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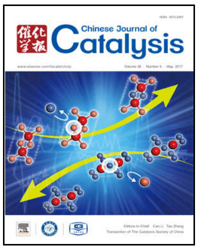

Article

Brønsted-acidic ionic liquids as efficient catalysts for the synthesis of polyoxymethylene dialkyl ethers

Heyuan Song [a,b], Meirong Kang [a], Fuxiang Jin [a], Guoqin Wang [a,b], Zhen Li [a], Jing Chen [a,*]

[a] *State Key Laboratory for Oxo Synthesis and Selective Oxidation, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou 730000, Gansu, China*

[b] *University of Chinese Academy of Sciences, Beijing 100049, China*

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ABSTRACT

Acetalation of formaldehyde (HCHO) with dialkyl formal or aliphatic alcohol to prepare polyoxymethylene dialkyl ethers ($RO(CH_2O)_nR$, $n \geq 1$) catalyzed by Brønsted-acidic ionic liquids has been developed. The correlation between the structure and acidity activity of various ionic liquids was studied. Among the ionic liquids investigated, 1-(4-sulfonic acid)butyl-3-methylimidazolium hydrogen sulfate ([MIMBs]HSO_4) exhibited the best catalytic performance in the reaction of diethoxymethane (DEM_1) with trioxane. The influences of ionic liquid loading, molar ratio of DEM_1 to HCHO, reaction temperature, pressure, time, and reactant source on the catalytic reaction were explored using [MIMBs]HSO_4 as the catalyst. Under the optimal conditions of n([MIMBs]HSO_4):n(DEM_1):n(HCHO) = 1:80:80, 140 °C, and 4 h, the conversion of HCHO and selectivity for DEM_{2-8} were 92.6% and 95.1%, respectively. The [MIMBs]HSO_4 catalyst could be easily separated and reused. A feasible mechanism for the catalytic performance of [MIMBs]HSO_4 was proposed.

1. Introduction

Polyoxymethylene dialkyl ethers ($RO(CH_2O)_nR$, $n \geq 1$) are polyether compounds with high oxygen contents and cetane numbers (CN), and are regarded as a promising diesel additive to improve the combustibility of diesel oil, enhance combustion efficiency, and lower the release of pollutants [1,2]. It has been reported that the emission of particulate matter and NO_x released upon combustion were lowered by 80%–90% and 50%, respectively, when polyoxymethylene dimethyl ethers ($CH_3O(CH_2O)_nCH_3$, n = 3–8, $PODE_{3-8}$, DMM_{3-8}) were added to diesel oil with a ratio of 20% [2]. The CN, calorific value, and flashing point gradually increase and density and condensation point decrease with increasing R chain length of $RO(CH_2O)_nR$ [3]. $RO(CH_2O)_nR$ also can display excellent solubilizing power, permeating ability, and miscibility with most organic compounds. Furthermore, they are very promising for use as green industrial solvents and pigment dispersants.

$RO(CH_2O)_nR$ can be synthesized from the end–group (–R) provider (e.g., aliphatic alcohol or dialkyl formal) and a compound that offers an oxymethylene group (–CH_2O–) as a chain segment, e.g., 1,3,5-trioxane (TOX), paraformaldehyde (PF), or formaldehyde (FA) [4]. In 1948, Gresham et al. [5] reported the first acetalation reaction of dialkyl formal with PF using a proton acid such as sulfuric acid as the catalyst, which mainly produced $RO(CH_2O)_nR$ with n = 2 or 3. Subsequently, there have been many reports on the synthesis of $PODE_n$. For example, Renata et al. [6–9] patented the acetalation reaction of PF or

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* Corresponding author. Tel: +86-931-4968068; Fax: +86-931-4968129; E-mail: chenj@licp.cas.cn

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TOX with methanol or methylal catalyzed by sulfuric or triflic acid. Heavy corrosion, difficult separation and recovery, and disposal of the spent catalyst are the disadvantages associated with the reported methods involving proton acid catalyst systems. To solve these problems, more environmentally friendly and easily separable solid acids, such as ion exchange resin Amberlyst 36 [10], cation resin NKC-9 [11], and molecular sieves [12–14] have been used as catalysts in PODE$_n$ formation. Unfortunately, the reported catalytic systems still suffer from one or more disadvantages, including poor reactivity (low catalytic activity and selectivity) and easy deactivation.

