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Short Communication

Synthesis of triethoxysilane imidazolium based ionic liquids and their application in the preparation of mesoporous ZSM-5

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1. Introduction

lonic liquids (ILs) have been attracting considerable attention in recent time due to their unique physico-chemical properties [1]. Physical and chemical properties of ILs can be tailored by varying cations and anions. Most of the common ILs are formed by reacting a nitrogen-containing heterocyclic compounds with an alkyl halide to form quaternary ammonium salts. Efforts have been made to explore the ability of ILs to serve as a catalyst [2,3]. A few efforts have been made to utilize ILs as a structure directing agent for the synthesis of nanostructured materials [4,5].

Zeolite has become an extremely successful catalyst for oil refining, petrochemistry, and organic synthesis in the production of fine and specialty chemicals, particularly for molecules having kinetic diameters below 1.5 nm [6–9]. Zeolites act as shape-selective catalysts due to their strong acidity and uniform microporosity. The presence of catalytic sites (Al) in micropores of zeolites imposes significant limitations on a range of reactions involving large reactant and product molecules. Diffusion limitation in the micropores can also lower the overall reaction rate even for the reactions in which reactants and products are smaller than the micropores [10], and potential of the zeolite is not fully utilized. Various synthesis procedures have been reported to improve the chemical and structural properties of zeolite [11–17]. Non-templating method involves post-synthesis etching of zeolites by acid/base/steam to achieve mesoporosity [17].

ABSTRACT

Triethoxysilane containing imidazole based ionic liquids were synthesized. These ionic liquids were utilized as a structure directing agent for the synthesis of mesoporous ZSM-5. ZSM-5 was characterized by a complementary combination of X-ray diffraction, N₂ adsorption/desorption, Scanning electron microscopy, Transmission electron microscopy, Temperature programmed desorption techniques, Infrared spectroscopy and Nuclear Magnetic Resonance spectroscopy. The resultant zeolites were mesoporous and showed unique characteristics of a fully crystalline microporous MFI zeolite framework. Mesoporous ZSM-5 synthesized from imidazole based ionic liquids exhibited higher catalytic activity than conventional ZSM-5 in alkylation and cracking reactions. Significantly high catalytic activity of the mesoporous ZSM-5 suggests that large external surface area and accessible acid sites are beneficial for catalytic reactions involving large organic molecules. © 2011 Elsevier B.V. All rights reserved.

> Among the templating methods, hard templating has been first employed to create mesopores inside zeolites [12]. However, in this method complicated multi steps are usually involved because of the incompatibility between hard substrates and precursor species. In recent years, a soft templating method including cationic or silylated polymer and amphiphilic organosilane as the templates has been drawing increasing attention for its ease of use and high efficiency to create mesoporosity [13–16].

> Very less effort has been made to prepare and utilize the silane containing ionic liquids [18,19]. The objectives of this study is to prepare a variety of silane containing imidazole based ionic liquids (SIMILs) and explore their potential in the synthesis of mesoporous ZSM-5. Further, the catalytic activities of mesoporous ZSM-5 were investigated and compared with conventional ZSM-5 in acid catalyzed alkylation and cracking reactions.

2. Experimental

2.1. Synthesis of structure directing agents

1-Methyl-3-(triethoxysilyl propyl) imidazolium chloride (SIMIL1) was synthesized by following the reported procedure (Yield = 89%) [18]. First N-dodecylimidazole was prepared for the synthesis of 1-dodecyl-3-(triethoxysilyl propyl) imidazolium chloride (SIMIL2). Then SIMIL2 was prepared by following the reported procedure (Yield = 71%) [19] (Scheme 1). Experimental details and spectroscopic characteristic data of SIMILs are given in the supporting information.

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Scheme 1. Schematic representation for the synthesis of SIMILs.

