Direct Synthesis of Ionic liquid (N-methylimidazole) onto Mesoporous SBA-15 and Base Catalytic Applications

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Introduction

Ionic liquids (ILs) have received great attention as green solvent in the fields of organic synthesis, enzyme activation and catalysis because of their unique properties such as non-volatility, non-flammability, high thermal and chemical stability [1]. Specially, ILs had shown great potential as catalysts when it was immobilized onto the mesoporous silica which have high surface area, turnable pore size and nerrowed pore size distribution. This strategy could minimize the amount of ILs used while maintaining their catalytic properties, and additionally easy to separate and recycle the supported ILs [2]. So far the immobilization of ILs was mainly applied post method like as simple impregnation, covalent linking of the cation, sol-gel method and so on [3]. To the best of our knowledge no trials for the direct immobilization of ionic liquid during the synthesis of mesoporous silica has been reported and morphosynthesis with ionic liquid functionality.

In this paper, [N-methylimidazole][Cl] was directly immobilized onto by co-condensation of as prepared organosilane and sodium metasilicate in the strong acid condition via microwave synthesis. The [N-methylimidazole][Cl] functionalized mesoporous silicas were tested as organocatalyst in the Knovenagel reactions.

Materials and Methods

Ionic liquid type organosilane was synthesized by heating the mixture of [N-methylimidazole][Cl] and chloropropyl silane at 70 ℃ for 48 h under Ar environment. This orgnosilane was added to the water solution of sodium metasilicate and P123. To the mixture Con. HCl was added and stirred at 40 ℃ for 3 h. The gel was transferred into Teflon vessel for microwave heating (100 ℃, 1h). The precipitate was filtered, subsequently washed with distilled water and dried at 80 ℃. The template was removed by soxlet extractor using acidic EtOH for 24h. The samples prepared were denoted as X%-IL-SBA-15 (X was the molar ratio of IL to sodium metasilicate.). The Knovenagel condensation of benzaldehyde and ethyl cyanoacetate was followed previous method [4].

Results and Discussion

X-ray diffraction patterns of the N-methyl-3-(3-triethoxysilypropyl)imidazole chloride functionalized SBA-15 with different ILs to silica molar ratios showed well-resolved diffraction peaks at 2 θ = 0.8-1° and two peaks at higher degrees which were indexed to the 100, 110, 200 planes. This is the characteristic of the long range ordered mesostructure of hexagonal space group symmetry P6mm. However, N_2 full isotherm showed type IV hysteresis with the tail in the low relative pressures which indicated the cavitation due to the formation plugs in pores. That pretended to show a bimodal pore size distribution likewise in the case of l-proline functionalized SBA-15 [5], which also had plugged and disk type morphology due to the basicity of organofunctional group and different silica source under the microwave synthesis. SEM images showed uniform hexagonal platelet type morphology in the case 7.5%-IL-SBA-15 with the thickness of 100-300 nm. Such phenomena have been observed in the direct synthesis of amine functionalized SBA-15 with the co-condensation of organosilane and sodium metasilicate [4]. This morphology became unclear and particles stacked heavily when the amounts of immobilized ILs were increased to 10 %. The catalytic activity of prepared samples was tested in the Knovenagel condensation of benzaldehyde and ethyl cyanoacetate. The 7.5%-IL-SBA-15 having thin disk type morphology and pluggs gave the better activity in the short time due to the short channel of platelet crystals as well as the confinement effect by the presence of plug in mesopores.

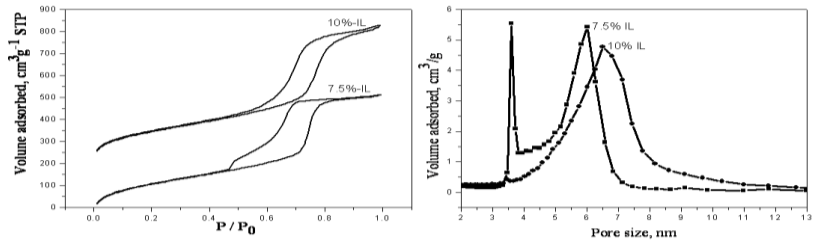

Figure 1. N_2 full isotherms of 7.5%-IL-SBA-15 and 10%-SBA-15.

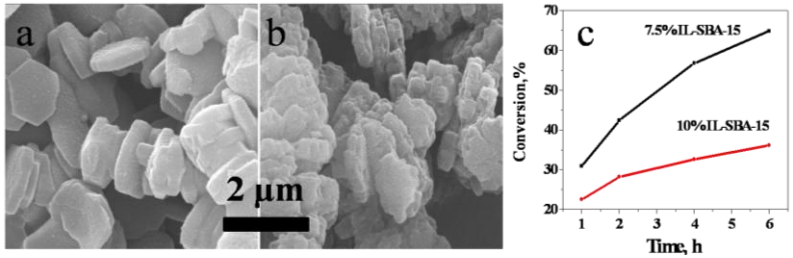

Figure 2. SEM images and Knovenagel condensation of benzaldehyde and ethyl cyanoacetate.

Significance

The N-methylimidazole][Cl] was directly immobilized into the short channel of SBA-15 with hexagonal platelet morphology. 7.5%-IL-SBA-15 with such morphology gave better catalytic activity due to the reactants could easily diffuse to the IL active sites in the channel.

References

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