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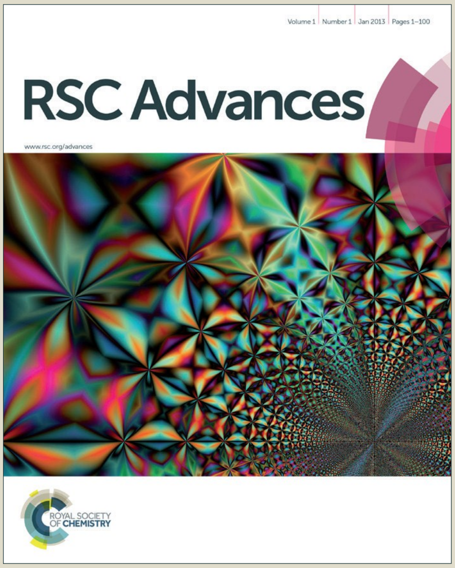

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Synthesis of methylal from methanol and formaldehyde catalyzed by Brønsted acid ionic liquids with different alkyl groups

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Catalytic reaction of methanol with formaldehyde for preparation of methylal was investigated in various Brønsted acid ionic liquids with different carbon chain length of alkyl groups. The structures, acidities, and properties of ionic liquids were experimentally characterized and theoretically analyzed. The Brønsted acidity-viscosity-activity correlation for the ionic liquids was studied. Among all these ionic liquids, [C_6ImBS][HSO_4] exhibited the best catalytic performance, which was ascribed to its strong Brønsted acidity and low viscosity. The catalytic activity of ionic liquid was near to that of concentrated sulfuric acid. The influences of ionic liquid dosage, reaction temperature and molar ratio of methanol to formaldehyde were explored using [C_6ImBS]HSO_4 as the catalyst. Under the optimal conditions of n(methanol) : n(formaldehyde) : n(ILs)= 2.5: 1: 0.0258, 60 °C, and 4h, the conversion of formaldehyde can reach 63.37 %. The ionic liquid [C_6ImBS]HSO_4 could be reused.

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Introduction

Methylal (dimethoxymethane, DMM) is an excellent green solvent and chemical intermediate because of its extremely low toxicity, good solubility and intersolubility with water. With a boiling point of 315.3 K under atmospheric pressure, DMM can also be considered as a convenient antifreeze additive in fuel cells[1]. It has been widely used in pharmaceutical, perfume industries and organic synthesis[2,3]. Methylal has low vapor pressure, high oxygen content, high cetane number and reducing pollutants, which can be used as promising green diesel additive. Thus methylal has the potential scientific values and application prospects for petrochemical industry[4,5].

Methylal is usually produced through the reaction of methanol with formaldehyde in the presence of acid catalyst, such as homogeneous or heterogeneous acid catalyst[6,7]. Conventionally, this reaction is carried out using homogeneous acid catalysts, such as concentrated sulfuric acid or *p*-toluenesulfonic acid. However, homogeneous liquid catalysts are corrosive and are not easily recovered leading to the release of environmentally unfriendly effluents, which inevitably leads to a series of environmental problems[8]. On account of the detrimental effects of these catalysts, great efforts directed toward the development of environmentally friendly catalysts have been made. Solid acid catalyst has been of great interest due to its environment friendliness. Solid acid catalyst has easy separation, no corrosion of apparatus and no pollution, but it exists some shortages, such as low activity, rapid loss of activity and short catalyst life. Therefore, the development of environmental and efficient catalysts for synthesis of methylal is extremely urgent.

In recent years, ionic liquid (ILs), including functionalized ones, have attracted considerable research attention[9,10]. Ionic liquids are organic salts that may be liquid at room temperature or at relatively low temperatures (<100 °C), generally known as room temperature ILs[11,12]. They are finding increasing use and interest owing to their unique properties such as negligible vapor pressure, thermal stability over a wide temperature range, large electrochemical window, wide liquid-phase temperature range and being also recyclable[13-15]. They are also described as “designer solvents”[16] since their properties may be appropriately tuned and developed for specific needs by the proper selection of the anion–cation couples. Many organic reactions involving alkylation[17-20], esterification[21,22], nitration[23], hydrogenation[24], epoxidation[25] or Diels-Alder[26] have been performed in room temperature ionic liquids with excellent yields and selectivity.

In this work, Brønsted acid ionic liquids with different carbon chain length of alkyl groups were synthesized. They were characterized by infrared spectrum (IR), nuclear magnetic resonance (NMR), electrospray ionization mass spectrum (ESI-MS), differential thermal analysis (TG-DTA). Their Brønsted acidity was determined through UV-vis spectroscopy. Their catalytic performances for the synthesis of methylal from methanol and formaldehyde were investigated in various Brønsted acid ionic liquids with different carbon chain length of alkyl groups by gas chromatography. Correlations between the carbon chain length of alkyl groups of ionic liquids, Brønsted acidic strength, the viscosity and catalytic activity were discussed. The effects of reaction conditions on the production in the selected ionic liquids were extensively studied.

