

CONVERSION OF GLUCOSE INTO PLATFORM CHEMICALS USING ALUMINOPHOSPHATES (SAPO-5 and MeAPO-5) IN [BMIM]Cl IONIC LIQUID

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ABSTRACT. The conversion of glucose into platform chemicals such as 5-hydroxymethylfurfural, levulinic acid and formic acid has been investigated using two aluminophosphate based zeotypes (SAPO-5 and MeAPO-5) catalysts in 1-butyl-3-methylimidazolium chloride [BMIM]Cl ionic liquid as a reaction medium. The silico aluminophosphates (SAPO-5) and metal aluminophosphates (MeAPO-5) were designed and chosen for their tunable amount and strength of acid sites. The dehydration of glucose using each catalyst gave more than 90% glucose conversion. Among all the catalysts tested, the most hydrophilic SAPO-5 (1.5T) results in a better 5-HMF yield of 8% at 100 °C and 6 h reaction time. Contrary to this, the more hydrophobic SAPO-5 gives higher yield of levulinic acid and formic acid and no 5-HMF yield at this particular reaction time. In general, despite the higher glucose conversion attained by these aluminophosphate based catalysts, the lower yield obtained by these materials can be attributed to the type of acidity and the incompatibility of the pore diameter of the AFI channels of the catalysts and the desired products.

KEY WORDS: Biomass, 5-Hydroxymethylfurfural, Levulinic acid, Formic acid, Ionic liquids, Aluminophosphate

INTRODUCTION

The world's economic and geopolitical factors together with an increase in demand for energy, fuels and materials by society lead scientists to investigate new and renewable energy resources [1]. Renewable and vastly abundant biomass resources have the potential to serve as a sustainable supply of fuels and chemical intermediates by developing cost effective processing methods to transform highly functionalized carbohydrate moieties into value added chemicals. Among other primary renewable building blocks, 5-hydroxymethylfurfural (5-HMF) is considered an important intermediate due to its rich chemistry and potential availability from carbohydrates such as fructose, glucose, sucrose, cellulose and inulin. 5-HMF is very useful not only as intermediate for the production of the biofuel 2,5-dimethylfuran (DMF) and other molecules, but also for important molecules such as levulinic acid, 2,5-furandicarboxylic acid (FDA), 2,5-diformylfuran (DFF), dihydroxymethylfuran and 5-hydroxy-4-keto-2-pentenoic acid [2, 3].

Recently, considerable improvement has been reported for the conversion of fructose to 5-HMF, whereas the transformation of glucose, sucrose and cellulose remains difficult. More efficient reaction conditions (lower temperature, and higher carbohydrate initial concentration), higher conversions and 5-HMF selectivity are desirable, and these processes have to be environmentally friendly [4-8]. Recent work on glucose dehydration to platform chemicals such as 5-hydroxymethylfurfural over phosphate of aluminum, titanium, zirconium and niobium catalysts showed the synergistic effect of Brønsted and Lewis acids, which result in 5-HMF selectivity range of 30-60% [9]. In this direction, apart from several attempts in using zeolites [10], no other microporous solids have been tested. Zeotypes are aluminophosphate based crystalline microporous solids whose acidity can be controlled from the synthesis conditions. Silicoaluminophosphates (SAPOs) and aluminophosphates (MeAPOs) can be designed by

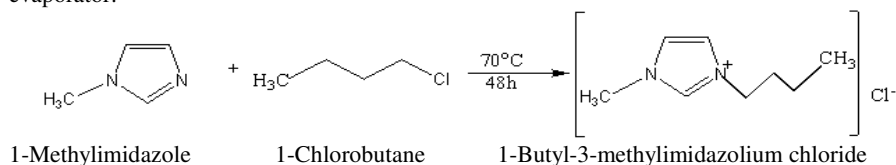
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different mechanisms of silicon and metal insertion to obtain tuned acidity including both Lewis and Brønsted acid sites [11, 12]. Among the zeolitic materials reported in the literature, mordenite zeolites with moderate acidity have shown promising fructose conversion with maximum selectivity to 5-HMF (90%) [13]. On the other hand, Chloride based IL like [BMIM]Cl have an exceptionally high capacity for dissolving carbohydrate since the extensive hydrogen bonding network that constituent the structure of the solid carbohydrate is disrupted. It can also open up the possibility of 'one-pot' reactions directly from crude biomass [14, 15]. Therefore, the present study explores the catalytic activity of tuned SAPO-5 and MeAPO-5 molecular sieves with AlPO-5 (AFI) structure having similar pore size and channels structure as mordenite, in the presence of ionic liquid [BMIM]Cl instead of conventional solvents like water and DMSO because of its unique dissolving properties for crude biomass such as glucose.

