the four ionic liquids in the positive and negative ion modes, providing a basis for identifying the molecular structure, molecular weight, and the presence of anions and cations of the synthesized ionic liquids. First, we found that there were ion peaks at m/z 176 in the negative ion mode, which was consistent with the molar weight of our anion structure [p-TSA]⁻. In addition, the ion peak at m/z 169.02 shown in Fig. S3a1† was assumed to be the cation structure of ILa [COO(CH₂)₃-MIM]⁺. As shown in Fig. S3b1,† the ion peak at m/z 144.82 may be the cation structure of ILb [BMIM]⁺. As shown in Fig. S3c1,† the ion peak at m/z 210.57 was inferred to be the cation structure of ILc $[HSO_3-PMIM]^+$. Fig. S3d1[†] shows an ion peak at m/z 224.60 that may be the cation structure of ILd $[HSO_3-BMIM]^+$. Through the above data analysis, it can be seen that the molar anions and cations in the ionic liquid were consistent with the theoretical value, indicating that the four ionic liquids have been successfully synthesized.

TG-DSC analysis

The thermogravimetric (TG) curves of Bi(10)-SBA-16 and 1.2ILs@Bi(10)-SBA-16 are shown in Fig. 7. As can be seen from the figure that the mass of all the samples decreased significantly from room temperature to 100 °C, which may be due to the evaporation of crystal water in the sample. With the rise of temperature, the TG curve of Bi(10)-SBA-16 tends to be stable, while the four composite catalysts 1.2ILs@Bi(10)-SBA-16 experience secondary weight loss. When the temperature increases from 350 to 600 °C, the mass of the ionic liquids in Bi(10)-SBA-16 decreased by 11.361%, 13.819%, 21.528% and 15.558%, respectively. Compared to Bi(10)-SBA-16, it was found that this phenomenon should be caused by the degradation of ionic liquid. It also can be seen from the figure that the loading rate of ILc was the highest under the same load. According to the literature, the melting point is a key parameter to evaluate the characteristics of ionic liquids. The melting point of ionic liquids is closely related to the composition of cations and anions, and increases with the improve-



Fig. 7 TG-DSC curves of (a) Bi(10)-SBA-16 and (b-e) 1.2ILs@Bi(10)-SBA-16

ment in the degree of cation symmetry and intermolecular force.^{49–51} The TG curve of the composite material does not change significantly as the temperature continues to rise. The TG analysis showed that the ionic liquid was successfully encapsulated in Bi(10)-SBA-16 and had good thermal stability.

Catalytic activity evaluation

Effect of different catalysts on Friedel–Crafts acylation. Table 2 lists the conversion rates of the reactants and the product yields of all samples involved in the acylation reaction of anisole with acetic anhydride. The main product of the reaction is *p*-methoxybenzophenone (*p*-MAP) and the by-product is *o*-methoxybenzophenone (*o*-MAP). *p*-MAP was the target product of the reaction.^{52,53} The reaction mechanism is shown in Fig. S6.[†] The results of the blank experiment and that with concentrated sulfuric acid as a catalyst are also listed in Table 2. The reaction conditions for all the catalytic reactions listed in Table 2 are as follows: temperature = 80 °C, *n*(AN)/

 Table 2
 Performance of various catalysts in Friedel-Crafts acylation reaction

Catalyst	Conversion of anisole (%)	Yield of aromatic ketones (%)
Blank	45.19	23.61
Concentrated sulfuric acid	65.30	48.22
Bi(5)-SBA-16	52.93	35.67
Bi(10)-SBA-16	55.11	40.13
Bi(15)-SBA-16	52.40	36.55
1.2ILa@Bi(10)-SBA-16	60.09	46.36
1.2ILb@Bi(10)-SBA-16	62.17	47.55
1.2ILc@Bi(10)-SBA-16	69.85	50.41
1.2ILd@Bi(10)-SBA-16	61.23	45.20
OCH3 + Contraction of the catalyst solvent-free	eH3CO	O-MAP OCH ₃