Experimental

Materials

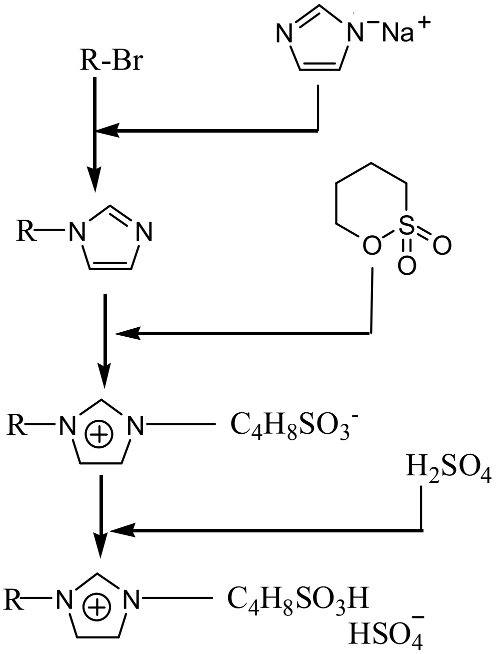
Sodium, formaldehyde, bromomethane, bromoethane, 1-bromobutane, 1-bromohexane and 1-bromononane were purchased from Sionpharm Chemical Reagent Co., Ltd. 1-bromodecane, 1-bromododecane, methylal were obtained from Alfa Aesa. 1,4-butane sultone(99 %) were purchased from Wuhan Fengfan Chemical Co, Ltd. Imidazole was obtained from Linhai Kaile Chemical Factory. Ethanol, acetone, dichloromethane, ethyl acetate, *p*-toluenesulfonic acid, toluene, methanol and concentrated sulfuric acid were received from Beijing Chemical Co., Ltd. All reagents and raw materials were commercially available and used without any further purification.

Methods

IR spectra were run on a Perkin-Elmer Spectrum, which used KBr windows suitable for Fourier transform infrared (FTIR) transmittance technology to form a liquid film. ^1H NMR spectra were obtained on a varian mercury-plus 400MHz nuclear magnetic resonance spectrometer. Chemical shifts were reported in parts per million(ppm, δ). ESI-MS spectra were obtained on Vavian 500MS instrument. The thermal decomposition temperature was determined by Perkin-Elmer TGA7 TG-DTA analysis, with a heating rate of 10 °C/min from room temperature to 700 °C.

Preparation of Brønsted acid ionic liquids with different alkyl groups

The synthetic procedure of Brønsted acid ionic liquids with different alkyl groups is illustrated in Scheme 1.



R：C_nH_{2n+1}

n=1、2、4、6、8、10、12、14、16

Scheme 1 Synthetic procedure of Brønsted acid ionic liquids with different alkyl groups

（1）Preparation of alkylimidazole with different carbon chain(RIm)

The sodium was slowly added to ethanol. The produced sodium ethoxide solution, which was colorless transparent liquid, was purified through filtration.

The imidazole was added to sodium ethoxide solution, and the mixture was stirred in the oil bath pan for eight hours, resulting in the formationof the sodium imidazole. The sodium imidazole was purified through filtration.

A stoichiometric amount of RBr was added to the ethanol solution of sodium imidazole, and the mixture was stirred in the oil bath pan for two days, resulting in the formation of the alkylimidazole (RIm). The RIm was washed repeatedly with ethanol, acetone and dichloromethane, leached and distilled accordingly. Finally, the RIm was purified by column chromatography on silica gel.

（2）Preparation of acidic ionic liquids ([RImBs][HSO_4])

A stoichiometric amount of 1,4-butane sultone was added dropwise to the RIm at 0 °C and the mixture was stirred at 50 °C for 2-3 days. The zwitterions BsImR produced, all of which were white solids, were washed three times with ethyl acetate and ether to remove unreacted material and dried for 12 hours in a vacuum.

A stoichiometric amount of concentrated sulfuric acid was added dropwise to the zwitterions at 0 °C, and the mixture was stirred at 50 °C for 1-2 days, resulting in the formation of the [RImBs][HSO_4] ionic liquids. The ionic liquids were washed repeatedly with ethyl acetate and ether to remove unreacted material and dried under vacuum[27].

The ionic liquids were fully characterized by FT-IR, NMR, ESI-MS and TG-DTA, and the spectral data agreed with their structures.

Spectral data for [C_1ImBs]HSO_4. IR(KBr, ν/cm^{-1}): ν 3108, 1515, 1234, 1167, 1054, 571. ^{1}H NMR (400 MHz, DMSO-d_6): δ 1.540(m, 2H), 1.877(m, 2H), 2.496(t, 2H), 3.852(s,3H), 4.183(t, 2H), 7. 707(s, 1H) , 7.772(s, 1H) , 9.137(s, 1H). Positive-ion ESI-MS m/z: 317.1 (C_1ImBs^+), Negative-ion ESI-MS m/z: 96.9 (HSO_4^-). TG-DTA (N_2, 10 °C/min): Td 311 °C.

Spectral data for [C_2ImBs]HSO_4. IR(KBr, ν/cm^{-1}): ν 3105, 1513, 1216, 1167, 1054, 580. ^{1}H NMR (400 MHz, DMSO-d_6): δ 1.420(m, 3H), 1.547(m, 2H ,), 1.871 (m, 2H,), 2.510 (t, 2H), 4.201(m, 4H) , 7.807 (s, 1H), 7.833 (s, 1H), 9.250 (s, 1H). Positive-ion ESI-MS m/z: 233.1 (C_2ImBs^+), Negative-ion ESI-MS m/z: 96.9 (HSO_4^-). TG-DTA (N_2, 10 °C/min): Td 301 °C.