2.2. Synthesis of mesoporous ZSM-5 and conventional ZSM-5

In a typical synthesis, required amount of SIMILs, 1.33 g of tetrapropylammonium bromide (TPABr), and 0.40 g of NaOH were completely dissolved in 18.2 g of H₂O and mixed with 27.8 g of diluted sodium silicate solution (Si/Na=1.75; 10 wt.% SiO₂). A solution containing 0.24 g of sodium aluminate (53 wt.% Al₂O₃, 43 wt.% Na₂O; Riedel-deHaën) and 13.3 g of H₂O was added drop wise under stirring to the resultant mixture. Then, 13 g of 10 wt.% H₂SO₄ solution was added to the synthesis mixture under vigorous stirring. The final molar composition of the mixture was 2.5 Al₂O₃/40 Na₂O/93 SiO₂/10 TPABr/26 H₂SO₄/9000 H₂O/7 SIMILs. The mixture was heated under stirring at 423 K for 3 days in a Teflon-coated stainless steel autoclave. The precipitated product was filtered and washed with distilled water. The product was dried in an oven at 373 K and subsequently calcined in air at 823 K (Yield: ZSM-5-SIMIL1 = 73%; ZSM-5-SIMIL2 = 77%). Conventional ZSM-5 was synthesized at 443 K using the synthesis composition 2.5 Al₂O₃/40 Na₂O/100 SiO₂/10 TPABr/26 H₂SO₄/9000 H₂O by following the synthesis procedure described above (Yield = 64%). Samples were ion-exchanged into the NH_4^+ using 1 M aqueous NH₄NO₃ solution, followed by calcinations at 823 K for 6 h to convert it to the H⁺ form.

2.3. Material characterizations and catalytic measurements

Material characterizations and catalytic measurements are given in the supporting information.

3. Results and discussion

In this study SIMILs were synthesized using one-step/two-step synthetic routes (Scheme 1). SIMIL1 is oily liquid whereas SIMIL2 is sticky solid at ambient condition. None of the SIMILs were soluble in hexane but both of them were soluble in methanol. It may be noted that SIMIL1 was completely soluble in H₂O but SIMIL2 is sparingly soluble in water. In this study, SIMILs were utilized in the synthesis of mesoporous ZSM-5 in which they act as a structure directing agent (SDA). Zeolites were designated as ZSM-5-SIMIL1 and ZSM-5-SIMIL2 when SIMIL1 and SIMIL2, respectively were used as SDA.

Both SDA were successful in synthesizing mesoporous ZSM-5. Mesoporous ZSM-5 had the MFI framework structure with high phase purity, which was confirmed by using XRD (Fig. 1). The XRD pattern of ZSM-5-SIMIL2 is broad in nature when compared with the conventional ZSM-5 and ZSM-5-SIMIL1. This shows that the particle size of sample synthesized by using SIMIL2 is smaller in size than by using SIMIL1. The N₂-adsoption isotherm of ZSM-5-SIMIL2 showed a typical type-IV isotherm with H1 hysteresis loop similar to the mesoporous materials (Fig. 2). The major difference in the isotherms of ZSM-5-SIMIL2 from that of conventional ZSM-5 is a distinct increase of N₂ adsorption in the region 0.4 < P/Po < 0.85, which is

interpreted as capillary condensation in mesoporous void spaces. ZSM-5-SIMIL1 shows N₂ sorption isotherm similar to conventional ZSM-5. However, its surface area and pore volume are higher than the conventional ZSM-5. Specific surface area and pore volume of ZSM-5-SIMIL2 were the highest, among the samples investigated in this study (Table 1). SEM and TEM investigations confirmed that the particle size of zeolite decreases in the order ZSM-5-ZSM-5-SIMIL1 > ZSM-5-SIMIL2 (Fig. 3). TEM images showed that the material has disordered mesopore structure and the sample looks like consisting of unshaped inter grown crystals.