Reaction conditions: (n(anisole)/n(acetic anhydride) = 1:1.5, catalyst dosage = 0.3 g, temperature = 80 °C, and time = 3 h).

n(AA) = 1:1.5, catalyst dosage = 0.3 g, and time = 3 h. As shown in Table 2, the SBA-16 carrier with 10% Bi doping has better catalytic performance compared to other doping amounts. With Bi(10)-SBA-16 as the carrier and doped with an ionic liquid, 1.2ILc@Bi(10)-SBA-16 showed the best catalytic performance under the above reaction conditions, the conversion rate of anisole was 69.85% and the product yield was 50.41%. It may be due to that the structure of cations has a certain influence on the acidity and solubility of the ionic liquids. The acidity and solubility of the ionic liquids are closely related to their catalytic activity. The mutual solubility of ionic liquids and reaction products determines the difficulty of phase separation, and phase separation performance has a great influence on the catalytic effect. Although the ionic liquid with a propane sulfonate group has the same activity as the traditional concentrated sulfuric acid catalyst, it has more advantages in terms of product selectivity, product separation and reuse.54-56

Table S1[†] presents some catalytic activity data collected from different articles of various catalysts for Friedel–Crafts acylation. Using HPW/MCM-41(60% loading) as a catalyst, although the reaction conditions were mild, the catalytic effect was negligible. With Nanocrystalline ZSM-5 of 90 nm particle size as the catalyst, more acetic anhydride was needed, which is not economical and good for the environment, and the catalytic effect is not obvious. The same was true with HPA/SiO₂ as the catalyst. When 20%IL/MIL-101 was used as the catalyst, the catalytic performance was higher but the amount of the catalyst needed was higher.

Effect of reaction temperature on the Friedel–Crafts acylation. Fig. 8 reveals the effect of temperature on the acylation of anisole with acetic anhydride. Based on the above results, 1.2ILc@Bi(10)-SBA-16 was selected as the catalyst, the molar ratio of anisole to acetic anhydride was 1.5, the catalyst dosage was 0.3 g, and the reaction time was 3 h. The change in catalytic performance at different reaction temperatures from 70 °C to 110 °C was explored. It can be seen from the figure that the conversion and yield improve with the increase in temperature, which may be due to the enhancement of the molecular collision and miscibility of reactants. When the temperature was 100 °C, the conversion and yield up were 78.94% and 57.52%, respectively. Obviously, the conversion and yield change a little when the temperature was increased from 100 °C to 110 °C, possibly due to the production of by-products (such as 2-methoxyacetophenone and phenol).^{52,53,57,58}

Effect of molar ratio on Friedel–Crafts acylation. The effect of the molar ratio of anisole to acetic anhydride on acylation is shown in Fig. 9. Under the reaction conditions of the temperature of 100 °C, the catalyst dosage of 0.3 g and the reaction time of 3 h, the influence of the molar ratio from 1 to 2 on the catalytic performance was studied. Apparently, conversion and yield increase significantly in the molar ratio range of 1 to 1.5, but decrease slightly in the range of 1.5 to 2. This may be because anisole was diluted with excessive acetic anhydride as the amount of acetic anhydride increased, which results in the inhibition of the effective collision between the two reactants.^{52,55,56} So the best molar ratio of anisole with acetic anhydride was 1.5.

Effect of catalyst dosage on Friedel–Crafts acylation. The influence of catalyst dosage on acylation is shown in Fig. 10. The amount of reaction variable catalyst is 0.2, 0.3, 0.4, 0.5 and 0.6 g, respectively. The reaction conditions were as follows: the temperature was 100 °C, the reaction time was 3 h, and the molar ratio was 1.5. As can be seen from the figure, the conversion and yield of the reaction increase as the catalyst dosage increased from 0.2 to 0.5 g. It can be inferred that the augment of catalytic activity enhances the effective collision of the reactants. As the amount of the catalyst continues to increase, the conversion and yield decrease slightly, which may be due to the excessive amount of catalyst leading to the occurrence of deep reaction.^{52,53} Therefore, the optimal amount of catalyst was 0.5 g.



