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Efficient and reusable zeolite-immobilized acidic ionic liquids for the synthesis of polyoxymethylene dimethyl ethers



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ABSTRACT

Keywords: Trioxane Polyoxymethylene dimethyl ethers Acetalation reaction Molecular sieve Supported ionic liquids A series of molecular sieve-immobilized Brønsted acidic ionic liquids (BAILs@MS) was prepared, characterized and utilized as efficient catalysts for the synthesis of polyoxymethylene dimethyl ethers (PODE_n or DMM_n) from methylal (DMM₁) and trioxane (TOX). Combined characterization results from fourier transform infrared (FT-IR) spectroscopy, elemental analysis, thermogravimetry (TG), N₂ adsorption-desorption (Brunauer-Emmett-Teller, BET) isotherms, X-ray diffraction (XRD), scanning electron microscopy (SEM) and temperature-programmed desorption of ammonia (NH₃-TPD), suggested that the synthesized BAILs were successfully immobilized on the surface of molecular sieves through covalent bonds. Moreover, the catalytic performance tests demonstrated that NaZSM-5 immobilized SO₃H-functionalized ionic liquids (ILs) i.e., BAILs@NaZSM-5, exhibited excellent activity for the acetalation of DMM₁ with TOX, compared to the homogeneous catalysis of the precursors ([MIMBs] HSO₄) as well as other molecular sieve-supported ILs. The influence of catalyst concentration, molar ratio of DMM₁ to HCHO, temperature and reaction duration on the catalytic activity were investigated by employing [NaZSM-5IMBs]HSO₄ as the catalyst. It was demonstrated that a superior conversion of formaldehyde (FA) (90.3%) and excellent selectivity for DMM₃₋₈ (53.5%) has been achieved in mild conditions (110 °C, 2.5 MPa for 2 h). Additionally, the catalyst can be effortlessly separated by filtration and reused more than ten times without significant loss of activity.

1. Introduction

Polyoxymethylene dimethyl ethers (CH₃O(CH₂O)_nCH₃, $n \ge 2$; referred to as PODE_n or DMM_n) have been considered as promising diesel additives because of their high oxygen contents and cetane numbers (CN), making them suitable for improving the combustibility and enhancing the efficiency of combustion, as well as reducing the release of pollutants [1-3]. Especially, the physicochemical properties of DMM₃₋₈ are comparable to that of diesel oil, thus allowing their use in modern diesel engines without any modification of the engine infrastructure. Compared with the usage of diesel fuel alone, the particulate matter and NO_x emissions are reduced by 80-90% and 50%, respectively with 20% blend [2-4]. DMM₂, DMM₃, and DMM₄ also exhibit low toxicity [5], excellent volatility, low condensation point, great permeating ability, good solubilizing power and miscibility with nearly all organic compounds and water. Additionally, they have the potential to be used as environment-friendly industrial solvents. The conventional process for the synthesis of DMM_n is based on the acetalation of the end-group (-CH₃, -OCH₃) provider (methanol or methylal (DMM₁)) with a chain section (-CH₂O-) provider (1,3,5-trioxane (TOX), paraformaldehyde (PF) or formaldehyde (FA)) under acidic conditions [6]. All these raw

materials can be obtained economically on large scale from coal and

natural gas. In recent years, many routes have been reported to syn-

thesize DMM_n from methanol and FA, PF or TOX [7-14]. However,

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when methanol and water are present in the process, the separation of DMM_n is difficult because many side-products are produced. To avoid introducing or generating water, one particularly favorable route is, therefore, the water-free process using DMM_1 and TOX as starting materials. So far, many catalysts have been developed for the acetalation reaction of DMM_1 with TOX, such as liquid acids [15,16], ionexchange resins [17–19], molecular sieves [20], metal oxides [21], etc. In this context, our group has recently proposed a process catalyzed by Brønsted-acidic ionic liquids (BAILs) [22–25], which combines the advantages of both homogeneous and heterogeneous catalysts. Even though BAILs possess inherent advantages such as high acid density, broad liquid range, and uniform active catalytic sites, there are still some disadvantages, including high viscosity and losses in polar solvents.