²⁷Al MAS NMR results show that ZSM-5 contains only tetrahedral aluminum sites, whereas ZSM-5-SIMIL2 contains approximately 99% tetrahedral aluminum sites and only approximately 1% of octahedral Al (extra framework Al) (Fig. S1, supporting information). Pyridine IR studies confirm that materials contain Brönsted as well as Lewis acid sites. Pyridine chemisorbed on Brönsted acid sites results in IR bands at 1642 and 1550 cm⁻¹. Bands due to pyridine on Lewis acid sites are observed at 1610, and 1446 cm⁻¹. An intense band at 1486 cm⁻¹ was observed for pyridine chemisorbed on both Brönsted and Lewis acid sites. Acidity of the sample was investigated using NH₃-TPD (Fig. 4). The total acidity decreases in the order: ZSM-5>ZSM-5-SIMIL1>ZSM-5-SIMIL2 (Table 1). In the TPD profiles of



Fig. 1. XRD patterns of ZSM-5 samples synthesized in this study.



Fig. 2. (a) N₂-adsorption isotherms and (b) pore size distribution of ZSM-5 samples synthesized in this study.

ZSM-5 and ZSM-5-SIMIL1, two well-resolved symmetric peaks were observed. They dominate with maximum at 480 K and 650 K for ZSM-5 and 465 K and 670 K for ZSM-5-SIMIL1. These peaks demonstrate the presence of weak acid sites and strong acid sites. In ZSM-5-SIMIL2, the first peak becomes smaller and less well-resolved and the maxima of second peak shifts to slightly higher temperature (690 K). This indicates that the acid sites in ZSM-5-SIMIL2 are stronger than the acid sites present in ZSM-5-SIMIL1/ZSM-5.

It is true that when conventional mesoporous structure directing agent such as cetyltrimethylammonium bromide (CTMABr) is used along with TPABr, it is difficult for the mesopore structure director to participate in this zeolite crystallization [14]. During the crystallization process using such soft templates, phase separation between surfactant and zeolite crystals took place and resulted in the formation of amorphous mesoporous material, bulk zeolite without mesoporosity, or their physical mixtures. Hence, a suitable SDA is required that is capable of having a strong interaction with the growing crystal surface, which can effectively modulate the crystallization process by participating in it. The present synthesis strategy utilizes SIMILs for the generation of intercrystalline mesoporosity in ZSM-5. In ZSM-5-SIMILs, zeolite crystallization was mediated by the nanoscale segregation of organic-rich and organic-lean domains on the growing zeolite particles and intercrystalline mesopores are formed due to crystal packing of these growing zeolite particles. SIMILs contain only three hydrolysable moieties (with one hydrophobic alkyl imidazole group), which is disadvantage for the formation of extended tetrahedral SiO₂ linkages. Consequently, the zeolite growth might be significantly retarded at the organic and inorganic interfaces, resulting in the formation of intercrystalline mesoporous ZSM-5. ¹³C MAS NMR of ZSM-5-SIMIL2 (Fig. 5) and FT-IR of assynthesized samples (Fig. S2, supporting information) confirm the incorporation of SIMILs in the as-synthesized form of zeolites.

The catalytic activities of mesoporous ZSM-5 samples synthesized in this study were compared with conventional ZSM-5 for some important reactions such as alkylation and cracking. In the present work, zeolites were tested for the alkylation of toluene with benzyl chloride to obtain diphenylmethanes, which are important chemicals used in fine chemicals and pharmaceutical industries (Scheme 2). The C-C chain branching makes the cracking reaction more difficult in branch polyethylene. The cracking of polyethylene requires strong acid sites [20,21]. Catalytic cracking of HDPE (MW \approx 125000) was chosen to evaluate the efficiency of these catalysts. Catalytic cracking of HDPE produces a large variety of products such as alkanes, isoalkanes, alkenes, aromatics such as benzene derivatives, naphthalene derivatives, etc. [22]. Following order was obtained for the catalytic activity of these catalysts in the alkylation and cracking reactions: ZSM-5<ZSM-5-SIMIL1<ZSM-5-SIMIL2 (Tables 2 and 3). ZSM-5 exhibited the lowest activity whereas ZSM-5-SIMIL2 exhibited the

 Table 1

 Textural properties of ZSM-5 samples synthesized in this work.