Fig. 8 The effect of temperature on acylation of anisole with acetic anhydride over 1.2ILc@Bi(10)-SBA-16 catalyst (reaction conditions: n(AN)/n(AA) = 1:1.5, catalyst dosage = 0.3 g, and time = 3 h).



Fig. 9 The effect of molar ratio on acylation of anisole with acetic anhydride over 1.2ILc@Bi(10)-SBA-16 catalyst (reaction conditions: temperature = 100 °C, catalyst dosage = 0.3 g, and time = 3 h).



Fig. 10 The effect of catalyst dosage on acylation of anisole with acetic anhydride over 1.2ILc@Bi(10)-SBA-16 catalyst (reaction conditions: temperature = 100 °C, n(AN)/n(AA) = 1: 1.5, and time = 3 h).



Fig. 11 The effect of reaction time on acylation of anisole with acetic anhydride over 1.2ILc@Bi(10)-SBA-16 catalyst (reaction conditions: temperature = 100 °C, n(AN)/n(AA) = 1: 1.5, and catalyst dosage = 0.5 g).

Effect of reaction time on Friedel–Crafts acylation. As shown in Fig. 11, the 1.2ILc@Bi(10)-SBA-16 was used as the catalyst to explore the influence of reaction time on acylation under the corresponding test conditions. The reaction was carried out at a temperature of 100 °C with a catalyst dosage of 0.5 g and a molar ratio of 1.5. As can be seen from the figure, the conversion and yield of the reaction increased significantly with the increase in reaction time. When the reaction time was 4 h, the conversion and yield reached 85.41% and 69.19% respectively. However, when the reaction continued for a period of time, the conversion and yield showed a downward trend, which can be speculated that adverse reactions have occurred. Therefore, the optimal reaction time is 4 h.

Reusability of the catalyst. The stability of the catalyst was studied in the acylation of anisole with acetic anhydride. Under the optimum reaction conditions (temperature = 100 °C, n(AN)/n(AA) = 1:1.5, catalyst dosage = 0.5 g, time = 4 h), the catalyst used for the first time was recovered and then washed with anhydrous ethanol for several times to remove impurities. The



Fig. 12 The reusability of the 1.2ILc@Bi(10)-SBA-16 catalyst (reaction conditions: temperature = 100 °C, n(AN)/n(AA) = 1:1.5, catalyst dosage = 0.5 g, and time = 4 h).

performance of the regenerated catalyst was observed by a repeated performance test. The results are shown in Fig. 12. After 5 recycling runs, the conversion of the reactant and the yield of product decreased, but the overall ratio did not exceed 7.5%, indicating that 1.2ILc@Bi(10)-SBA-16 has good stability and reusability. The reduction in conversion may be due to the loss of catalyst quality during regeneration.

Conclusions

In this work, SBA-16 was modified by the in situ synthesis method for the synthesis of Bi(10)-SBA-16. Four kinds of *p*-toluenesulfonic acid functionalized imidazole ionic liquids were prepared by a two-step method. A series of composite catalysts (1.2ILs@Bi(10)-SBA-16 (ILs = ILa, ILb, ILc, and ILd)) were obtained by loading the ionic liquids into Bi-doped mesoporous carriers. After FT-IR, XRD, BET, XPS, MS, TG and other characterization studies, it was found that the filling of Bi and ionic liquid changed the pore volume and pore size, while the three-dimensional cubic pore structure of SBA-16 was not destroyed. It shows the good catalytic performance in the Friedel-Crafts acylation reaction of anisole with acetic anhydride. Under ideal conditions, not only the conversion rate of anisole and the yield of aromatic ketone were high, but also the repetitive utilization rate of the catalyst was high. Therefore, the metal-doped mesoporous molecular sieve coated acidic ionic liquid is of great significance to the production and use of industrial aromatic ketones.