EXPERIMENTAL

Preparation of ionic liquid ([BMIM]Cl)

The [BMIM]Cl ionic liquid used in this study was synthesized in our laboratory (Scheme 1) and characterized using NMR spectroscopy. 1-Methylimidazole (61.29 mL) and excess 1-chlorobutane (85.42 mL) were placed in a 250 mL round bottom flask, equipped with a thermometer, magnetic stirrer bar, condenser and drying tube. The flask was placed in an oil bath and its solution heated under reflux at 70 °C for 48 h and the product was washed with 1,1,1-trichloromethane three times to purify the product from unreacted methyl imidazole. Finally, the washing solvent was removed by evaporation under reduced pressure using rotary evaporator.



Scheme 1. Synthesis of [BMIM]Cl from 1-methylimidazole and 1-chlorobutane.

Synthesis and activation of SAPO-5 and MeAPO-5 catalysts

SAPO-5 and MeAPO-5 samples were kindly donated by the authors [11, 12] from the Institute of Catalysis and Petroleocochemistry, CSIC (Madrid, Spain). Each microporous material contains water molecules adsorbed on the surface, and is prepared in the presence of structure directing agent (SDA). This structure directing agent has to be removed to provide the material with the catalytic activity. The calcination of SAPO-5 and MeAPO-5 samples was carried out by putting the samples in a time and temperature controlled furnace for six hours in the temperature range of 550 to 600 °C to remove the structure directing agents. Complete removal of the SDA was confirmed by thermogravimetric analysis (TGA).

Experimental methods for conversion of glucose

In a typical run for the conversion of glucose into platform chemicals in the IL, a 250 mL two-necked round bottom flask was equipped with water cooled condenser, and magnetic stirrer under inert gas atmosphere. After an appropriate amount of glucose (5 g) was dissolved in [BMIM]Cl (16 g) for 15 min in the reactor, 0.5 g of the catalyst was added, and the reaction was

continued by heating the flask at a constant temperature of 100 °C. Samples were taken at 30 min, 1, 3, 6, and 12 h, and extracted three times with 5 mL ethyl acetate and diethyl ether. The extracting solvent was removed using rotary evaporator and the product was collected, and then dissolved in chloroform and kept in refrigerator for analysis.

Analysis of ionic liquid, glucose, products and its residues

The characterization of glucose, the synthesized ionic liquid ([BMIM]Cl), products and its residues were performed with NMR (Bruker 400 MHz) spectroscopy. The ^1H and ^{13}C NMR spectra of the synthesized [BMIM]Cl, and d-glucose were recorded in CDCl_3 and D_2O , respectively.

The ^1H and ^{13}C NMR spectra of 5-HMF and its residues were also recorded in CDCl_3 as solvent. The amount (mol %) of 5-HMF obtained from the reaction mixture was determined using mesitylene (1,3,5 trimethyl benzene) as an internal standard. Glucose conversion for each reaction interval was determined using the ^1H NMR of pure glucose as a reference. The yield of 5-HMF (mol %) and glucose conversion were calculated based on the mole of the glucose loaded into the reaction mixture using the following formula.

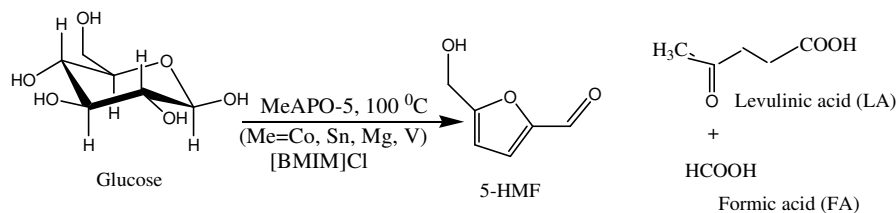
$$\text{(I) Mole of 5-HMF} = \frac{\text{Integral area of 5-HMF}}{\text{Integral area of std}} \times \frac{\text{Proton of std}}{\text{Proton of 5-HMF}} \times \text{mol of std}$$

$$\text{(II) 5-HMF yield} = \frac{\text{Mole of 5-HMF obtained}}{\text{Mole of glucose loaded}} \times 100\%$$

$$\text{(III) \% Conversion} = \left(1 - \frac{\text{Mole of unreacted glucose}}{\text{Mole of loaded glucose}}\right) \times 100\%$$

RESULTS AND DISCUSSION

5-Hydroxymethylfurfural (5-HMF), levulinic acid (LA), and formic acid (FA) have been produced from carbohydrates like glucose and fructose under various conditions catalyzed by mineral acids, organic acids, strong acidic resins and zeolite in different solvents, including water, organic solvents, organic/water mixtures, and ionic liquids. In this work, we have used different aluminophosphates (SAPO-5 and MeAPO-5) as catalysts in 1-butyl-3-methylimidazolium chloride [BMIM]Cl ionic liquid as a reaction medium (Scheme 2).