Spectral data for $[C_4ImBs]HSO_4$. IR(KBr, ν/cm^{-1}): ν 3107, 1514, 1221, 1166, 1037, 595. ^{1}H NMR (400 MHz, DMSO-d$_6$): δ 0.9160(m, 3H), 1.276 (m, 2H,), 1.536 (m, 2H,), 1.776(m, 2H), 1.886(m, 2H), 2.506 (t, 2H), 4.187(m, 4H), 7.815 (s, 2H), 9.237 (s, 1H). Positive-ion ESI-MS m/z: 261.1 (C_4ImBs^+), Negative-ion ESI-MS m/z: 96.9 (HSO_4^-). TG-DTA (N_2, 10 °C/min): Td 288 °C.

Spectral data for $[C_6ImBs]HSO_4$. IR(KBr, ν/cm^{-1}): ν 3107, 1510, 1225, 1165, 1046, 591. ^{1}H NMR (400 MHz, DMSO-d$_6$): δ 0.8020(m, 3H), 1.210(m, 6H), 1.510(m, 2H),1.738(m, 2H), 1.848 (m, 2H), 2.529 (t, 2H), 4.139(m, 4H), 7.775 (s, 2H), 9.228 (s, 1H). Positive-ion ESI-MS m/z: 289.1 (C_6ImBs^+), Negative-ion ESI-MS m/z: 97.0 (HSO_4^-). TG-DTA (N_2, 10 °C/min): Td 274 °C.

Spectral data for $[C_8ImBs]HSO_4$. IR(KBr, ν/cm^{-1}): ν 3105, 1508, 1228, 1167, 1051, 596. ^{1}H NMR (400 MHz, DMSO-d$_6$): δ 0.9120(m, 3H), 1.250(m, 10H), 1.521(m, 2H), 1.752(m, 2H), 1. 872 (m, 2H,) , 2.509 (t, 2H), 4.187(m, 4H), 7.812 (s, 2H) , 9.227 (s, 1H). Positive-ion ESI-MS m/z: 317.1 (C_8ImBs^+), Negative-ion ESI-MS m/z: 96.9 (HSO_4^-). TG-DTA (N_2, 10 °C/min): Td 273 °C.

Spectral data for $[C_{10}ImBs]HSO_4$. IR(KBr, ν/cm^{-1}): ν 3108, 1507, 1223, 1164, 1046, 580. ^{1}H NMR (400 MHz, DMSO-d$_6$): δ 0.8610(m, 3H), 1.282(m, 14H), 1.532(m,2H), 1.781(m, 2H), 1.852 (m, 2H), 2.521(t, 2H), 4.334(m, 4H), 7.781(s, 2H) , 9.208(s, 1H). Positive-ion ESI-MS m/z: 345.2 ($C_{10}ImBs^+$), Negative-ion ESI-MS m/z: 96.9 (HSO_4^-). TG-DTA (N_2, 10 °C/min): Td 280 °C.

Spectral data for $[C_{12}ImBs]HSO_4$. IR(KBr, ν/cm^{-1}): ν 3100, 1509, 1243, 1164, 1050, 592. ^{1}H NMR (400 MHz, DMSO-d$_6$): δ 0.8112(m, 3H), 1.253(m, 10H), 1.521-1.853(m,10H), 2.532 (t, 4H) ,4.139(m, 6H) , 7.775 (s, 2H) , 9.205 (s, 1H). Positive-ion ESI-MS m/z: 373.2 ($C_{12}ImBs^+$), Negative-ion ESI-MS m/z: 96.9 (HSO_4^-). TG-DTA (N_2, 10 °C/min): Td 296 °C.

Spectral data for $[C_{14}ImBs]HSO_4$. IR(KBr, ν/cm^{-1}): ν 3107, 1509, 1232, 1167, 1057, 596. ^{1}H NMR (400 MHz, DMSO-d$_6$): δ 0.8921(m, 3H), 1.117(m, 20H), 1.511-1.832(m, 6H), 2.532(t, 4H), 4.176(m, 4H), 7.871 (s, 2H), 9.204 (s, 1H). Positive-ion ESI-MS m/z: 401.3 ($C_{14}ImBs^+$), Negative-ion ESI-MS m/z: 97.0 (HSO_4^-). TG-DTA (N_2, 10 °C/min): Td 265 °C.

Spectral data for [C_{16}ImBs]HSO_4. IR(KBr, ν/cm^{-1}): ν 3113, 1503, 1239, 1168, 1055, 593. ^{1}H NMR (400 MHz, DMSO-d_6): δ 0.9612(m, 3H), 1.031(m, 22H), 1.511-1.801(m, 6H), 2.521 (t, 6H), 4.210(m, 4H), 7.775 (s, 2H)，9.119 (s, 1H). Positive-ion ESI-MS m/z: 429.3 ($C_{16}ImBs^+$), Negative-ion ESI-MS m/z: 96.9 (HSO_4^-). TG-DTA (N_2, 10 °C/min): Td 253 °C.

Brønsted acidity analysis of the ionic liquids

The Brønsted acidic strengths of ionic liquids were determined using UV-vis spectroscopy[28]. A series of different concentration of ionic liquids solutions were prepared, using p-nitroaniline as an indicator, and then the Hammett function (H_0) was calculated as follows:

$$H_0 = pK_a + \log([I]/[HI])$$

Where pK_a is the electrolytic constant of p-nitroaniline (pK_a =0.99), $[I]$ and $[HI]$ are percentage of unprotonated and protonated p-nitroaniline respectively.

