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

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ABSTRACT

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 (DMM_1) and trioxane (TOX). Combined characterization results from fourier transform infrared (FT-IR) spectroscopy, elemental analysis, thermogravimetry (TG), N_2 adsorption-desorption (Brunauer-Emmett-Teller, BET) isotherms, X-ray diffraction (XRD), scanning electron microscopy (SEM) and temperature-programmed desorption of ammonia (NH_3-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 SO_3H-functionalized ionic liquids (ILs) i.e., BAILs@NaZSM-5, exhibited excellent activity for the acetalation of DMM_1 with TOX, compared to the homogeneous catalysis of the precursors ([MIMBs] HSO_4) as well as other molecular sieve-supported ILs. The influence of catalyst concentration, molar ratio of DMM_1 to HCHO, temperature and reaction duration on the catalytic activity were investigated by employing [NaZSM-5IMBs]HSO_4 as the catalyst. It was demonstrated that a superior conversion of formaldehyde (FA) (90.3%) and excellent selectivity for $DMM_{3\text{-}8}$ (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 ($CH_3O(CH_2O)_nCH_3$, $n \geq 2$; 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 $DMM_{3–8}$ 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]. DMM_2, DMM_3, and DMM_4 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 ($–CH_3$, $–OCH_3$) provider (methanol or methylal (DMM_1)) with a chain section ($–CH_2O–$) 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 synthesize DMM_n from methanol and FA, PF or TOX [7–14]. However, 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], ion-exchange 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 CO_2 and epoxides, 80–99% yield and 97–99% selectivity of the products were obtained under mild conditions. J.B. Yang et al. [35] have developed –SO_3H 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 –SO_3H 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 -SO_3H functionalized BAILs (BAILs@MS) and its application in the acetalation reaction of DMM_1 with TOX (Scheme 1). Fourier transform infrared (FT-IR) spectroscopy, elemental analysis, thermogravimetry analysis (TG), N_2 adsorption-desorption (Brunauer-Emmett-Teller, BET) isotherm, X-ray diffraction (XRD), scanning electron microscopy (SEM) and temperature-programmed desorption of ammonia (NH_3-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

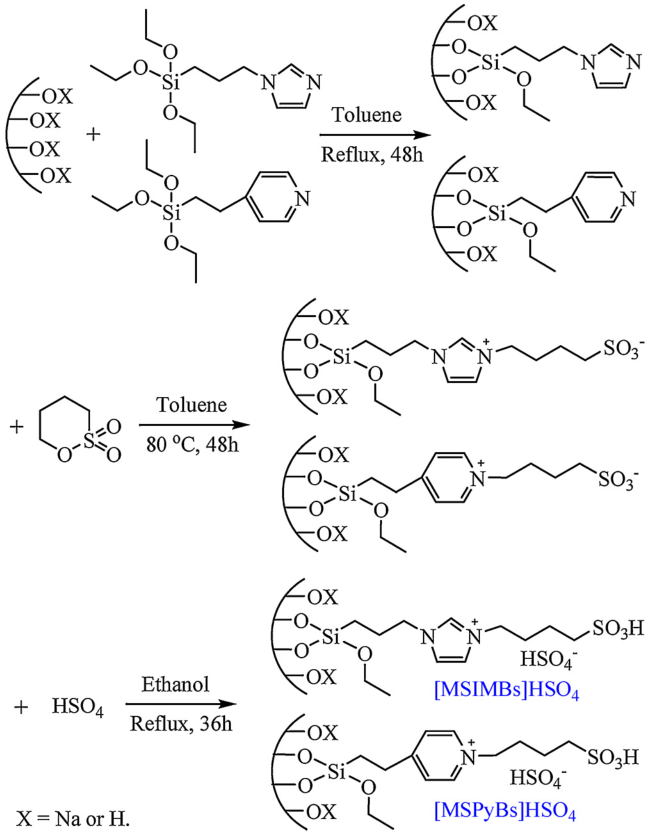
2.1. General

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. DMM_2 (> 99.5%), DMM_3 (> 99.5%), DMM_4 (> 99.5%) and DMM_5 (> 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 ^{13}C NMR spectra were 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). ^{13}C NMR (100 MHz, C_6D_6): δ 7.32, 18.16, 24.90, 48.31, 58.20, 118.08, 129.79, 137.06.



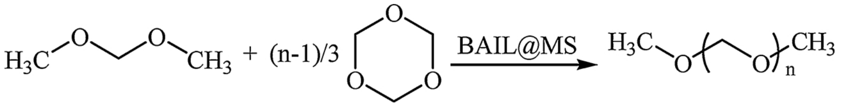
Scheme 2. Synthetic route of BAILs@MS.

2.2.2. Preparation of NaZSM-5

In a typical procedure, 1 M $NaNO_3$ 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.