Experimental section

Materials

The Bi-doped SBA-16 mesoporous molecular sieve (Bi(10)-SBA-16) was synthesized with the Pluronic F127 (poly(ethylene

oxide)–poly(propylene oxide)–poly(ethylene oxide) tri-block copolymer $EO_{106}PO_{70}EO_{106}$, $M_{aver.} = 12\,600$, Sigma) as the structure-directing agent and TEOS (tetraethoxysilane, 98%, Aldrich) as the silicate source under a hydrochloric acid (36%, Merck) solution. The ionic liquid was synthesized using *N*-methylimidazole (99%, Sigma), 1,3-propane sulfonate (99%, Aldrich), 1,4-butane sulfonate (98%, Aldrich), *N*-chlorobutane (99%, Aldrich), and *p*-toluenesulfonic acid (>99%). Other drugs used in the experiment include anisole (99%, Sigma) and acetic anhydride (99%, Sigma). All the above commercial chemicals were of analytical grade and were purchased from the Shanghai Chemical Reagent Corporation, China.

Preparation of Bi(x)-SBA-16 (x = 5, 10, 15)

High quality hexagonal ordered mesoporous Bi(x)-SBA-16 (x = 5, 10, and 15) was synthesized under acidic conditions using a triblock copolymer as the templating agent. The reaction was carried out according to the reaction ratio F127: HCl: TEOS: Bi $(NO_3)_3 \cdot 5H_2O = 0.0016 : 1.45 : 0.3841 : 0.0192 - 0.0576$. First, F127 was dissolved in dilute hydrochloric acid and stirred until it was clear and transparent; the concentration of dilute hydrochloric acid was 1.62 mol L⁻¹. The mixed solution was stirred vigorously in a 34 °C water bath for 2-3 h, TEOS was added dropwise, and then Bi(NO₃)₃·5H₂O was added and continuously stirred for 20 h. The sample was washed after the hydrolysis process and then transferred to a polytetrafluoroethylene reactor. Deionized water was added to disperse the sample and then the sample was hydrothermally crystallized at 100 °C for 24 h. After crystallization, the sample was filtered, washed, and dried. The resulting product was calcined at 550 °C to remove the templating agent, the heating rate was 1 $^{\circ}$ C min⁻¹, and the holding time was 6 h. After the calcination, the white powder was collected to obtain Bi(x)-SBA-16 (x = 5, 10, 15).

Preparation of ILs

Preparation of ILa intermediate 1-(3-carboxyl)butyl-3-methylimidazolium salt $[COO(CH_2)_2$ -MIM]⁺. The reaction was carried out with 1,4-butyrolactone and *N*-methylimidazole in a molar ratio of 1 : 1. First, 8.61 g of 1,4-butyrolactone was added into a 100 ml beaker and then was added 8.21 g of *N*-methylimidazole. The reaction was conducted at room temperature by the solvent free method for 30 min, and then washed with ethanol. The product was dried in a vacuum at 80 °C to obtain the product intermediate 1-(3-carboxyl) butyl-3-methylimidazolium salt $[COO(CH_2)_2$ -MIM]⁺.

Preparation of ILb intermediate 1-butyl-3-methylimidazolium salt [BMIM]Cl⁺. The reaction was carried out with 1-chlorobutane and *N*-methylimidazole in the molar ratio of 1.2 : 1. First, 8.2 g of *N*-methylimidazole was added to three flasks and quickly passed into nitrogen for a particular period of time and then slowly dripped into 11.1 g of 1-chlorobutane. After all the liquid was added into three batches of burnt products, the solution was heated directly to 80–85 °C by the solvent-free method and then stirred and refluxed for 48 h under nitrogen conditions. After the reaction, the lower layer of the pale yellow liquid was separated and washed repeatedly with 60 ml of ether. Then, the ionic liquid intermediate product 1-butyl-3-methylimidazole salt $[BMIM]^+$ can be dried for more than 12 h under vacuum at 80 °C. The product was light yellow or colorless with high viscosity.