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To overcome these drawbacks of ILs, there has been a great deal of attention recently to immobilization of ILs on a variety of polymeric [26-32] and inorganic supports [33-40]. The immobilization process aims to combine the desired catalytic properties of ILs with the easy recovery features of heterogeneous supports. Moreover, it is desirable to utilize properties of support materials such as surface and pore structure, achieving synergistic catalysis in the reaction system. Among the heterogeneous solid supports employed for ILs, molecular sieves are the most widely used, convenient, and acid stable, possessing several attractive advantages in terms of structure stability and recycling. W.G. Cheng et al. [34] have successfully synthesized an SBA-15 supported 1.2.4-triazolium-based IL for the preparation of cyclic carbonates from CO₂ and epoxides, 80-99% vield and 97-99% selectivity of the products were obtained under mild conditions. J.B. Yang et al. [35] have developed -SO3H functionalized BAILs supported onto SBA-15 and applied them as efficient catalysts in the transesterification of sec-butyl acetate and methanol for the synthesis of 2-butanol. Z.M. Li et al. [36] reported MOR zeolite immobilized -SO3H functionalized BAILs as efficient catalysts for the ketalization of cyclohexanone with diols. Therefore, we choose the hydrothermally stable molecular sieves as the solid support which can effectively promote the catalytic reactivity of acetalation reactions when compared to the corresponding homogeneous IL catalysts.

Herein, we report a novel heterogeneous catalyst i.e., molecular sieve-supported -SO₃H functionalized BAILs (BAILs@MS) and its application in the acetalation reaction of DMM₁ with TOX (Scheme 1). Fourier transform infrared (FT-IR) spectroscopy, elemental analysis, thermogravimetry analysis (TG), N₂ adsorption-desorption (Brunauer-Emmett-Teller, BET) isotherm, X-ray diffraction (XRD), scanning electron microscopy (SEM) and temperature-programmed desorption of ammonia (NH₃-TPD) were then utilized to characterize the catalyst in detail. Further, the effect of the reaction parameters including catalyst loading, material ratios, temperature, and reaction time were studied to obtain the optimum conditions and the recyclability of the catalyst was also investigated.

2. Experimental

2.1. General

The molecular sieves ZSM-5 (Si/Al = 500), Y (Si/Al = 5), and Si-MCM-41 were purchased from Nanjing XFNAON Materials Tech Co., Ltd. DMM₂ (> 99.5%), DMM₃ (> 99.5%), DMM₄ (> 99.5%) and DMM₅ (> 99.5%) were separated by rectification. Other chemicals were analytical grade and utilized without additional purification.

2.2. Catalyst preparation

2.2.1. Preparation of 1-(3-(triethoxysilyl)propyl)-1H-imidazole

A stoichiometric amount of imidazole (1 mol) in anhydrous furanidine (200 mL) was added dropwise to a suspension of NaH (1 mol) in anhydrous furanidine (100 mL) at room temperature under stirring, and the mixture was further heated at 40 °C for 12 h. Then, a stoichiometric amount of (3-chloropropyl)triethoxysilane (1 mol) was added dropwise to the mixture and stirred at 80 °C for 48 h to yield 1-(3-(triethoxysilyl) propyl)-1H-imidazole. After the reaction has completed, the reaction mixture was filtered and the filter cake was washed three times with furanidine. The filtrate was collected and dried for 12 h with anhydrous magnesium sulfate and 1-(3-(triethoxysilyl)propyl)-1H-imidazole was separated by distillation. The ¹H NMR and ¹³C NMR spectra were



Scheme 2. Synthetic route of BAILs@MS.

recorded on the INOVA-400 MHz spectrometer (Bruker, Switzerland) employing tetramethylsilane (TMS) as the internal standard. NMR spectra data in C_6D_6 is shown as follows. ¹H NMR (400 MHz, C_6D_6): δ 0.11–0.15 (t, J = 8.0 Hz, 2 H), 0.86–0.90 (t, J = 8.0 Hz, 9 H), 1.32–1.40 (h, J = 8.0 Hz, 2 H), 2.98–3.02(t, J = 8.0 Hz, 2 H), 3.43–3.49 (q, J = 8.0 Hz, 6 H), 6.26 (s, 1 H), 6.92 (s, 2 H). ¹³C NMR (100 MHz, C_6D_6): δ 7.32, 18.16, 24.90, 48.31, 58.20, 118.08, 129.79, 137.06.

2.2.2. Preparation of NaZSM-5

In a typical procedure, $1 \text{ M } \text{NaNO}_3$ solution (200 mL) was mixed with ZSM-5 (20 g) over a water bath at 80 °C with stirring for 4 h. The product was filtered, washed thoroughly with water and dried at 60 °C for 12 h. Next, the product was calcined in air at 550 °C for 5 h. The test was repeated three times.