Synthesis of methylal catalyzed by the [RImBs][HSO_4] ionic liquids

The reaction of formaldehyde with methanol was carried out in a 50 mL teflon-lined stainless-steel autoclave, equipped with thermostat and mechanical stirring. Formaldehyde, methanol, and [RImBs][HSO_4] ionic liquid catalyst with different molar rations were quantitatively introduced into the reactor successively. The reaction was allowed to proceed for 4h and kept at the desired temperature. After the reaction completed, the mixture was cooled and kept at 0 °C for 1 h and two phases were formed. The upper phase consisted of the produced methylal and the unreacted materials, and the lower phase contained the ionic liquid catalyst. The lower phase was simply separated from the upper phase by decantation.

The upper solution was analyzed by a Tianmei GC-7980T equipped with a Thermal Conductivity Detector (TCD). A packed column- Porapak T (60/80mesh 5m (L)*3mm (OD)*2mm (ID)) was used. Analytical conditons were as follows: injection port temperature, 140 °C；oven temperature, 150 °C; TCD temperature, 140 °C; carrier gas, hydrogen.

Results and discussion

Brønsted acidity analyses of the ionic liquids

The Brønsted acidic strengths of various ionic liquids are shown in Table 1. As could be seen from Table 1, with increasing the carbon chain length of ionic liquids, the Hammett function (H_0) are slightly increased at first and then slightly decreased. [C_6ImBs][HSO_4] shows the weakest Brønsted acidity. When the length of carbon chain increases from 4 to 12, the variation of acidic strength was in agreement with the results of references[29-31]. But the Hammett function of these ionic liquids have no great difference. The Brønsted acidic strength of these ionic liquids with different carbon chain of alkyl groups changes small. Therefore, for ionic liquids with the same anion, carbon chain length of alkyl groups has little effect on the Brønsted acidic strengths.

Table 1 The Brønsted Acidic Strengths of Various Ionic Liquids

Ionic liquids	A_{max}（AU）	[I](%)	[IH^+](%)	H_0
0	2.483	100	0	0
C_1-IL	2.145	86.40	13.59	1.793
C_2-IL	2.218	89.35	10.64	1.913
C_4-IL	2.275	91.64	8.351	2.030
C_6-IL	2.298	92.58	7.413	2.086
C_8-IL	2.194	88.36	11.63	1.870
C_{10}-IL	2.228	89.73	10.27	1.931
C_{12}-IL	2.185	87.98	12.01	1.854

Concentration: 20mmol/L; indicator: p-nitroaniline; Amax: Maximum absorbance of the indicator in various ionic liquids solutions; [I]: The percentage of unprotonated p-nitroaniline; $[IH^+]$: The percentage of protonated p-nitroaniline; H_0: The Hammett function.

Reaction of methanol with formaldehyde for preparation of methylal

Effect of ionic liquids with different carbon chain of alkyl groups on the catalytic reaction

The effect of ionic liquids with different carbon chain of alkyl groups on the catalytic reaction was studied (see Fig. 1). It is found that the conversion of formaldehyde is 0 and no methylal is obtained when there is no catalyst. The conversions of formaldehyde are distinctly different for the different carbon chain of ionic liquids. When the carbon chain length of ionic liquids is less than 6, the conversion of formaldehyde has a distinct increase with the increasing of carbon chain length. However, when the carbon chain length of ionic liquids increases from 6 to 16, the conversion of formaldehyde sharply decreases. The carbon chain length of ionic liquid has a significant effect on its catalytic activity. Among all the ionic liquids, $[C_6ImBS][HSO_4]$ shows the best catalytic performance. The catalytic activity of the ionic liquids is related to the viscosity of the ionic liquids[32]. When the viscosity of the ionic liquids is high, the collision rate between the ionic liquid catalyst and reactants becomes small. So, the reaction rate is slow. On the contrary ,when the viscosity of the ionic liquids is low, the reaction rate is fast. On the basis of the study of the viscosity of the ionic liquids, the carbon chain length of ionic liquids has important effect on the viscosity of the ionic liquids. When the carbon chain length of ionic liquids is less than 6, the viscosity of ionic liquid has a slight decrease. However, when the carbon chain length of ionic liquids increases from 6 to 16, the viscosity of ionic liquid sharply increases. The viscosity of $[C_6ImBS][HSO_4]$ ionic liquids is the lowest among all the ionic liquids. Therefore, the carbon chain length of ionic liquids have effect on the catalytic activity of the ionic liquids. Among all the ionic liquids, $[C_6ImBS][HSO_4]$ shows the best catalytic performance. With increasing the carbon chain length of ionic liquids, the variation trend of viscosity is contrary to that of catalytic activity. In addition, the hydrophobicity of ionic liquids becomes stronger with the increase of carbon chain length[32]. The catalytic activity of the ionic liquid may be related to the hydrophobicity. As the carbon chain length of ionic liquid increases, the solubility of ionic liquid catalyst in reactants decreases. The collision rate between the ionic liquid catalyst and reactants becomes small. Therefore, when the carbon chain length of ionic liquids increases from 6 to 16, the conversion of formaldehyde sharply decreases. Moreover, when the carbon chain length of ionic liquids is greater than 6, the effect of steric hindrance on reaction reduces catalytic activity. Therefore, the carbon chain length of ionic liquids have effect on the catalytic activity of the ionic liquids. Among all the ionic liquids, $[C_6ImBS][HSO_4]$ shows the best catalytic performance and the conversion of formaldehyde is 55.03 %. To investigate the influence of various factors synthesizing of methylal from methanol and formaldehyde, $[C_6ImBS][HSO_4]$ was chosen as the catalyst.