Preparation of ILc intermediate 1-(3-sulfonyl) propyl-3methylimidazolium salt [SO₃-PMIM]⁺. The intermediate of ionic liquid was prepared by a two-step synthesis method: 30 ml of toluene solvent was measured in a beaker, 6.1 g of 1,3-propanesulfonic acid was dispersed in the beaker and 4.1 g of *N*-methylimidazole was slowly added in an ice water bath, followed by magnetic agitation. Then the temperature was slowly raised to 60 °C and continue stirred with a magnetic stirrer for 5 h. The mixture was filtered to obtain a white solid, washed with ether for several times and dried at 60 °C for 6 h to obtain the intermediate 1-(3-sulfonyl) propyl-3-methylimidazolium salt [SO₃-PMIM]⁺.

Preparation of ILd intermediate 1-(4-sulfonyl) butyl-3methylimidazolium salt $[SO_3-BMIM]^+$. The preparation of ILd intermediate 1-(4-sulfonyl) butyl-3-methylimidazolium salt $[SO_3-BMIM]^+$ is similar to the preparation of ILc intermediate.

Prepartion of ILa, ILb, ILc, and ILd. The prepared ionic liquid intermediate was added to the flask and *p*-toluenesulfonic acid (*p*-TSA) was added dropwise according to the ratio of 1:1 to the intermediate. The ionic liquids were heated to 80 °C in a water bath and stirred for 5–6 h until all ionic liquid intermediates were dissolved. After the reaction, the product was washed with ethyl acetate for three times and dried in a vacuum at 100 °C to obtain sulfonic acid functionalized ionic liquids [COOH(CH₂)₂-MIM]*p*-TSA (ILa), [BMIM]*p*-TSA (ILb), [HSO₃-PMIM]*p*-TSA (ILC), and [HSO₃-BMIM]*p*-TSA (ILd).

Synthesis of 1.2ILs@Bi(*x*)-SBA-16 (x = 5, 10, and 15) composites. The above four ionic liquids, 1.2 g each, were dissolved in 20 ml of deionized water, respectively. The solution was magnetically stirred at 80 °C in an isothermal oil bath pot. Then 1 g of Bi(x)-SBA-16 (x = 5, 10, and 15) was added to the solution. After 6 h, the water in the mixture was heated and evaporated to obtain solids that were respectively washed with methanol, ethyl acetate, and anhydrous ether, and then dried in a vacuum for 10 h to obtain 1.2ILs@Bi(x)-SBA-16 (ILs = ILa, ILb, ILc, and ILd) (x = 5, 10, and 15) composite catalysts.

Catalyst characterization

The X-ray diffraction (XRD) patterns of samples were recorded with an X-ray powder diffractometer made in Germany BRUKER with Cu K α radiation (λ = 0.15418 nm). It was operated at 40 kV and 50 mA, the scanning speed was 1° min⁻¹ and the scanning was done in the 2 theta range of 0.5–10°. The specific surface area, total pore volume and pore size distribution were measured using a Micromeritics Tristar II 3020 surface area and pore analyzer. The specific surface area of the sample was calculated by the BET (Brunauer–Emmett–Teller) formula and the pore size and pore volume of the sample were measured by the BJH (Barrett–Joyner–Halenda) formula. The Fourier transform infrared (FT-IR) spectra of the samples in the range of 400–4000 cm⁻¹ were obtained using a Nexus FT-IR 470 spectrometer made by the Nicolet Corporation with