2.2.3. Preparation of molecular sieve supported ionic liquids (ILs@MS)

The molecular sieve supported ionic liquids (ILs@MS) were synthesized in three steps, as shown in Scheme 2. Firstly, a mixture of molecular sieves (10.0 g) with 1-(3-(triethoxysilyl)propyl)-1H-imidazole or 4-(2-(triethoxysilyl)ethyl)pyridine (0.04 mol) in anhydrous toluene (100 mL) was stirred and refluxed for 48 h. Secondly, the reaction mixture was cooled to 80 °C and 1,4-butylene sulfone (0.04 mol) was added dropwise to the reaction system, the mixture was stirred for 48 h at 80 °C. After the reaction has completed, the reaction mixture was collected by filtration and washed thrice with toluene to remove any unconverted reactants. After drying in vacuum (70 °C, 5.3 K Pa for 12 h), the white powder (intermediate) was obtained. Finally, the intermediate was added in a round-bottom flask containing ethanol



Scheme 1. Acetalation reaction of methylal with trioxane catalyzed by BAILs@MS.

(100 mL) and sulphuric acid (0.04 mol) in ethanol (50 mL) was gradually added to the flask at room temperature while stirring. Next, the mixture was steadily heated to reflux and allowed to react for 36 h. The mixture was further filtered and washed with toluene (50 mL \times 2) and ethanol (50 mL \times 12) until the p^H reached 7.0. Finally, the prepared ILs@MS was dried under vacuum to entirely eliminate the residual volatiles and moisture prior to use.

2.3. Catalyst characterization

FT-IR spectra were recorded on a NEXUS 870 FT-IR infrared spectrometer (Nicolet Instruments Co., USA) in dry air at room temperature with anhydrous KBr as standard. Sulfur (S, wt.%) was determined by elemental microanalysis technique using a Vario EL cube elemental analyzer (Elementar Analysensysteme Co., Ltd., Hanau, Germany), and the loading amount of ILs on the molecular sieve was calculated by the content of S element. TG analysis was carried out using a Netzsch STA449F3 simultaneous thermal analyzer (Netzsch Co., Ltd., Selb, Germany) in a N2 atmosphere between 50 and 1000 °C. The BET sorption of N2 was determined using Micromeritics ASAP2010 equipment (Micromeritics Instrument Co., Ltd., Norcross, USA). The XRD was measured on a Panalytical X'PERT PRO X-ray diffractometer (Panalytical B V, Almelo, Netherlands). The particle size and morphology was assessed by SEM using Hitachi SU8020 equipment (Hitachi, Tokyo, Japan). The acidity of BAIL@NaZSM-5 was measured by NH₃-TPD using an AutoChem 2910 apparatus (Micromeritics Instrument Co., Ltd., Norcross, USA). A 100 mg sample was treated in situ at 300 °C for 1 h under a Helium (He) stream (30 mL/min), purged by He (30 mL/min) for 0.5 h to clean its surface, and then cooled to 50 °C. The sample was further saturated with NH₃ for 1 h, followed by flushing with He until a stable baseline was obtained. TPD measurements were then conducted from 50 to 800 °C with a rate of 10 °C/min. The release of NH₃ was monitored by a thermal conductivity detector.

2.4. Typical acetalation procedure

Catalytic activity experiments were conducted in a 100 mL Teflonlined stainless-steel autoclave provided with a thermometer and mechanical stirrer. It is thermostated using an electric heater. Initially, DMM₁ (0.36 mol), TOX (0.1 mol), and catalyst (1.8 g) were added into the autoclave, which was then closed and flushed thrice with N₂ (1.5 MPa) at room temperature. The reaction mixture was preheated to the desired temperature before starting the reaction, after which, the mechanical stirrer was immediately turned on, and the timing began. After completion of the reaction, the products have been characterized and quantitatively determined using gas chromatography/mass spectrometry (GC/MS) (Agilent 7890 A/5975C) and GC (Agilent 6890), respectively. An SE-54 capillary column with a FID detector was used in an Agilent 6890 gas chromatograph. The GC quantitative analysis of TOX, DMM_n, methanol, and methyl formate was determined with the internal standard method: a specific quantity of furanidine was used as the internal standard for the samples prior to GC analyses. FA was analyzed using titration by the sodium sulfite method and formic acid content was analyzed using titration by potassium methylate.