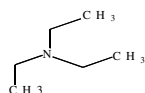
Scheme 2. Dehydration of glucose to 5-HMF, levulinic acid (LA) and, formic acid (FA) [3].

The catalysts with the structure directing agent employed are listed in Table 1. After calcination of all the materials, they were dried overnight at 100 °C to remove water molecules.

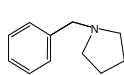
The reaction setup included an initial contact time (15 min) between the glucose and ionic liquid in order to allow proper solution and any possible catalytic effect of the ionic liquid. Prior studies in our laboratory have shown no conversion at all of the glucose in the presence of ionic liquid at 100 °C (blank). After this initial contact time, the catalyst was added under continuous stirring and under nitrogen flow. The evolution of the catalytic reaction was followed by taking samples at 30 min, 1, 3, 6, and 12 h.

Table 1. Calcination data of SAPO-5, ALPO-5 and MeAPO-5 catalysts.

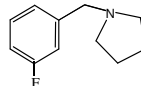
Sample	SDA	Time (h)	T (°C)	Weight loss TGA (%)
SAPO-5 1.5T	TEA	6	550	10
SAPO-5 1.5B	BP	6	600	15.7
SAPO-5 0.5T,1B	TEA:BP	12	600	12
SAPO-5 1T,0.5B	TEA:BP	6	600	12
SAPO-5 0.75T,0.75B	TEA:BP	7	600	11.5
SAPO-5 mFBP	FBP	6	600	15.3
SAPO-5 MCHA	MCHA	6	600	13.5
ALPO-5	MCHA	6	600	13.6
CoAPO-5*	TPA	18	550	11
CoAPO-5	MCHA	6	550	-
MgAPO-5	MCHA	12	550	14
MnAPO-5	MCHA	6	550	13
SnAPO-5	MCHA	6	550	14
VAPO-5	MCHA	6	550	25



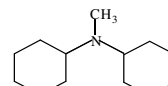
Triethylamine
(TEA)



Benzylpyrrolidine (BP)



Meta-fluoro-Benzyl
pyrrolidine (mFBP)



N-methyl-dicyclo
hexylamine (MCHA)

For initial comparison with previous experiments undertaken with commercial zeolites, the sample taken at 3 h was first analyzed by NMR. Table 2 shows the results obtained at 3 h reaction time for the SAPO-5 and MeAPO-5 catalyst prepared with TEA, BP and different ratios of the mixtures of the two templates.

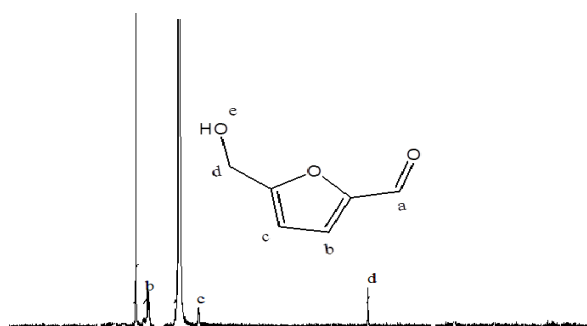
The 3 h reaction product of ¹H NMR analysis results in Table 2 show that all catalysts converted glucose more than 90% at this specific reaction time, but the corresponding yield is rather low. Despite this low formation of 5-HMF, there are differences in the catalysts depending on the synthesis method that are to be remarked. The highest yield, 0.63%, is obtained for SAPO-5 catalyst with triethylamine (1.5T) as a template. The ¹H NMR spectrum of 1.5T catalyzed reaction (Figure 1) shows the major peaks of the 5-HMF δ 9.87 (s, 1H), 7.106 (d, 1H), 6.79 (d, 1H), 4.93 (s, 2H) and 3.373 (br, 1H) although the peaks are very weak compared to the peaks of the IL which could not be purified from our product.

This sample is reported to contain higher number of Brønsted acid sites but weaker and more hydrophilic [11]. This mild acidity could be responsible for a better performance of this catalyst. On the other hand, SAPO-5 1.5B sample with less but strong Brønsted acid site brought very small 5-HMF yield at this reaction time. Although, SAPO-5 catalyst with equimolar composition of templates (0.75T, 0.75B) showed the maximum glucose conversion (99.25%), its yield was the least compared to the others at this specific reaction time.