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anhydrous KBr as the standard. The particle morphology was characterized using a scanning electron microscope (SEM) with a Hitachi S-3400N microscope at 4 kV. EDS allows the qualitative and semi-quantitative analyses of samples through the difference in the characteristic energy of the X-ray photons of the elements. Before analysis, the samples were coated with gold for a thickness of about 10 nm by cathodic sputtering. A transmission electron microscopy (TEM) study was performed using a JEOL JEM 2100 transmission electron microscope operated at 200 kV. The finely powdered samples were suspended in ethanol and dispersed by ultrasound, and then dried on a porous carbon gate at room temperature for transmission electron microscope observation. The types of surface elements and the chemical states of the surface atoms were analyzed and determined using an AXIS-U1tra DLD X-ray photoelectron spectroscope (XPS) from Shimadzu, Japan. The radiation source was Al-Ka (1486.6 eV). The type of surface elements was qualitatively determined by XPS and the carbon pollution peak was found to be 284.8 eV. The chemical environment of the element was analyzed by peaking the high resolution spectra of the specific element. The ionic liquid was determined by ¹H NMR using an AVANCE II 400 Hz superconducting nuclear magnetic resonance spectrometer from BRUKER, Switzerland. D₂O was used as the solvent and the sample was dissolved into a special nuclear magnetic tube. The data were analyzed by the MestReNova software. The molecular structure and molecular weight of the ionic liquids were analyzed using a liquid chromatography-ion trap mass spectrometer manufactured by the Thermo Fisher ScientificCompany. Water was used as the solvent and filtered through a 0.22 micron membrane in the range of m/z 50–2000. The thermogravimetric analysis (TGA) of the active ionic liquid in the catalyst was performed using a NETZSCH STA 449C thermogravimetric analyzer. Under an atmosphere of nitrogen, the temperature ranged from room temperature to 800 °C and the heating rate was 10 °C min⁻¹. The DSC curve was used to observe the heat change during the heating process.

Catalytic activity test

The performance evaluation of the catalyst was carried out in a round bottom flask equipped with magnetic stirring and a reflux condenser. We chose the acylation of acetic anhydride and anisole as the template reaction. The specific operation was as follows: 0.15 mol acetic anhydride (AA) and 0.1 mol anisole (AN) were added into a 25 ml three mouthed bottle, 0.3 g (about 5 wt% of acetic anhydride) of catalyst was added under stirring, and the reaction time was 3 h at 80 °C. The catalyst was obtained by centrifugation after the reaction liquid was cooled to room temperature. The catalyst was washed with 20 ml of ether and dried for a repeated effect test. An Agilent 8090A gas chromatograph, SE-54 column and FID were used to analyze the conversion of the reactants and the yield of products. In the analysis process, high purity N₂ was used as the carrier gas. The heating conditions were as follows: the initial temperature was kept at 100 °C for 1 minute, then the initial temperature was raised to 280 °C at

the rate of 20 °C min⁻¹, and the injection volume was 2 μ l each time. The product was analyzed by gas chromatography using the internal standard method and the internal standard used was *p*-xylene.

Conflicts of interest

There are no conflicts to declare.