Conversion of FA (Con. FA) and the selectivity for products (Sele. DMM_{3-8}) were determined using the following equations:

Con. FA(%) =
$$\frac{W_{(TOX+FA),0} - W_{(TOX+FA)}}{W_{(TOX+FA),0}} \times 100\%$$

Sele. DMM₃₋₈ =
$$\frac{w_{DMM_{3-8}}}{w_{DMM_{2-10}} + w_{MeOH} + w_{MA} + w_{MF}} \times 100\%$$

FA, formaldehyde; MA, formic acid; MF, methyl formate.



Fig. 1. Fourier transform infrared spectroscopy spectra of molecular sieves and BAILs@MS.

3. Results and discussion

3.1. Catalyst characterization

3.1.1. Fourier transform infrared (FT-IR) spectroscopy

The FT-IR spectra of NaZSM-5, Si-MCM-41, Y, [NaZSM-5IMBs] HSO₄, [NaZSM-5PyBs]HSO₄, [Si-MCM-411MBs]HSO₄ and [YIMBs] HSO₄ are illustrated in Fig. 1. As shown in Fig. 1(a), the absorption bands at about 447.2, 801.7 and 1089.6.0 cm⁻¹ were characteristic of SiO₂ [36,37], whereas the bands at 1640.0 and 3443.8 cm⁻¹ were

attributed to the stretching frequency of Si-OH and physisorbed water [36,38]. For [NaZSM-5IMBs]HSO₄, the characteristic peaks were found at 3154.4, 1566.6 and 1458.0 cm^{-1} , which can be assigned to the C-H, C=N and C=C stretching vibrations of the imidazole ring [36,39]. The bands around 1232.1 and 1092.9 cm⁻¹ were associated with the signals of C-S and S=O bonds, which overlap with the characteristic peaks of SiO₂, where the peaks become wider and stronger. These results indicate the existence of the -SO₃H group [40]. In comparison with NaZSM-5, [NaZSM-5IMBs]HSO4 exhibited the same characteristic bands such as the Si–O–Si vibrations (789.3 and 1092.9 cm⁻¹) and the stretching vibration of -OH (1646.9, 3445.0 cm⁻¹). Moreover, the bands around 3445.0 cm⁻¹ become wider and stronger after loading ILs. which indicates the existence hydrogen bonds with ILs on the surface of the zeolite. Similar results were obtained in [NaZSM-5PyBs]HSO4; it displays peaks at 3060.5, 1515.8 and 1471.4 cm⁻¹ related to the stretching frequencies of C-H, C=N and C=C on the pyridine ring while the characteristic peaks of the -SO3H group are detected at 1232.1 and 1095.5 cm⁻¹. Therefore, these results confirm that the ILs have been successfully immobilized on the NaZSM-5 via covalent bonds.

Fig. 1(b) and (c) depict the FT-IR spectra of $[Si-MCM-411MBs]HSO_4$ and $[YIMBs]HSO_4$, as well as Si-MCM-41 and Y for comparison, respectively. Similar results were obtained, providing further evidence of ILs grafted onto the surface of molecular sieves.

3.1.2. Elemental analysis

The fraction of the ILs grafted onto molecular sieves was measured by an elemental analyzer through the amount of S element and the results were presented in Table 1. The results of [NaZSM-5IMBs]HSO₄ show that 17.7% of the IL ([PIM]HSO₄) were immobilized on NaZSM-5 according to the content of S element (3.3 wt.%) in the catalyst. Furthermore, the grafted percentages of [NaZSM-5PyBs]HSO₄, [Si-MCM-41IMBs]HSO₄ and [YIMBs]HSO₄ were 9.6%, 28.5% and 8.1%, respectively.

3.1.3. Thermal stability

The thermal stability of molecular sieve-grafted acidic ILs was determined by TG, and the weight losses of the samples were depicted in Fig. 2. For NaZSM-5, a slight weight loss of 2.8% at the temperature range of 50-1000 °C occurred due to the residual moisture in pores. When -SO₃H functionalized imidazolium ILs was immobilized on zeolite, an initial weight loss of \sim 5.3% occurred at the temperature range of 50-310 °C, which was attributed to the release of physisorbed water as well as the dehydration of unreacted silanol groups. Further, a considerable weight loss of ~18.5% was seen at 310-510 °C as the organic structure of the ILs decomposed from the surface of NaZSM-5. Therefore, the catalyst can be operated stably at temperatures under 310 °C. Similar results were obtained when -SO₃H functionalized pyridine ILs was immobilized on NaZSM-5 ([NaZSM-5PyBs]HSO₄); a weight loss of ~5.6% at 50–280 °C was attributed to the loss of water and unreacted silanol groups. Further, a weight loss of $\sim 9.7\%$ was found at 280–500 °C brought about by the decomposition of ILs. When -SO₃H functionalized imidazolium ILs was immobilized on Si-MCM-41 and Y, the weight loss temperatures were 320 °C and 350 °C, respectively. Consequently, we arrived at a conclusion that all of these BAILs@MS demonstrate high thermal stability and could be potentially

Table 1

Elemental analysis of NaZSN-5 and BAILs@MS.