Table 2. Conversion of glucose into 5-HMF, levulinic (LA) and formic (FA) in [BMIM]Cl at 3 h.

Catalyst	Conversion (%)	5-HMF yield (%)	Other products
SAPO-5 1.5T	95.8	0.63	LA, FA
SAPO-5 1.5B	94.9	0.15	LA, FA
SAPO-5 1B, 0.5T	98.0	0.15	LA, FA
SAPO-5 1T, 0.5B	96.9	0.16	LA, FA
SAPO-5 0.75B, 0.75T	99.2	0.13	LA, FA
SAPO-5 mFBP	99.4	1.99	
SAPO-5 MCHA	93.2	1.03	
AlPO-5	-	-	
CoAPO-5*	96	-	
CoAPO-5	96	0.12	
MgAPO-5	95	-	
MnAPO-5	96	-	
SnAPO-5	96	0.1	
VAPO-5	-	-	

Reaction conditions: 16 g ionic liquid, 5 g glucose, 0.5 g catalyst, 100 °C, 3 h.

Figure 1. ¹H NMR spectra of 5-HMF produced by SAPO-5 1.5T at 3 h reaction time.

In the analysis of the 6h reaction product (Table 3) the maximum 5-HMF yield (7.96%) was obtained by the SAPO-5 1.5T catalyst. On the other hand, SAPO-5 1.5B showed the maximum glucose conversion (99.9 %), but gave no 5-HMF yield at this specific reaction time. Instead, peaks of other products, levulinic and formic acid, showed dominance. This could be related to the strong Brønsted acid sites of the catalyst as a result of its hydrophobicity that brings the further conversion of glucose and 5-HMF to LA and FA.

Table 3. SAPO-5 and MeAPO-5 catalyzed dehydration of glucose in [BMIM]Cl.

Types of catalyst	Glucose conversion (%)	5-HMF yield (%)	Other products
SAPO 1.5T	99.8	7.96	LA, FA
SAPO 1.5B	99.9	0	LA, FA
CoAPO-5*	95	0	LA, FA
CoAPO-5	95	0.46	LA, FA
SnAPO-5	98	0.24	LA, FA

Reaction conditions: 16 g ionic liquid, 5 g glucose, 0.5 g catalyst, 100 °C, 6 h.

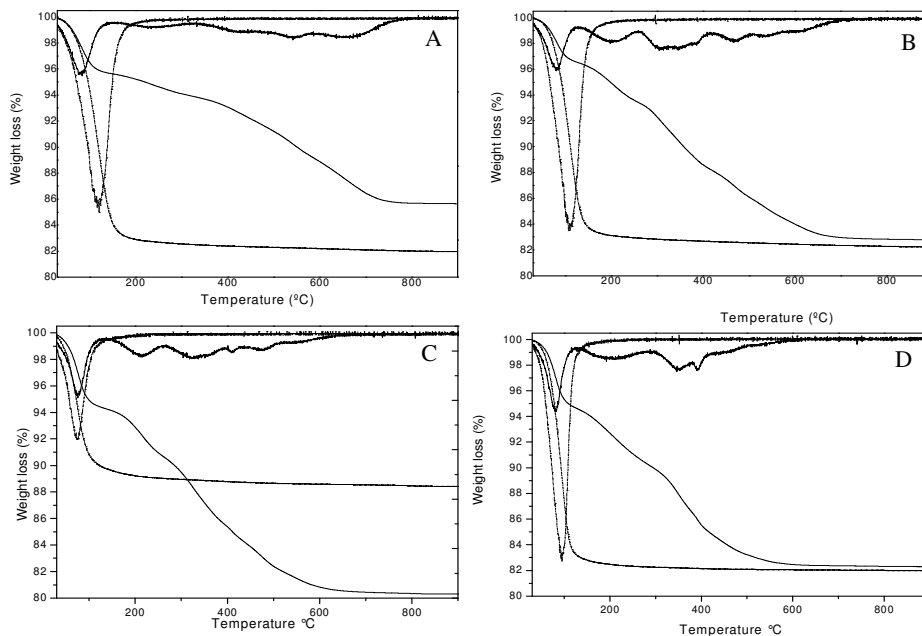


Figure 2. Thermogravimetric analysis of the recovered catalysts SAPO-5 1.5T (A), SAPO-5 1.5B (B), CoAPO-5 (C) and CoAPO-5*(D). Dotted lines correspond to calcined samples, whereas solid lines are the recovered ones.