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References

- 1 S. P. Art, K. Okuro, M. Miura, S. Murata and M. Nomura, *J. Chem. Soc., Perkin Trans.* 1, 1994, 1, 1703–1707.
- 2 M. L. Kantam, K. V. S. Ranganath, M. Sateesh, K. B. S. Kumar and B. M. Choudary, *J. Mol. Catal. A: Chem.*, 2005, **225**, 15–20.
- 3 Y. M. Chung, H. Y. Kim and W. S. Ahn, *Catal. Lett.*, 2014, 144, 817–824.
- 4 M. Mu, W. Fang, Y. Liu and L. Chen, *Ind. Eng. Chem. Res.*, 2015, 54, 8893–8899.
- 5 N. Chalotra, S. Sultan and B. A. Shah, *Asian J. Org. Chem.*, 2020, **9**, 863–881.
- 6 Y. K. Mahendra, P. Kapoor, M. Yanagi, T. Yokoyama,
 S. Inagaki, T. Shimada, H. Nanbu and L. R. Juneja, *Microporous Mesoporous Mater.*, 2007, 101, 231–239.
- 7 G. Losfeld, V. Escande, P. V. Blache, L. L'Huillier and C. Grison, *Catal. Today*, 2012, **189**, 111–116.
- 8 M. V. Khedkar, T. Sasaki and B. M. Bhanage, *RSC Adv.*, 2013, **3**, 7791–7797.
- 9 H. Naeimi and L. Moradi, J. Mol. Catal. A: Chem., 2006, 256, 242–246.
- 10 J. Sun, Y. Gui, Y. Huang, J. Li, Z. Zha, Y. Yang and Z. Wang, *ACS Omega*, 2020, 5, 11962–11970.
- 11 X. Song, F. Liu, H. Wang, C. Wang, S. Yu and S. Liu, *Polym. Degrad. Stab.*, 2018, 147, 215–221.
- 12 G. Y. Bai, H. Y. Dou, M. D. Qiu, F. He, X. X. Fan and Z. Ma, *Res. Chem. Intermed.*, 2010, **36**, 483–490.
- 13 T. Jaimol, P. Moreau, A. Finiels, A. V. Ramaswamy and A. P. Singh, *Appl. Catal.*, A, 2001, 215, 1–10.
- 14 L. T. L. Nguyen, K. K. A. Le and N. T. S. Phan, *Chin. J. Catal.*, 2012, 33, 688–696.
- 15 X. Rao, H. Ishitani, W. J. Yoo and S. Kobayashi, Asian J. Org. Chem., 2019, 8, 316-319.
- 16 J. Ross and J. L. Xiao, Green Chem., 2002, 4, 129-133.
- 17 T. Tsuchimoto, T. Maeda, E. Shirakawa and Y. Kawakami, *Chem. Commun.*, 2000, 1573–1574.
- 18 M. Ammar, S. Jiang and S. Ji, J. Solid State Chem., 2016, 233, 303–310.

- 19 H. Yang, X. Qi, L. Wen, C. Lu and G. Cheng, *Ind. Eng. Chem. Res.*, 2011, **50**, 11440–11444.
- 20 N. Jiao, Z. Li, Y. Wang, J. Liu and C. Xia, *RSC Adv.*, 2015, 5, 26913–26922.
- 21 D. Zheng, L. Dong, W. Huang, X. Wu and N. Nie, *Renewable Sustainable Energy Rev.*, 2014, **37**, 47–68.
- 22 Y. Tian, X. Meng and L. Shi, *Ind. Eng. Chem. Res.*, 2013, **52**, 6655–6661.
- 23 P. H. Tran, N. B. Do and T. N. Le, *Tetrahedron Lett.*, 2014, 55, 205–208.
- 24 K. S. Yeung, M. E. Farkas, Z. Qiu and Z. Yang, *Tetrahedron Lett.*, 2002, **43**, 5793–5795.
- 25 A. Filiz, Mater. Chem. Phys., 2019, 227, 21-28.
- 26 H. Zhang, J. Han, F. Tian, Q. Chen, C. Wang, H. Jin and G. Bai, *Res. Chem. Intermed.*, 2014, **41**, 6731–6739.
- 27 F. Martínez, G. Morales, A. Martín and R. Grieken, *Appl. Catal.*, A, 2008, 347, 169–178.
- 28 M. Karaki, A. Karout, J. Toufaily, F. Rataboul, N. Essayem and B. Lebeau, *J. Catal.*, 2013, **305**, 204–216.
- 29 M. Jinmei, W. Hui, S. Yanbing, G. Guofeng and X. Bin, J. Mol. Catal. A: Chem., 2011, 348, 77–82.
- 30 L. Yu, Z. Ziming, W. Li, L. Sha, W. He, W. Wei, Z. Hongbo and M. Jiantai, *Mol. Catal.*, 2017, 433, 291–300.
- 31 Y. Long, Y. H. Liu, Z. M. Zhao, S. Luo, W. Wu, L. Wu, H. Wen, R. Q. Wang and J. T. Ma, *J. Colloid Interface Sci.*, 2107, **496**, 465–473.
- 32 A. F. Guzik, P. Szczyglewska and I. Nowak, *Catal. Today*, 2019, **325**, 61–67.
- 33 K. Bachari, R. Chebout, R. M. Guerroudj and M. Lamouchi, *Res. Chem. Intermed.*, 2011, **38**, 367–381.
- 34 K. Bachari, R. Chebout, R. M. Guerroudj and M. Lamouchi, *J. Porous Mater.*, 2011, **19**, 615–622.
- 35 Y. J. Xie, Q. Zhao, G. F. Gao and T. S. Jiang, *Dalton Trans.*, 2019, **48**, 17106–17116.
- 36 S. Madadia, L. Charbonneau, J. Y. Bergeron and S. Kaliaguine, *Appl. Catal., B*, 2020, **260**, 118049.
- 37 L. M. Dai, Q. Zhao, M. L. Fang, R. F. Liu, M. F. Dong and T. S. Jiang, *RSC Adv.*, 2017, 7, 32427–32435.
- 38 L. Zhang, Y. D. Cui, C. Zhang, L. Wan, H. Wan and G. F. Guan, *Ind. Eng. Chem. Res.*, 2012, 51, 16590–16596.
- 39 R. Mohan, Nat. Chem., 2010, 2, 336.