Sample	S content (wt.%)	IL content (wt.%)
NaZSM-5	0	0
[NaZSM-5IMBs]HSO ₄	3.3	17.7
[NaZSM–5PyBs]HSO ₄	1.8	9.6
[Si-MCM-41IMBs]HSO4	5.3	28.5
[YIMBs]HSO ₄	1.5	8.1



Fig. 2. Thermal stability of molecular sieves and BAILs@MS.



Fig. 3. N2 Adsorption-desorption isotherms of NaZSM-5 and BAILs@NaZSM-5.

employed as catalysts.

3.1.4. N₂ adsorption-desorption (BET)

The BET isotherms of the support before and after grafting are presented in Fig. 3. It can be observed that all the curves exhibit typical type IV isotherms and the H1 hysteresis loop of NaZSM-5 was at the pressures of $P/P_0 = 0.45 - 0.8$, which was characteristic of a mesopores structure [41]. Moreover, the hysteresis loops of BAILs@NaZSM-5 became smaller, which was attributed to the immobilization of ILs onto the zeolite and filling into some mesopores of the zeolite. The surface area and pore size of the samples were calculated by the BET equation and shown in Table 2. It can be seen that the surface area and total pore volume were reduced after ILs were grafted on the molecular sieves,

Table 2	
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Sample	BET Surface	Total pore	Average pore
	area	volume	width
	(m²/g)	(cm ³ /g)	(Å)
NaZSM-5	416.43	0.22	20.89
[NaZSM-5IMBs]HSO ₄	40.19	0.06	56.39
[NaZSM-5PyBs]HSO ₄	218.06	0.11	20.67
Si-MCM-41	1122.95	1.02	36.32
[Si-MCM-411MBs]HSO ₄	10.69	0.02	60.84
Y	723.47	0.37	20.36
[YIMBs]HSO ₄	9.20	0.02	82.40



Fig. 4. XRD patterns of NaZSM-5 and BAILs@NaZSM-5.

while the average pore width increased as a small fraction of the pores were blocked off after grafting $[PIMBs]HSO_4$.

3.1.5. X-Ray diffraction (XRD) studies

Fig. 4 displays the high-angle powder XRD patterns of NaZSM-5 and NaZSM-5 grafted with various ILs. It was clear that the diffraction peak decreased apparently after the ILs was grafted on NaZSM-5; moreover, the type of XRD pattern has not altered. The higher the amount of ILs loaded, the weaker the peak intensity. This result indicates that the framework of the zeolite was not damaged and only the crystallinity was reduced when ILs were grafted on NaZSM-5.

3.1.6. Scanning electron microscopy (SEM) studies

SEM was performed to characterize the morphology of BAILs@ NaZSM-5 and NaZSM-5, and the images were shown in Fig. 5. The SEM image showed that there was no obvious change in the size of NaZSM-5 particles after the introduction of the ILs. These results indicated that the morphological homogeneity of the NaZSM-5 particles was maintained after BAILs grafting. However, the SEM images also revealed that some NaZSM-5 particles have coalesced in BAILs@NaZSM-5, which is



Fig. 6. NH₃-TPD profiles of NaZSM-5 and BAILs@NaZSM-5.

possibly due to the binding of BAILs to the zeolite crystals.

3.1.7. Acidity analysis

NH₃-TPD was employed to determine the acidity of BAILs@NaZSM-5 and NaZSM-5, and the images were depicted in Fig. 6. As shown in the NH₃-TPD profiles, the ammonia desorption peaks at about 120–250 °C and 300–450 °C correspond to the weak acid sites and the strong acid sites, respectively [20]. The peak intensity has obviously increased when ILs were grafted onto the surface of the zeolite. Furthermore, the peak intensity representing the density of acid sites was enhanced with an increase in the loading of ILs, especially for the strong acid sites. Based on the aforementioned results, we have obtained the order of acidity for BAILs@NaZSM-5 and NaZSM-5: [NaZSM-5IMBs] HSO₄ > [NaZSM-5PyBs]HSO₄ > NaZSM-5.

