In-situ FTIR Study of the Effect of Hydration on Ionic Liquids Confined in Mesoporous Silica Thin Films

Yuxin He, Daudi Saang'onyo, Folami Ladipo, Barbara L. Knutson and Stephen E. Rankin

Room temperature ionic liquids (ILs) have been widely investigated as solvents due to their low volatility, good thermal stability, and tunable solvent properties, they have been employed as media for catalytic dehydration of glucose into 5-hydroxymethylfurfural (HMF). [1][2][3] However, their high price, unknown toxicity and difficulty of solute recovery inhibit their large-scale application. Supported ionic liquid systems (SILPs) overcome many disadvantages of bulk ILs and allow their properties to be utilized as solvents and for heterogeneous catalysis. [4][5] The long-term goal of the present study is to understand the effect of confinement of ILs in mesoporous silica thin films with a goal of tailoring supported ILs for membrane and catalysis applications.

Many ILs are hygroscopic and the presence of water can dramatically alter their solvent properties. Complete water removal is often not feasible, particularly when water is a byproduct of a reaction. The effect of the presence of water on ILs and their interaction in confined pores of thin films is largely unknown. Here, *in situ* transmission FT-IR is developed as a technique to characterize the interactions of water with IL (1-butyl-3-methylimidazolium chloride (BMIM-Cl)) supported by mesoporous silica thin films. The approach is to use thin silicon wafers as supports to allow direct transmission monitoring of ionic liquid response to solvent vapors. Changes in the interaction of bulk IL on unmodified silicon wafers were measured with respect to relative humidity (RH). This establishes the amount of water absorbed and the mode of interaction with the ionic liquid, as well as the reversibility of hydration upon changes in relative humidity. [6] Confinement of ILs was investigated using mesoporous silica thin films prepared by templating with Pluronic surfactant P123. Vertically oriented, accessible pores (8 – 9 nm in diameter) were achieved by synthesizing the thin films on a neutral chemically modified surface of crosslinked layer of P123. [7] Hydration of BMIM-Cl as well as dry BMIM-Cl with and without silica mesopore confinement are compared. Significant peak shifts of the Cl^- interacting C-H stretching bands are observed, which suggests changes in interaction between imidazolium ring and Cl^- occurs when confinement is applied and during hydration. Both regular and deuterated water were used for RH control to allow all bands from the ionic liquid to be clearly resolved. The changes in the interaction of supported ILs can affect their solvent properties for separation and catalysis.

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