- 40 C. Z. Yu, J. Fan, G. D. Stucky and D. Y. Zhao, J. Am. Chem. Soc., 2002, 124, 4556–4557.
- 41 D. Y. Zhao, J. L. Feng, B. F. Chmelka and G. D. Stucky, J. Am. Chem. Soc., 1998, 120, 6024–6036.
- 42 Q. Zhao, C. Yang, M. L. Fang and T. S. Jiang, *Appl. Catal.*, *A*, 2020, **594**, 117470.
- 43 M. Gotić, S. Popović and S. Musić, *Mater. Lett.*, 2007, **61**, 709–714.
- 44 K. Belkacemi and S. HamoudiInd, *Eng. Chem. Res.*, 2010, **49**, 6878–6889.
- 45 I. C. Quarmby and R. A. Osteryoung, J. Am. Chem. Soc., 1994, **116**, 2649–2650.
- 46 I. C. Quarmby, R. A. Mantz, L. M. Goldenberg and R. A. Osteryoung, *Anal. Chem.*, 1994, 66, 3558– 3561.
- 47 R. Kumar, N. Enjamuri, J. K. Pandey, D. Sen, S. Mazumder,
 A. Bhaumik and B. Chowdhury, *Appl. Catal.*, A, 2015, 497, 51–57.
- 48 A. S. Amarasekara and B. Wiredu, *Sustainable Energy Fuels*, 2014, 2, 102–107.
- 49 K. R. Seddon, J. Chem. Technol. Biotechnol., 1997, 68, 351– 356.
- 50 P. BonhÔte, A. P. Dias, N. Papageorgiou,
 K. Kalyanasundaram and M. Grätzel, *Inorg. Chem.*, 1996, 35, 1168–1178.
- 51 H. Stegemann, A. Rohde, A. Rekhe, A. Schnittke and H. Fullbie, *Electrochim. Acta*, 1992, **37**, 379–383.
- 52 K. M. Parida, S. Mallick and G. C. Pradhan, *J. Mol. Catal. A: Chem.*, 2009, **297**, 93–100.
- 53 F. Martínez, G. Morales, A. Martín and R. Grieken, *Appl. Catal.*, A, 2008, 347, 169–178.
- 54 P. Wasserscheid and W. Keim, Angew. Chem., Int. Ed., 2000, 39, 3772–3789.
- 55 K. Ala'a, S. Abdul, M. Anthony, K. R. Greenway and T. Seddon, *Org. Mass Spectrom.*, 1993, 28, 759–765.
- 56 Y. L. Gu, F. Shi and Y. Q. Deng, J. Mol. Catal. A: Chem., 2004, 212, 71–75.
- 57 A. Padmanabhan, R. Selvin, H. L. Hsu and L. W. Xiao, *Chem. Eng. Technol.*, 2010, **33**, 998–1002.
- 58 D. P. Serrano, R. A. García and D. Otero, *Appl. Catal., A*, 2009, **359**, 69–78.