One pot conversion of glucose to 5- Hydroxymethyl furfural using dual functional catalyst

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Abstract: One-pot conversion of Glucose 5-hydroxymethyl furfural (HMF) was carried out using multifunctional catalyst having basic and acidic sites. Basic sites catalyze the glucose isomerization to fructose and acidic sites are responsible for dehydration of fructose to 5-HMF. Maximum yield of HMF 44% was achieved at 160°C and 1atm pressure. The study of detailed reaction mechanism using Density Functional Theory (DFT) was studied and the transformation of glucose ring to ene-diol intermediate found to be the rate limiting step.

Keywords: One-pot, Glucose, HMF.

1. Introduction (11-point boldface)

Alternative fuel is the immediate solution for the current problem of depletion of fossil fuels and global warming [1,2]. Dimethyl furan is an alternative fuel having high energy density of (31.5 MJ/L) better than ethanol (23 MJ/L) [3,4]. Hydroxymethyl furfural is a precursor of DMF that can be obtained from glucose isomerization to fructose and its subsequent dehydration to HMF. Isomerization process is catalyzed by basic sites/ Lewis acid and dehydration of fructose to HMF is catalyzed by Bronsted acidity [5]. Multifunctional catalysts having both acidic and basic sites found to be the potential catalyst for one-pot conversion of glucose to 5-HMF. Glucose is isomerized to fructose following the Lobry de Bruyn Van Ekenstein rearrangement. Fructose then dehydrated to the 5-HMF by losing three water molecules.

2.a Experimental

Glucose, multifunctional catalyst were taken in a Teflon lined autoclave with 2:8 aqueous to organic layers as a solvent. A mixture of saturated NaCl solution and DMSO (7:3 v/v) was used as an aqueous layer and methyl isobutyl ketone was used as an organic layer. The reaction is carried out at different temperature for different intervals of time and the products are analyzed with HPLC using Hi-plex column at a temperature of 65°C and RI detector at temperature of 35°C using glucose and HMF as an external indicator.

2.b The geometries of all the reactants, products and intermediate have been optimized using B3LYP 6311G basis set of Density Functional Theory employed in Gaussian 09 program.

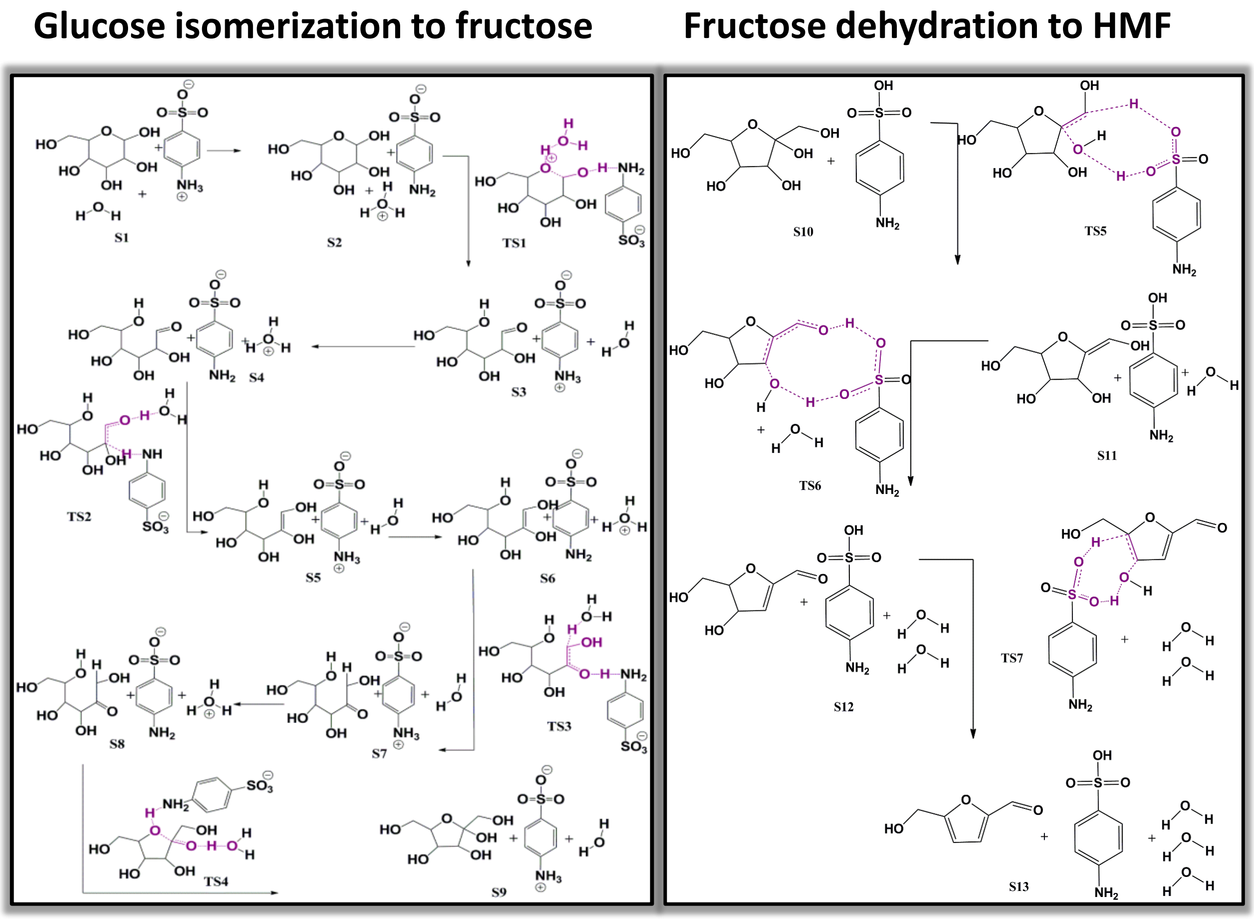
3. Results and discussion

The reaction is catalyzed in two steps (i) glucose isomerization to fructose and (ii) fructose dehydration to HMF as shown in Figure 1. Maximum conversion of glucose to HMF was achieved using multifunctional catalyst having both acidic and basic sites at a temperature of 160°C and 30 min of time as shown in Figure 2. The detailed reaction mechanism studied using DFT studies revealed that glucose isomerization to fructose is a rate limiting step as depicted from the data reported in Table 1

Table 1. Mechanistic details for glucose conversion to HMF

Reactions	**Energy Barrier (kcal/mol)**
Opening of glucose ring	22.2
Open chain glucose to ene-diol intermediate	25.0
Keto-enol tautomerization	22.0

Loss of 1st water molecule from fructose	20.8
Loss of 2nd water molecule	6.9
Loss of 3rd water molecule	27.1


Glucose isomerization to fructose

Fructose dehydration to HMF

Figure 1. Mechanism for glucose dehydration to HMF

4. Conclusions

Glucose conversion was studied using multifunctional catalyst having both basic and Bronsted acidic functionalities. Glucose conversion to HMF was achieved with 44% yield at 160 °C and 30 min reaction time using multifunctional catalyst. The detailed study of reaction mechanism was studied using Density Functional Theory (DFT). Glucose isomerization to fructose following the Lobry de Bruyn–van Ekenstein rearrangement was found to be the rate limiting step with an activation energy of 25.2 kcal/mol.

References

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