3.2. Performance of the synthesized BAILs@MS catalysts

The catalytic activity of BAILs@MS for the preparation of



Fig. 5. The whole and magnified SEM images of NaZSM-5 and BAILs@NaZSM-5. (a) NaZSM-5, (b)[NaZSM-5IMBs]HSO4, (c) [NaZSM-5PyBs]HSO4.

Table 3 Effect of catalysts on the reaction

Catalysts	Produc	t distribut	tion (%)												Con.	Sele. for
	$\hline CH_3O(CH_2O)_nCH_3, DMM_n, n = MeOH MF TOX FA$								(%)	(%)						
	1	2	3	4	5	6	7	8	9	10						
NaZSM–5	74.0	1.1	0.1	0.09	0	0	0	0	0	0	0.06	0.04	24.5	0.1	0.8	16.8
*[MIMBs]HSO ₄	65.4	13.6	3.0	0.7	0.1	0	0	0	0	0	0.6	0.3	19.8	0.6	17.8	21.5
[NaZSM–5IMBs]HSO ₄	43.1	24.8	14.8	8.3	3.4	1.6	0.6	0.2	0.07	0.01	0.8	0.1	2.2	0.2	90.3	53.5
[NaZSM–5PyBs]HSO ₄	48.0	23.8	12.4	6.5	2.7	1.4	0.6	0.2	0.1	0.02	1.6	0.08	2.0	0.5	89.9	49.8
[YIMBs]HSO ₄	72.6	2.7	0.3	0.03	0	0	0	0	0	0	0.7	0.4	22.4	0.9	6.1	10.0
[Si-MCM–41IMBs]HSO ₄	75.1	0.5	0.09	0.03	0	0	0	0	0	0	0.04	0.02	24.0	0.1	2.8	17.9

Reaction conditions: Catalyst: 5.0 wt.%, HCHO (TOX):DMM₁ = 1:1.2 M ratio, 110°C, 2.5 M Pa, 2 h. *[MIMBs]HSO₄: 0.9 wt.%.

polyoxymethylene dimethyl ethers (CH₃O(CH₂O)_nCH₃, DMM_n, n = 2-8) via acetalation of DMM₁ with TOX were evaluated and compared with that of NaZSM-5 and [MIMBs]HSO4. The probe reaction of DMM₁ and TOX was carried out at 110 °C and 2.5 MPa for 2 h (DMM₁: HCHO = 1.2 M ratio, one TOX molecule is equivalent to three HCHO molecules) and the observations are presented in Table 3. The major products were DMM_n (n = 2–8), while the byproducts of methanol, methyl formate and formic acid were also detected in the reaction mixture. As shown in Table 3, only traces of DMM₂₋₄ were formed when NaZSM-5 zeolite was used as the catalyst, which proves that the support has almost no catalytic activity. In contrast, [NaZSM-5IMBs]HSO4 fabricated through the immobilization of -SO₃H functionalized ILs onto the NaZSM-5 support, produced a drastic increase in the catalytic activity while the FA conversion and selectivity for DMM₃₋₈ were at 90.3% and 53.5%, respectively. However, the corresponding homogeneous catalysis of [MIMBs]HSO4 (0.9 wt.%, with the same amount of loading on [NaZSM-5IMBs]HSO4) under the same conditions produced only 17.8% and 21.5%, respectively. This is mainly due to the cooperation of Brønsted acid site from BAILs and the pore structure of the NaZSM-5 zeolite, besides, [MIMBs]HSO4 is viscous and immiscible with the substrate which gose against mass transfer. Furthermore, when [NaZSM-5PyBs]HSO4 was used as the catalyst, 89.9% FA conversion and 49.8% DMM₃₋₈ selectivity were obtained, which were slightly inferior to those of [NaZSM-5IMBs]HSO₄. This is mainly attributed to the stronger surface acidity displayed by [NaZSM-5IMBs]HSO₄ compared to [NaZSM-5PyBs]HSO₄, which can effectively promote the dissociation of TOX to FA species [42]. Moreover, the insertion step of FA species into DMM₁ and lower DMM_n to form higher DMM_n is an acid-catalyzed carbocation mechanism [22]. Hence, it was inferred that the catalytic performance of BAILs@NaZSM-5 was related to its acidic properties.