In addition, as could be seen from Fig. 1, the catalytic activity of the ionic liquid $[C_6ImBS][HSO_4]$ was near to that of concentrated sulfuric acid and *p*-toluenesulfonic acid. Concentrated sulfuric acid is corrosive and as a catalyst, is not easily recovered and its recovery gives the release of environmentally unfriendly effluents. It inevitably leads to a series of serious environment problems. On the contrary, ionic liquids are environmentally friendly catalysts that possess important attributes, such as negligible vapor pressure, high catalytic activity, excellent chemical and thermal stability, potential recoverability, design possibilities and ease of separation of the products from reactants. Therefore, considering the catalytic activity and environmental benefit, the ionic liquid catalyst is superior to concentrated sulfuric acid.

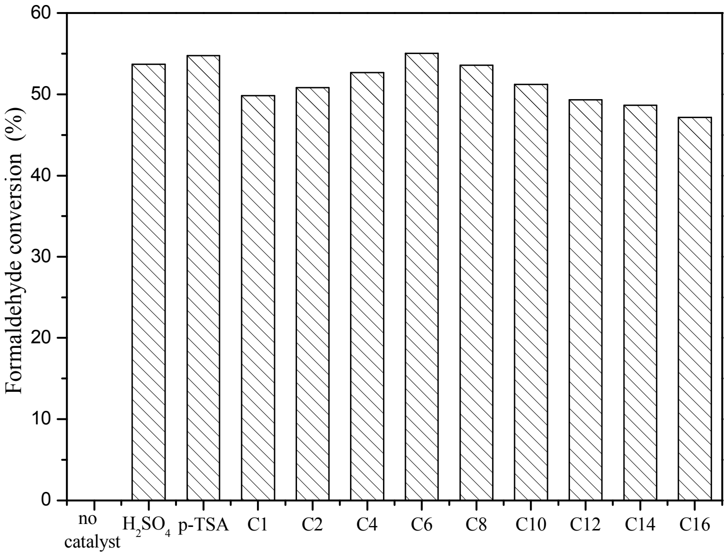


Fig. 1. Effect of ionic liquids with different carbon chain of alkyl groups on the catalytic reaction

Reaction conditions: n(methanol) : n(formaldehyde) : n(ILs) =2.4: 1: 0.0186, 60 °C, 4h.

Effect of catalyst dosage on the catalytic reaction

A series of experiments were conducted using the best catalyst [C_6ImBS][HSO_4] with different dosages (Fig. 2). The amount of ionic liquid is denoted by ILs/ formaldehyde molar ratio. As shown in Fig. 2， when the amount of ionic liquid is less than 0.0258, with an increase in the relative amount of ionic liquids, the rate of reaction is enhanced, resulting in a higher conversion of formaldehyde. The amount of ionic liquids had a significant effect on the catalytic performance. This is attributed to the increase in acidity in the reaction system. However, when the amount of ionic liquid is more than 0.0258, the conversion of formaldehyde is basically unchanged, which indicates that the reaction has probably approached equilibrium. From the point of view of economy in the industrial applications, the increase in catalyst dosage would undoubtedly increase operation cost. Thus, considering the reaction rate and the cost of ionic liquids, the optimum catalyst dosage is 0.0258.

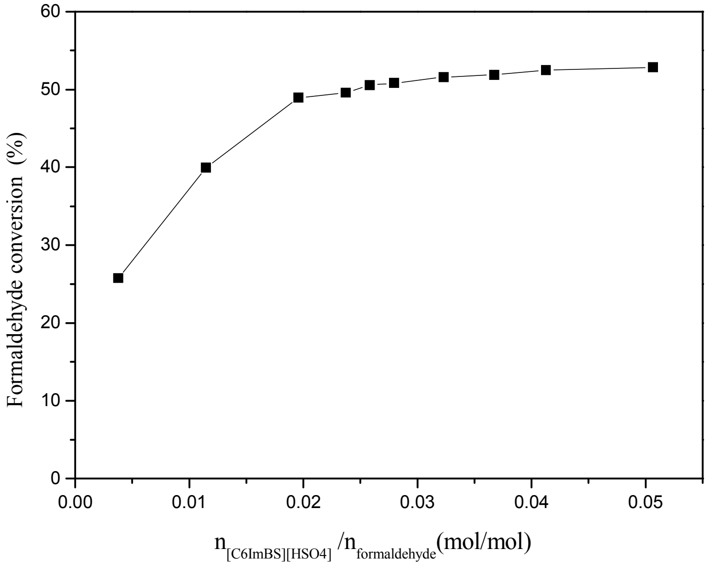


Fig. 2. Effect of catalyst dosage on the catalytic reaction

Reaction conditions: n(methanol) : n(formaldehyde) =2:1, 60 °C, 4h.

