Glucose isomerization to fructose over Ba-Zr mixed metal oxide catalyst

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Abstract: This study investigated various barium mixed metals *viz*. Zn, Zr, W oxide catalysts for glucose isomerization. The results showed that Ba-Zr (1-1) as most efficient catalyst for glucose isomerisation in terms of 56% glucose conversion and 92% fructose selectivity. Characterization data from XPS, TEM and TPD reveals new insight for the Lewis acid-base assisted glucose isomerization which further illustrates plausible reaction mechanism by structure activity correlation.

Keywords: Isomerization,Glucose, Fructose, Mixed metal oxide.

1.Introduction

Fructose is not only an important food and beverage ingredients, but also a renewable resource for production of 5-hydroxymethylfurfural (HMF), which is a versatile platform chemical for production of chemicals and liquid fuels [1]. Even though, fructose is industrially important it is not found in the natural resources in large abundance as compare to other carbohydrates. Hence, isomerisation of glucose to obtain fructose was widely studied as glucose is found in large abundance as well as available at cheaper cost in the biological cycle.Industrially fructose is produced by immobilized glucose isomerases [2].Nevertheless, enzymatic isomerization process has several drawbacks, including high-cost, longer reaction time, need for buffers, and irreversible deactivation. To overcome these drawbacks several heterogeneous catalysts were studied including Sn-β zeolite, yielded approximately 31% fructose [3, 4].

2. Experimental

All the mixed metal oxidecatalysts were prepared by co-precipitation method using appropriate calculated amount of respective metal nitrate solutions and K_2CO_3 solutions were used as precipitating agent.The pH of solution was maintained in between the range of 9-10.The precipitate obtained was kept under continuous stirring for 3h at room temperature. Then obtained cake was filtered, washed with DI water and dried at about 110 ^oC for 12h. The obtained powder was calcined at 550 ^oC for 3h.

The catalytic reactions were performed in 50 ml round bottom flask equipped with condenser. Then it was charged with 0.180g of glucose, 0.1g of catalyst and 6 ml of solvent. It was kept under stirring at about 100 ^oC for 6h. Liquid samples were analysed using HPLC(Agilent 1260) equipped withHi-Plex H columnand RI detector. Only water was used as a mobile phase with 0.5 mL/min flow rate having column temperature 50 ^oC.

3. Results and discussion

Table 1 showed that impregnation of 20% PWA over Ba-Zr (1-1) catalyst enhanced total acidity from0.1805 mmol/g to 0.7521 mmol/g of NH_3 desorbed and total basicity showed reverse order. **Figure 1** displays XRD patterns of prepared catalyst in comparison with bare metal oxide (BaO and ZrO_2). Which clearly suggest that in case of Ba-Zr (1-1) catalyst other than BaO and ZrO_2 phases, there was a formation of $BaZrO_3$ phase with reflections at 2θ = 23.9 (211), 27.7 (220), 34.6 (222) and 44.5 (420) [PCPDF # 030632].

Table1. NH_3 and CO_2 TPD of prepared catalysts.

Sr. No.	Catalyst	NH_3 desorbed (mmol/g)	CO_2 desorbed (mmol/g)
1	Ba-Zr (1-1)	0.1805	0.3952
2	20 % PWA Ba-Zr (1-1)	0.7521	0.2527

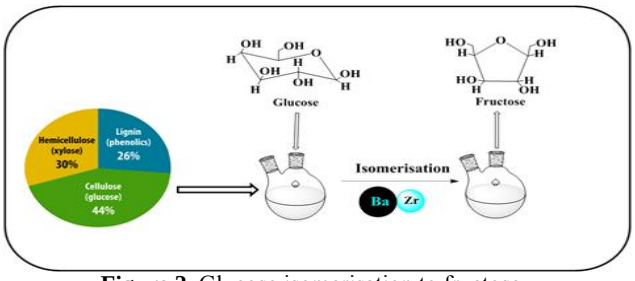

Figure 2. Glucose isomerisation to fructose.

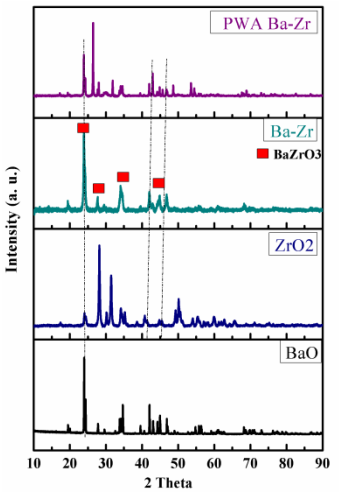

Figure 1. XRD pattern for prepared catalysts.

In present work, glucose isomerization to fructose was studied over various mixed metal (Ba, Zr, Zn, W) oxide catalysts to obtain maximum glucose conversion and fructose selectivity. Initially, Ba-Zn (1-1) catalyst showed lower glucose conversion (18 %). Further replacement of Zn to more acidic Zr in Ba-Zr (1-1) catalyst showed excellent activity in terms of 56% glucose conversion and 92% fructose selectivity (**Table 2**). However, impregnation of Brønsted acidic PWA over Ba-Zr (1-1) catalyst does not improvedactivity although it is having total acidity seven times more than Ba-Zr catalyst as revealed from NH_3-TPD results (**Table 1**).

Table2. Isomerisation of glucose to fructoseover different mixed metal oxide catalysts.

Sr. No.	Catalyst	Solvent	Conversion (%)	Selectivity (%)
1	Zr-W(1-1)	water	-	-
2	Ba-Zn(1-1)	water	18	90
3	**Ba-Zr(1-1)**	**water**	**56**	**94**
4	Ba-Zr(1-1)	DMSO: water	59	92
5	20% PWA Ba-Zr(1-1)	water	50	65

Reaction Conditions: Glucose, 0.180g; cat., 0.1g; temp., 100 ^oC; time, 6h; solvent, 6 ml.

4. Conclusions

The study demonstrated that mixed metal oxides can be applied as efficient heterogeneous, green and recyclable catalyst for glucose isomerization in water.By various combinations of metals in order to tune the acid-base ratio, we have arrived at best combination of acid-base ratio in Ba-Zr (1-1) catalyst for the glucose aqueous isomerisation with 56 % glucose conversion and 94% fructose selectivity.

References

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