For comparison, the acetalation of DMM₁ with TOX was also studied using [YIMBs]HSO₄ and [Si-MCM-41IMBs]HSO₄ as catalysts. It has been found that the conversion of FA for these catalysts were 6.1% and 2.8%, respectively. This result is attributed to the fact that the support confinement in the channel has a significant effect on the activity of a reaction. The increase in the orbital energy of organic molecules is more significant when the size of the guest molecule is similar to the pore size of the support, which indicates their improved ability to provide electrons in the reaction along with superior reactivity [43-45]. The structure of DMM_n is linear with \sim 3.4 Å width, which was determined using a density functional theory (DFT) method (Fig. 7) [46]. The zeolite of NaZSM-5 with the three-dimensional intersecting channel system (a straight channel of 5.6×5.3 Å and a sinusoidal channel of 5.5×5.1 Å) [47], MCM-41 possesses a hexagonal array of uniform mesopores with regularly channels of 20-100 Å [48]. The pore structure of zeolite Y is characterized by supercages approximately 12 Å in diameter and open channel width of about 7.4 Å [49,50]. The pore structure and size of NaZSM-5 are close to those of the reactant and product molecules which possess linear chain structure. The diffusion rate of the reactants and products in NaZSM-5 channels is faster, so [NaZSM-5IMBs]HSO4 exhibited superior catalytic activity.

Using [NaZSM-5IMBs]HSO4 as the catalyst, the effect of reaction parameters such as catalyst concentration, the M ratio of DMM₁ to HCHO, temperature and duration were examined in detail and the results were presented in Table 4. Initially, we studied the effect of catalyst concentration on the acetalation of DMM₁ with TOX and found that the conversion of FA increased with an increase in catalyst loading (Table 4, entries 1-4), and the highest conversion of FA (90.7%) was obtained when the amount of [NaZSM-5IMBs]HSO4 was 6 wt.% (Table 4, entry 4). Initially, the selectivity for DMM₃₋₈ increased and then decreased, which approached a maximum (53.5%) when the amount of [NaZSM-5IMBs]HSO4 was 5 wt.% (Table 4, entry 3). This behavior indicates the importance of using an appropriate quantity of catalyst in this reaction system. On the other hand, the excess acid may enhance the formation of byproducts such as methanol, FA and methyl formate. In addition, the M ratio of DMM₁ to HCHO had a remarkable impact on the reaction; the conversion of FA gradually increased from 84.6% to 92.3% and the selectivity for DMM₃₋₈ decreased from 55.6% to 43.9% when the M ratio of DMM₁ to HCHO was increased from 1:1 to 1.6:1 (Table 4, entries 3, 5–7). The most favorable M ratio of DMM_1 to HCHO is determined to be 1.2:1, at which the FA conversion was 90.3%, and the selectivity for DMM_{3-8} was 53.5%. The reaction temperature also had an immense effect on the results; the conversion of FA enhanced with an increase in the reaction temperature (from 100 to 120 °C) and the selectivity for DMM₃₋₈ reached the maximum at 110 °C (Table 4, entries 3 and 8-9). The results suggested that the products depolymerized into byproducts at higher temperatures and the best reaction temperature was 110 °C. The impact of reaction time on the preparation of DMM_n was also explored ranging from 1 to 4 h. (Table 4, entries 3 and 10-12). The FA conversion and selectivity for DMM₃₋₈ has improved rapidly by extending the reaction time from 1 to 2h and reached 90.3% and 53.5%, respectively, at 2 h. Further extending the reaction time led to only a slight augmentation in the conversion of FA, hence, an optimum reaction time of 2 h was selected for saving energy.

3.3. Reusability of [NaZSM-5IMBs]HSO₄

From environmental and economic points of view, the stability and sustained activity of the catalyst are of great importance. Thus, a series of repetitive experiments were carried out to explore the reusability of the zeolite-immobilized acidic ILs in the acetalation reaction of DMM₁ with TOX (the loading of [NaZSM-5IMBs]HSO₄ is 5.0 wt.%, HCHO (TOX): DMM₁ = 1:1.2 M ratio, 110 °C, 2.5 MPa, 2 h). In each cycle, [NaZSM-5IMBs]HSO₄ was separated from the reaction mixture by filtration and reused in the next run under the same conditions without any further treatment. The FA conversion and selectivity for DMM₃₋₈ from ten consecutive runs is shown in Fig. 8. The results demonstrated that [NaZSM-5IMBs]HSO₄ can be recycled up to ten times with no appreciable decrease in the FA conversion and selectivity for DMM₃₋₈, indicating that [NaZSM-5IMBs]HSO₄ owns excellent reusability and sustained activity. Additionally, the FT-IR and XRD spectrum of fresh [NaZSM-5IMBs]HSO₄ were compared with that of the catalyst which



Fig. 7. Structure of DMM_n calculated by density function theory (DFT) method.

