Dehydration of glucose into HMF by Lewis acidic metal chlorides: development of a heterogeneous $MeCl_x$/ionic liquid/SBA-15 catalyst

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Introduction

Cellulosic biomass is a promising renewable feedstock for energy and chemicals supply. In the future biorefinery abundant and cheap biomass feedstock replaces current fossil based hydrocarbons. 5-Hydroxymethylfurfural (HMF) has recently been proposed as a platform chemical which can be converted into a variety of useful intermediates including fuels and polymers [1]. Although HMF can be readily produced from fructose by acid-catalyzed dehydration, selective conversion of glucose, the dominant sugar in cellulose, to HMF remains a challenge. Recently, metal chlorides and especially $CrCl_2$ have been reported to exhibit very good yields for the conversion of glucose to HMF in the ethylmethylimidazolium chloride ([EMIM]Cl) ionic liquid medium [2]. In industrial scale processes heterogeneous catalysts have clear advantages related to catalyst recovery and continuous operation.

Materials and Methods

Ionic liquids can be immobilized on inorganic supports whilst maintaining their useful catalytic properties [3]. To this end, we prepared ordered mesoporous SBA-15 silica by established methods [4]. Afterwards, the ionic liquid was immobilized by stirring a suspension of 4 g of SBA-15 support in dried toluene together with 2 g of 1-(triethoxy-silyl-propyl)-3-methyl-imidazolium chloride at 90°C for 24 h. The excess reagents were removed by Soxhlet extraction with boiling CH_2Cl_2 and dried under vacuum. Then the metal chloride ($MeCl_x$: $CrCl_2$, $CuCl_2$, $AlCl_3$, and $FeCl_3$) was added to a 50 mL toluene solution with the dried support and reacted at room temperature overnight. The excess $MeCl_x$ was removed by Soxhlet extraction with boiling CH_2Cl_2.

The immobilized catalysts were characterized by XRD, ^{29}Si and ^{13}C CP MAS NMR spectroscopy, TEM and nitrogen physisorption. Elemental analyses were carried out via ICP-OES. The coordination chemistry of Cr in the immobilized system was studied by X-ray absorption spectroscopy at the Cr K edge and compared to in situ X-ray absorption spectroscopic measurements of $CrCl_2$ in the homogeneous $CrCl_2$:[EMIM]Cl system.

Results and Discussion

The comparison of the ^{29}Si CP MAS NMR spectra of SBA-15 and ionic liquid immobilized SBA-15 (Im-SBA-15) clearly show that the immobilization of ionic liquid was successful. Two additional bands appeared at -54 and -66 ppm with a weak shoulder at -51 ppm (Figure 1a) besides the regular Q bands of silica. These peaks are assigned to R-Si(OEt)$(OSi)_2$, R-Si(OEt)$(OSi)_3$ and R-Si$(OEt)_2$(OSi), respectively. Im-SBA-15 has a surface area of 408 m^2/g, and exhibits ordered structure as confirmed by low angle XRD and TEM picture (Figure 1b).

Table 1. Glucose conversion and HMF yields over $MeCl_x$-Im-SBA-15 catalysts.

Catalyst	Glucose Converison (%)	HMF Yield (%)
$CrCl_2$-Im-SBA-15	46	22
$AlCl_3$-Im-SBA-15	59	8
$CuCl_2$-Im-SBA-15	12	3
$FeCl_3$-Im-SBA-15	0	0

This ionic liquid support is a useful platform to evaluate the activity of various metal chlorides, *viz.* $CrCl_2$, $CuCl_2$, $AlCl_3$, $FeCl_2$, $FeCl_3$, in the aqueous phase dehydration of glucose to HMF. We found that the HMF yield of $MeCl_x$-Im-SBA-15 catalysts increases in the order: $FeCl_3$ < $CuCl_2$ < $AlCl_3$ < $CrCl_2$, which follows the same trend as the homogeneous case [2]. The yield however is lower than of the homogeneous catalyst. The $CrCl_2$-Im-SBA-15 catalyst was investigated in more detail. The metal chloride is retained by the immobilized ionic liquid, based on the observation that the filtrate of the reaction mixture did not convert glucose further. Current efforts aim to improve the yield by increasing the hydrophobicity of the SBA-15 support and extracting the HMF product in a biphasic system.

Interestingly, Cr K edge XAS results indicate that under reaction conditions a large part of the chlorine ligands of the homogeneous and immobilized Cr(II) are replaced by oxygen of the reacting sugar.

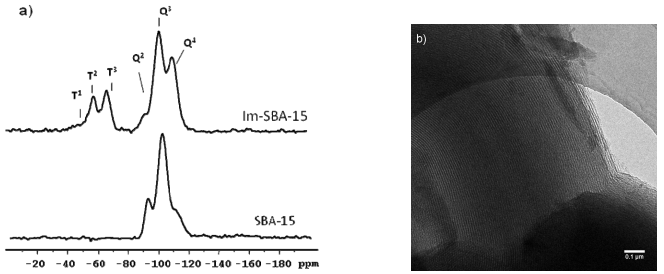

Figure 1. (a) ^{29}Si CP MAS NMR spectra of SBA-15 and ionic liquid immobilized on the SBA-15 surface and (b) electron micrograph of ionic liquid immobilized SBA-15.

Significance

Heterogenization of the homogeneous $CrCl_2$:EMIMCl glucose dehydration catalyst is possible by grafting the ionic liquid to a silica support.

References

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