Effect of Reaction Temperature on the Catalytic Reaction

In general, the reaction temperature has an important effect on the kinetics and thermodynamics of the reaction. Therefore, the effect of reaction temperature on the synthesis of methylal was investigated in detail (see Fig. 3). With the increasing of reaction temperature, the conversion of formaldehyde increases at first and then slightly decreases, which is up to maximum value when reaction temperature is 60 °C. When reaction temperature is high, the collision rate between the ionic liquid catalyst and reactants becomes fast. So, the reaction rate is fast and the conversion of formaldehyde increases. In addition, when reaction temperature is high, the viscosity of the ionic liquid becomes low. So, the collision rate between the ionic liquid catalyst and reactants becomes fast. The reaction rate is fast and the conversion of formaldehyde increases. However, the reaction is a slight exothermic reaction and the increase of temperature will reduce the reaction performance. Therefore, when reaction temperature is more than 60 °C, the conversion of formaldehyde slightly decreases. For this reason, the preferred reaction temperature is 60 °C.

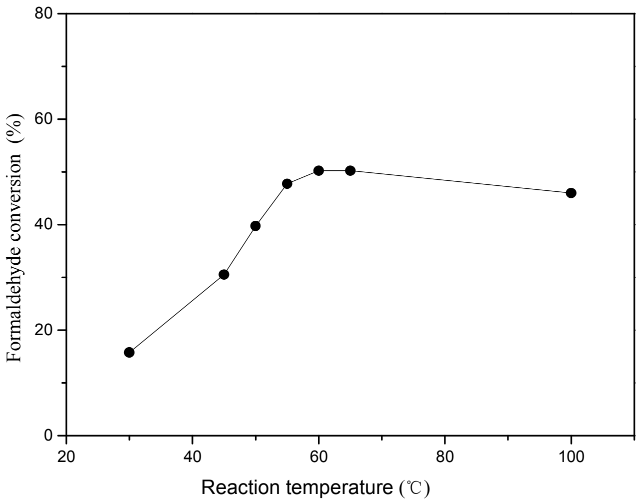


Fig. 3. Effect of the reaction temperature on the catalytic reaction

Reaction conditions: n(methanol) : n(formaldehyde) : n(ILs)=2:1: 0.0258, 4h.

Effect of the molar ratio of methanol to formaldehyde on the catalytic reaction

A series of experiments were conducted using the best catalyst [C_6ImBS][HSO_4]. Fig. 4 shows the effect of the molar ratio of methanol to formaldehyde on the catalytic reaction. As the molar ratio of methanol to formaldehyde increases, the conversion of formaldehyde was increased. When the mole ratio of methanol to formaldehyde is less than 2.5, the conversion of formaldehyde has a obvious increase with the increasing of methanol. However, when the mole ratio of methanol to formaldehyde is more than 2.5, the conversion of formaldehyde has a slight increase. Based on the chemical equilibrium theory, increasing the amount of methanol is beneficial to the forward reaction, resulting in a higher rate of reaction. However, if this ratio was further increased, the concentration of catalyst will be greatly diluted, resulting in a slight increase in the rate of reaction. Therefore, when the molar ratio of methanol to formaldehyde was more than 2.5, the amount of methanol had a slight effect on the catalytic performance. Moreover, a higher molar ratio of methanol to formaldehyde will cause a larger amount of methanol to be separated from the ionic liquid during recycling. For this reason, the optimal molar ratio of methanol to formaldehyde 2.5 is preferable. The conversion of formaldehyde was obtained as high as 63.37 %.

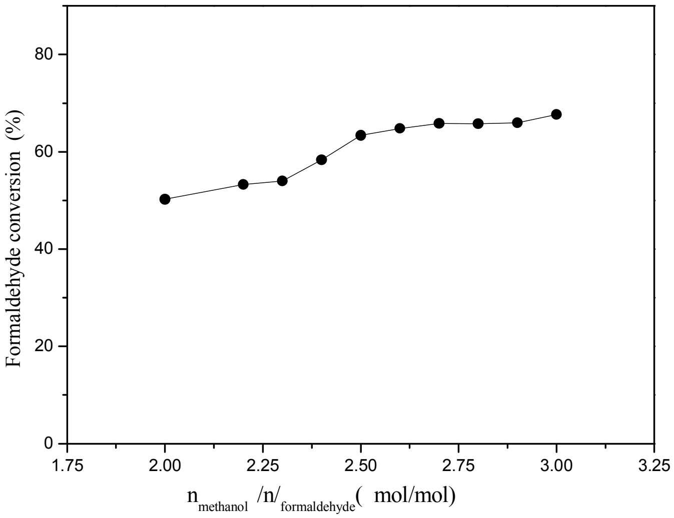


Fig. 4. Effect of methanol/formaldehyde molar ration on the catalytic reaction

Reaction conditions: n(ILs): n(formaldehyde) = 0.0258, 60 °C, 4h.

The reuse of ionic liquid

In order to investigate the potential reusability of the ionic liquids in the synthesis of methylal, a series of recycle experiments were conducted with a methanol to formaldehyde molar ratio of 2.5 and ionic liquid to formaldehyde molar ratio of 0.0258 at 60°C for 4h. After each recycle reaction, the ionic liquid was simply separated from the reactants by distillation and was dried in vacuum. As shown in Fig. 5, the [C_6ImBS][HSO_4] was used five times and its catalytic activity changed very little. Therefore, the [C_6ImBS][HSO_4] as the catalyst for the synthesis of methylal is recyclable and stable.

In addition, the catalytic activity of the ionic liquid [C_6ImBS][HSO_4] was near to that of concentrated sulfuric acid and *p*-toluenesulfonic acid from Fig. 1. Concentrated sulfuric acid is corrosive and as a catalyst, is not easily recovered and its recovery gives the release of environmentally unfriendly effluents. It inevitably leads to a series of serious environment problems. Although the cost of [C_6ImBS][HSO_4] is about 30 times the cost of H_2SO_4, ionic liquids are environmentally friendly catalysts that possess important attributes, such as negligible vapor pressure, high catalytic activity, excellent chemical and thermal stability, potential recoverability and ease of separation of the products from reactants. Therefore, considering the catalytic activity and environmental benefit, the ionic liquid catalyst is superior to concentrated sulfuric acid.