The table also indicated that, among the MeAPO-5 catalysts, CoAPO-5 catalyst (synthesized with MCHA as SDA) gave better yield of 5-HMF compared to other MeAPO-5 catalysts. On the contrary, CoAPO-5* (synthesized with TPA as SDA) gave no 5-HMF. The difference in their catalytic activities might be attributed to the difference in their structure directing agent and therefore, in the crystal size and mesoporosity generated therein. Moreover, SnAPO-5 gave clearly observable ^1H NMR spectra of the product at 6 h reaction time, even though the amount of 5-HMF obtained remains very small. This indicates that SnAPO-5 is a promising catalyst for the clean conversion of glucose to 5-HMF, in the same trend observed for Sn-Beta zeolite [10]. Although, among these platform chemicals high attention was given to the production of 5-HMF which could serve as a sustainable source of liquid fuels and chemicals, none of the explored catalysts improved the yield to 5-HMF neither by increasing the reaction temperature or the reaction time. Thus the explanation to this low yields together with very high conversions and short reactions times must be related to the microporous structure of the zeotypes as well as the type of acidity. The unidimensional structure of the AFI type (SAPO-5 and MeAPO-5) catalysts and their small pore size (7.3\AA) [16] compared to the starting material glucose (8.6\AA) and the product, 5-hydroxymethylfurfural (9.3\AA) [17] itself, seems to be hindering the accessibility of glucose to the catalytic sites for its partial dehydration to 5-HMF and the rapid diffusion of 5-HMF once formed inside the channels of the catalysts. Moreover, the ionic liquid used here as a solvent ([BMIM]Cl) is polar, and might compete for substrate (glucose) with the catalysts. This can reduce the free movement of glucose on the surface of the catalyst. The solvent also interfered with the extraction of 5-HMF from the reaction mixture, due to the polarity nature of 5-HMF. In an attempt to close the mass balance, we recovered the catalysts

after the first cycle of reaction and among the recycled catalysts, those showing some tendencies, SAPO 1.5T, SAPO 1.5B, CoAPO-5 and CoAPO-5* were selected for thermogravimetric analysis. Figure 2 shows the thermogravimetric curves for both the calcined and recycled catalysts.

The TGA of the four calcined catalyst showed only one sharp weight loss below 100 °C that is attributed to the removal of the physisorbed water molecules. Moreover, the TGA of the calcined sample showed no weight loss above 100 °C indicating that the calcination of the catalyst was completed under the temperature employed, and there was no organic templates remaining prior to the catalytic reaction. On the other hand, all the recovered catalysts showed other important weight losses, besides to weight loss due to water molecules. The weight losses observed in the recovered catalyst above 100 °C might be due to the decomposition of some organic molecules stacked in the pore of the catalysts. These organic molecules might be the ionic liquids, or products of glucose dehydration such as 5-HMF, levulinic acid, or other reaction intermediates and condensation products.

Table 4 summarizes the total weight losses of the recovered catalysts, which interestingly are very similar to those of the initial as made samples, indicating that the entire micro pore volume is filled by organic molecules. However, further studies will be needed to investigate the reaction mechanism leading to 5-HMF, LA, FA and/or ionic liquids being stacked in the pores of the catalyst.

Table 4. The recovered catalyst and the total weight losses.

The type of catalyst	Total weight loss (%)
SAPO 1.5T (A)	14
SAPO 1.5B (B)	17
CoAPO-5 (C)	19
CoAPO-5* (D)	17

The surface properties and type of acidity of the catalyst also limit the yield of 5-HMF obtained compared to LA and FA. For example from Table 3 it is possible to see that 1.5B resulted no 5-HMF at 6 h reaction time rather it gave LA and FA that can be remarked to the strong Brønsted acid sites of the catalyst that brings the further conversion of glucose and 5-HMF to LA and FA.

CONCLUSION

In this work, the efficiency of different zeotypes (SAPO-5 and MeAPO-5) catalysts in converting glucose into 5-hydroxymethylfurfural and other bulk chemicals levulinic acid and formic acid is investigated. The differences in efficiency of these materials are related to the difference in their synthesis method which results in difference in the acidity and surface properties of the catalysts. Glucose conversion of greater than 90% was obtained with all the catalyst. The high glucose conversion with each catalyst indicates that, even the amount of 5-HMF obtained is small, the catalysts interacts with glucose molecules and led to the formation of certain reaction intermediates. The presence of organic molecules was observed from the TGA of the recovered catalyst indicates that diffusion of product is limiting the yield and selectivity values.

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