Acid Catalyzed Monosaccharide Dehydration in the Condensed Phase

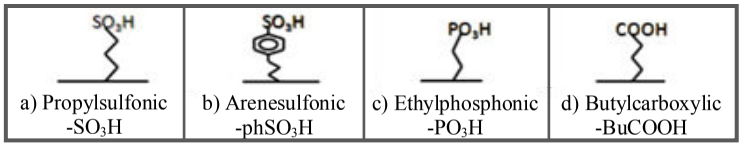
Basak Cinlar and Brent H. Shanks*
Iowa State University, Ames, IA 50011 (USA)
*bshanks@iastate.edu

Introduction

Integrating new catalyst technologies into monosaccharide dehydration is of great importance for the conversion of biomass into liquid alkane fuels and/or multitude of chemicals to substitute for petroleum-based building blocks in plastics and fine chemicals industry [1, 2]. Organic acid functionalized mesoporous silica catalysts are potential candidates for the reaction system. Recently, dehydration of xylose was performed successfully using a sulfonic acid functionalized MCM-41 [2]. Extension of the study to other monosaccharides and further tailoring of the textural and chemical properties of the catalyst remains challenging. Design of the catalyst requires knowledge about the reaction system, such as the effects of the nature of the acid and its initial acidity. Unfortunately, systematic data outlining these effects are not available and a common framework for a catalytic activity comparison is missing. The current work addresses the effect of the nature of acid and its initial acidity on dehydration kinetics using a variety of homogeneous acids and thereby begins to build a platform that allows activity comparison of heterogeneous catalyst to their homogenous analogs. The outcome of the study was used for the design of mesoporous silica catalysts for the dehydration reaction and their performance was studied on C-5 and C-6 carbohydrates, such as xylose, fructose and glucose.

Materials and Methods

To test the effect of the nature of the acid and initial pH, organic and mineral acids of different strength were selected. Sulfuric acid, hydrochloric acid, phosphoric acid, maleic acid and 1-propylsulfonic acid were tested for their activity on glucose, fructose and xylose at two different initial acidities, pH 1.5 and 3.6. The data on substrate conversion were used to calculate the activation energies (Ea), which provided a reference point for heterogeneous acid activity comparison. Organic acid functional groups of different acidic strength (as shown in Figure 1) were incorporated onto SBA-15 type mesoporous silica via co-condensation at 10% loading as described in the literature [3] and characterized for their textural and acidic properties. These catalysts were then tested for their activity for dehydration of fructose, glucose and xylose.



a) Propylsulfonic -SO_3H	b) Arenesulfonic -phSO_3H	c) Ethylphosphonic -PO_3H	d) Butylcarboxylic -BuCOOH

Figure 1. Organic acid groups incorporated onto SBA-15

All kinetic runs were conducted in lab scale batch reactors at 145, 160 and 175˚C. Samples drawn during the kinetic runs were analyzed using Hi-Plex H^+ column (Polymer Laboratories) on HPLC system equipped with RI and UV- detectors.

Results and Discussion

The Ea for glucose changed for pH value of 3.6 according to the strength of the acid as shown in Table 1. Whether the acid is organic or mineral, completely dissociating acids led to a different mechanism for glucose degradation than weaker acids. Such a mechanism change was not observed for fructose or xylose. Regardless of the acid type and strength, the Eas were 140 and 138 kJ/mol for fructose and xylose respectively.

Table 1. Activation energies (kJ/mol) for glucose degradation

	pH: 1.5	pH: 3.6	*Literature values*	
Hydrochloric acid	138	137	*153mM Sulfuric acid [4] (pH:0.7)*	137
Sulfuric acid	142	138	*50 mM Sulfuric acid [5] (pH:1.1)*	118
Phosphoric acid	145	82	*50 mM Maleic acid [5] (pH:2.1)*	73
Maleic acid	138	78	*20% SBA-15-BuCOOH [3]*	76
1-Propylsulfonic acid	148	83	*15% SBA-SO_3H [3]*	65

The reaction rate constants at 160˚C are shown in Figure 2, when mesoporous silica catalysts were used. Rates at 145˚C and 175˚C revealed similar trends as well. Surprisingly, the rates with different functional groups were the same as no effect of acidic strength was observed. It was suspected that hydrothermal stability problems arose for the heterogeneous catalysts. Future work is focused on improving the hydrothermal stability.

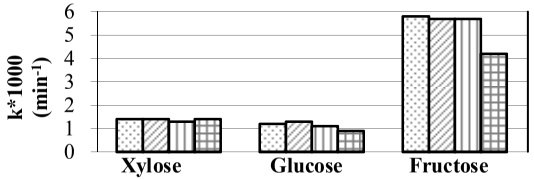


Figure 2. Monosaccharide consumption rates in the presence of mesoporous silica catalyst at 160°C (SBA-15-SO_3H, SBA-15-phSO_3H, SBA-15-PO_3H, SBA-15-BuCOOH)

Significance

This study demonstrated a change in the activation energy of glucose due to the acid strength at the pH values usually attained by organic acid functionalized mesoporous silica catalyst. A common framework for catalytic activity comparison was built and hence fine tuning of mesoporous silica catalysts for dehydration of monosaccharides was enabled.

References

1. J.N. Chheda, and J.A. Dumesic, Catal Today 123, 59 (2007).
2. A.S. Dias, M. Pillinger, and A.A. Valente, J Catal 229, 414 (2005).
3. J.A. Bootsma, and B.H. Shanks, Appl Catal A-Gen 327, 44 (2007).
4. N. Bhandari, D.G. Macdonald, and N.N. Bakhshi, Biotechnol Bioeng 26, 320 (1984).
5. N.S. Mosier, C.M. Ladisch, and M.R. Ladisch, Biotechnol Bioeng 79, 610 (2002).