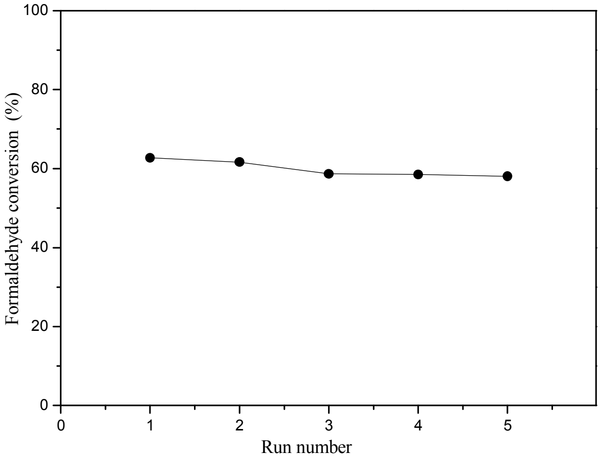


Fig. 5. The reuse of ionic liquid

Conclusions

Several ionic liquids with different carbon chain length of alkyl groups were synthesized successfully and were characterized by IR, NMR, ESI-MS, TG-DTA, UV-vis spectroscopy and capillary viscometer. Catalytic reaction of methanol with formaldehyde for preparation of methylal was investigated in various ionic liquids with different carbon chain length of alkyl groups. It was found that their structures were consistent with the designed structures. These acidic ionic liquids showed excellent catalytic performance for synthesis of methylal. The catalytic activity of each ILs is dependent on the carbon chain length of alkyl groups. The conversion of formaldehyde increased at first and then decreased with lengthening carbon chain of ionic liquids. The ionic liquid [C_6ImBs][HSO_4] showed the best catalytic performance.

From various parametric studies, such as catalyst dosage, reaction temperature and the methanol/ formaldehyde mole ratio, an optimum reaction condition was established. The Brønsted acidic ionic liquids had a potential application in the production of methylal.

Acknowledgments

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Captions

Scheme 1 Synthetic procedure of Brønsted acid ionic liquids with different alkyl groups

Fig. 1. Effect of ionic liquids with different carbon chain of alkyl groups on the catalytic reaction

Reaction conditions: n(methanol) : n(formaldehyde) : n(ILs) =2.4: 1: 0.0186, 60 °C, 4h.

Fig. 2. Effect of catalyst dosage on the catalytic reaction

Reaction conditions: n(methanol) : n(formaldehyde) =2:1, 60 °C, 4h.

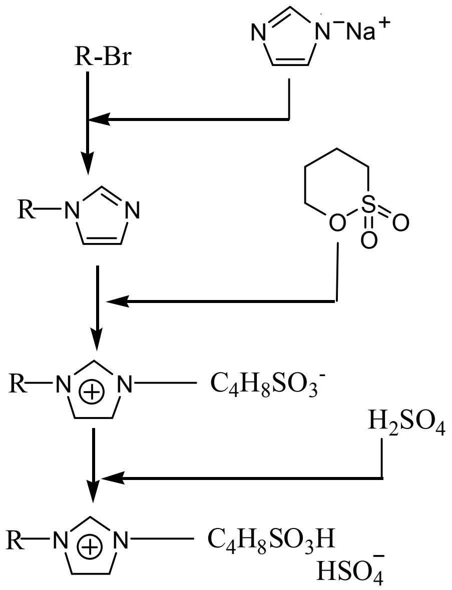
Fig. 3. Effect of the reaction temperature on the catalytic reaction

Reaction conditions: n(methanol) : n(formaldehyde) : n(ILs)=2:1: 0.0258, 4h.

Fig. 4. Effect of methanol/formaldehyde molar ration on the catalytic reaction

Reaction conditions: n(ILs): n(formaldehyde) = 0.0258, 60 °C, 4h.

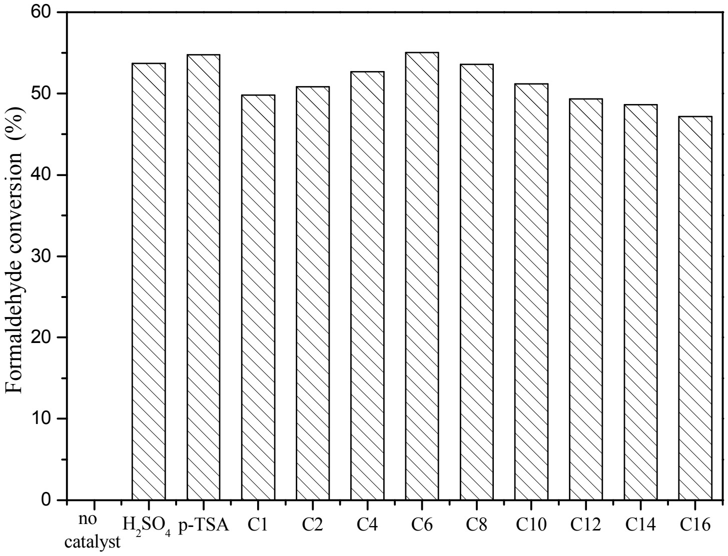
Fig. 5. The reuse of ionic liquid



R：C_nH_{2n+1}

n=1、2、4、6、8、10、12、14、16

Scheme 1 Synthetic procedure of Brønsted acid ionic liquids with different alkyl groups