Catalyst	Si/Al ^a	$S_{BET}\left(m^2/g\right)$	Ext. surface area (m²/g)	Total pore volume (ml/g)	Mesopore volume (ml/g)	Total acidity (mmol/g) ^b	Ratio of strong/weak acid sites ^b
ZSM-5	19.5	330	63	0.18	0.08	0.27	1.06
ZSM-5-SIMIL1	24.3	462	202	0.40	0.27	0.22	1.17
ZSM-5-SIMIL2	26.4	565	307	0.64	0.50	0.20	1.67

^a Obtained from ICP analysis.

^b Obtained from NH₃-TPD.



Fig. 3. SEM (a-c) and TEM (d-f) images of ZSM-5 samples synthesized in this study.



Fig. 4. NH₃-TPD profiles of ZSM-5 samples investigated in this study.



Fig. 5. ¹³C MAS NMR of the as-synthesized ZSM-5-SIMIL2.

highest activity. Although, the activity of ZSM-5-SIMIL1 was found to be low but its activity was much higher than the ZSM-5. The acidity of mesoporous ZSM-5 samples was less than the acidity of ZSM-5 (Table 1), but they were found to be more active than the ZSM-5. High activity of these materials is due to the presence of acid sites located on the large external surface. Since the sizes of reactant



Mono-alkylation Di-alkylation

Scheme 2. Alkylation of toluene with benzyl chloride using ZSM-5 catalysts investigated in this study.

Table 2

Comparison of the catalytic activity of various catalysts in the alkylation of toluene with benzyl chloride.

Catalyst	Conv. with respect	Selectivity (%)		
	to benzyl chloride (mol.%)	Mono-alkylation	Di-alkylation	
ZSM-5	0.9	100	-	
ZSM-5-SIMIL1	30.5	91	9	
ZSM-5-SIMIL2	64.7	87	13	

Reaction conditions: benzyl chloride (5 mmol); toluene (50 mmol); catalyst (100 mg); temperature (413 K); time (2 h).

Table 3

Catalytic cracking of HDPE into volatile products using ZSM-5 samples synthesized in this study.

Catalyst	Reaction time (min)	Conversion of HDPE (%) ^a
ZSM-5	30	6.5
ZSM-5	60	9.7
ZSM-5-SIMIL1	30	38.0
ZSM-5-SIMIL1	60	65.4
ZSM-5-SIMIL2	30	63.8
ZSM-5-SIMIL2	60	100

Reaction conditions: PE (10 g); catalyst (100 mg); temperature (653 K).

^a Calculated from the mass balance of HDPE before and after the reaction.

molecules are larger than the ZSM-5 pores, the alkylation/cracking occurs on the acid sites located on the external surface of the crystals. The low activity of ZSM-5 is attributable to very small external surface area. The high catalytic activity of ZSM-5-SIMIL2 indicates that the reaction took place at the large external surface of the catalyst. It may be noted that ZSM-5-SIMIL1 is less active than ZSM-5-SIMIL2. This can be correlated well with the external surface area. These investigations confirm that ZSM-5-SIMIL2 having mesoporous structure, large external surface area with accessible acid sites is more suitable for these reactions. Hence, it can be concluded that for most of the acid catalyzed reactions, strong acid sites, large external surface area, and accessibility of reactant molecules to the strong acid sites are the desirable criteria for the catalyst to exhibit high activity.

4. Conclusions

Triethoxysilane containing imidazole based ionic liquids were synthesized and utilized for the synthesis of ZSM-5. Textural characterization confirms that mesoporous ZSM-5 samples have intercrystalline mesopores with large external surface area. Remarkably high catalytic activity of mesoporous ZSM-5 in these reactions is due to the combined effect of accessible strong acid sites and large external surface area.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at doi:10. 1016/j.catcom.2011.11.012.

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