Table 4	
Effect of reaction conditions using [NaZSM-5IMBs]HSO ₄ as catalyst.	

Entry	[NaZSM- 5IMBs] HSO ₄ (wt.%)	DMM ₁ :HCHO (M ratio)	Temperature (°C)	Time (h)	Con. of FA (%)	Sele. for DMM ₃₋₈ (%)
1	2	1.2	110	2	78.9	46.6
2	4	1.2	110	2	89.0	52.1
3	5	1.2	110	2	90.3	53.5
4	6	1.2	110	2	90.7	50.5
5	5	1	110	2	84.6	55.6
6	5	1.4	110	2	90.6	46.6
7	5	1.6	110	2	92.3	43.9
8	5	1.2	100	2	82.1	47.5
9	5	1.2	120	2	90.7	50.0
10	5	1.2	110	1	85.2	49.4
11	5	1.2	110	3	91.0	50.0
12	5	1.2	110	4	91.8	50.8

Reaction conditions: the source of formaldehyde is TOX.



Fig. 8. The recycle test of [NaZSM–5IMBs]HSO₄ in the acetalation reaction of DMM₁ with TOX. Reaction conditions:[NaZSM–5IMBs]HSO₄. 5.0 wt.%, HCHO (TOX):DMM₁ = 1:1.2 M ratio, 110°C, 2.5 M Pa, 2 h.

was reused ten times. As shown in Figs. 9 and 10, the absence of apparent change in the FT-IR and XRD spectra reveals that the structure of [NaZSM-5IMBs]HSO₄ has not altered even after reusing ten times. To investigate the real loss of acidity, acid-base titration was adopted to determine the acid capacity of the fresh and the ten times reused [NaZSM–5IMBs]HSO₄ using NaCl solution as an ion-exchange agent, the loading of ILs was also compared and the results were presented in Table 5. After ten runs, the acid capacity of [NaZSM–5IMBs]HSO₄ has slightly decreased from 9.8 mmol/g to 9.1 mmol/g and the fraction of the ILs grafted onto NaZSM-5 decreased from 17.7% to 16.7%. According these comparative experiments, the prepared zeolite–immobilized acidic ILs possesses excellent stability and reusability. In this



Fig. 9. FT–IR spectra comparison of the fresh and the ten times reused $[\rm NaZSM-5IMBs]\rm HSO_4.$



Fig. 10. XRD spectrum comparison of the fresh and the ten times reused $[NaZSM-5IMBs]HSO_4$.

Table 5

Acid capacity and elemental analysis comparison of the fresh and the ten times reused $[NaZSM-5IMBs]HSO_4$.

Sample	Acid capacity (mmol/g)	Results of elemental analysis (wt.%)	
		S content	IL content
Fresh [NaZSM-5IMBs] HSO ₄	9.8	3.3	17.7
[NaZSM-5IMBs]HSO ₄ reused for 10 times	9.1	3.1	16.7



Scheme 3. The possible mechanism for hydrogen bond between anion of ILs and support.

situation, the cation of the ILs was firmly immobilized to the surface of the support through covalent bonds; anion was also not easily dissociated because of ionic bonding with cation and hydrogen bonding with the support (Scheme 3) [51].

4. Conclusion

In conclusion, novel molecular sieve-immobilized acidic ILs were successfully prepared, characterized and utilized in the acetalation reaction of DMM₁ with TOX. On the basis of the characterization results, the acidic ILs were proved to be immobilized successfully onto the molecular sieve. Moreover, zeolite NaZSM-5 supported -SO₃H functionalized ILs showed excellent catalytic efficiency for the preparation of polyoxymethylene dimethyl ethers. [NaZSM-5IMBs]HSO₄ displayed the best catalytic efficiency for acetalation, producing a high conversion of FA (90.5%) and selectivity for DMM₃₋₈ (53.5%). In addition, the catalyst can simply be separated and reused for ten times without any evident loss of its catalytic activity. Zeolite-immobilized acidic ILs, therefore, are efficient and promising catalysts for the acetalation reaction.

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