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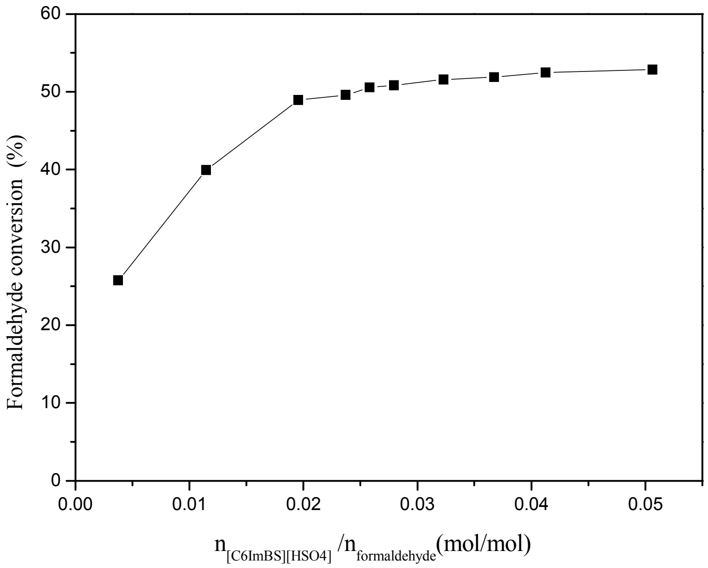

Fig. 2. Effect of catalyst dosage on the catalytic reaction

Reaction conditions: n(methanol) : n(formaldehyde) =2:1, 60 °C, 4h.

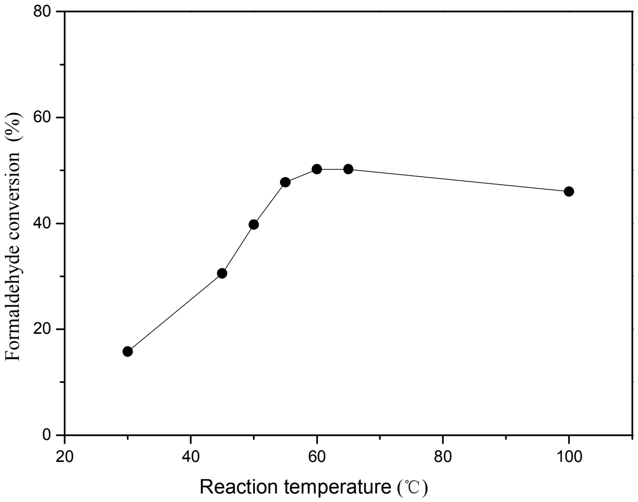

Fig. 3. Effect of the reaction temperature on the catalytic reaction

Reaction conditions: n(methanol) : n(formaldehyde) : n(ILs)=2:1: 0.0258, 4h.

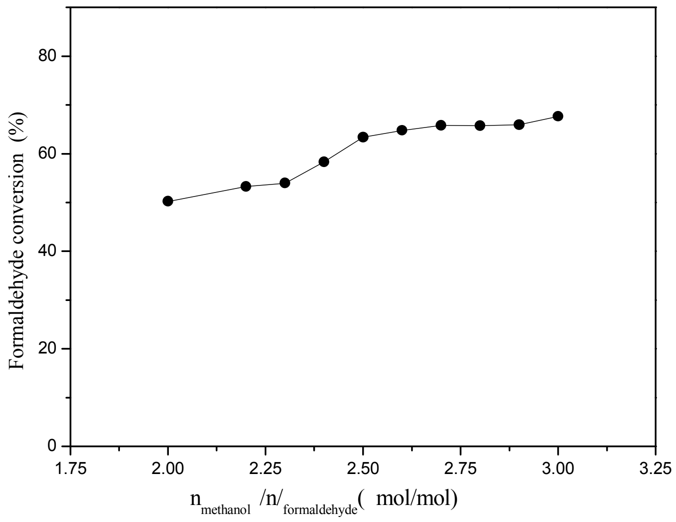

Fig. 4. Effect of methanol/formaldehyde molar ration on the catalytic reaction

Reaction conditions: n(ILs): n(formaldehyde) = 0.0258, 60 °C, 4h.

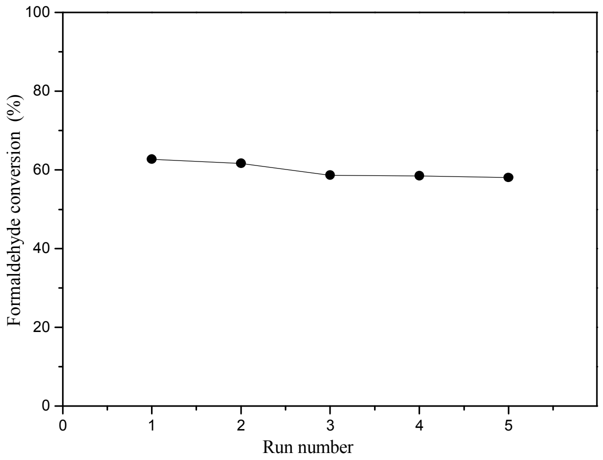

Fig. 5. The reuse of ionic liquid