Recently, ionic liquids (ILs) have attracted great interest as a novel catalyst because of their favorable properties. ILs combine the advantageous characteristics of both homogenous and heterogeneous catalysts, such as high acidic or alkali density, wide liquid range, uniform catalytic active sites, easy separation, and reusability [15]. As a result, ILs have been widely used in catalytic processes such as material synthesis, organic reactions, and biomass conversion [16–22]. Our group developed a method to synthesize PODE$_{3-8}$ using acidic ILs as catalysts with TOX, PF, or FA and methanol or methylal as raw materials [23–28]. Recently, acid ILs [PyBs]HSO$_4$ and [MIMBs]HSO$_4$ have been reported as catalysts for acetalation of TOX and methylal [29]. The conversion of TOX and selectivity of PODE$_{3-8}$ were 91.2% and 70.9%, respectively, under the conditions of n(ILs):n(methylal):n(TOX) = 1:180:60, 170 °C, and 10 h. Here, we investigate the potential applications of Brønsted-acidic IL in the acetalation reaction of FA and diethoxymethane ($C_2H_5OCH_2OC_2H_5$, DEM$_1$) or aliphatic alcohol ($C_nH_{2n+1}OH$, $n \geq 2$) (Scheme 1). Ideal yields of $RO(CH_2O)_nR$ (n = 2–8) are obtained in the presence of –SO_3H functionalized ILs and a possible reaction mechanism for this reaction system is proposed based on the experimental results. The recyclability of the catalyst system is also examined.

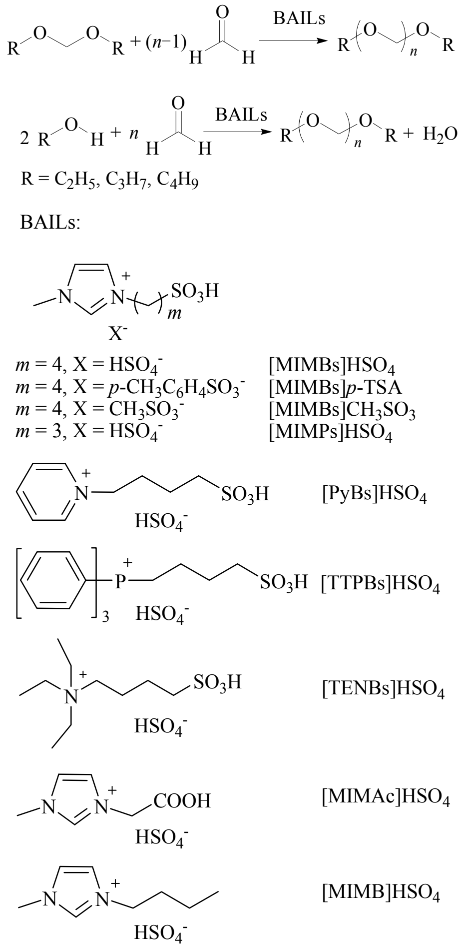
2. Experimental

2.1. General

All chemicals were analytical grade and used without further purification. Both ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AVIII HD 400 MHz NMR spectrometer (Switzerland) using tetramethylsilane as an internal standard. Fourier transform infrared (FT-IR) measurements were performed using KBr tablets on a Nicolet NEXUS 870 FT-IR infrared spectrometer (Madison, America). Absorbance spectra of 4-nitroaniline were obtained with a PerkinElmer Lambda 35 UV/VIS spectrometer (America).

2.2. Ionic liquid preparation

ILs were prepared according to a previous report [30] and their structures are shown in Scheme 1. A stoichiometric amount of 1,4-butane sultone, 1,3-propane sultone, bromobutane, or a solution of chloroacetic acid in chloroform was added dropwise to a stirred solution of N-methylimidazole, pyridine, or triphenylphosphine in toluene at room temperature, and then the mixture was heated at 60 °C for 12 h. The formed solid zwitterion was centrifuged and washed three times with toluene to remove unreacted non-ionic residues. After drying under vacuum (70 °C, 5.3 kPa, 12 h), white solid zwitterionic samples were obtained. A stoichiometric amount of concentrated sulfuric acid or methanesulfonic acid was then added dropwise to each zwitterionic sample in anhydrous toluene, and stirred at 80 °C for 12 h to form the IL. The IL phase was then washed repeatedly with toluene and dried under vacuum (70 °C, 5.3 kPa, 12 h) to give each viscous clear IL. When using p-toluenesulfonic acid (p-TSA) as the anion source, the preparation of ILs was carried out in water and the system was heated under reflux for 12 h. The mixture was dried under vacuum to form corresponding ILs.



Scheme 1. Acetalation reaction of FA with dialkyl formal or aliphatic alcohol catalyzed by Brønsted-acidic ionic liquids.

NMR spectral data in CD_3OD or D_2O and FT-IR spectral data for ILs are presented as follows. Chemical shifts are reported in parts per million (ppm, δ) and referenced to D_2O (δ = 4.73) or CD_3OD (δ = 3.31).

[MIMBs]HSO$_4$. ^{1}H NMR (400 MHz, D_2O): δ 1.66 (h, J = 8.0 Hz, 2H), 1.94 (h, J = 7.0 Hz, 2H), 2.86 (t, J = 8.0 Hz, 2H), 3.81 (s, 3H), 4.16 (t, J = 8.0 Hz, 2H), 7.35 (d, J = 4.0 Hz, 1H), 7.40 (d, J = 4.0 Hz, 1H), 8.64 (s, 1H). ^{13}C NMR (100 MHz, D_2O): δ 21.0, 28.14, 35.75, 49.0, 50.14, 122.25, 123.75, 136.09. IR (KBr, ν/cm^{-1}): 3156 (C–H stretching vibration, MIM), 2963 (C–H stretching vibra-