

Isomerization of Glucose in the Presence of Solid Base Catalysts at Hydrothermal Condition

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ABSTRACT

To produce 5-HMF from glucose, a two-step process is considered. In step 1, glucose is isomerized by base catalyst. In step 2, fructose is dehydrated by acid catalyst. In this work, we report on step 1, glucose isomerization. Alkaline-earth metal carbonates are effective for isomerizing lactose. We used alkaline-earth metal carbonate for glucose isomerization and studied catalyst and reaction conditions. Catalysts selected were CaCO_3 , MgCO_3 , and dolomite ($\text{CaMg}(\text{CO}_3)_2$). For comparison, TiO_2 , ZrO_2 and ZrO_2 solid solutions (CaO or TiO_2 were solubilized in ZrO_2 matrix) catalysts were also used. As a result, fructose selectivity decreased with increasing glucose conversion. For glucose conversions greater than 50%, fructose selectivity was highest for CaCO_3 and dolomite solid base catalysts. Probably, this can be explained by isomerization being inhibited by acid sites and accelerated by base sites. Therefore, one of the most important factors for isomerization seems to be the ratio of base to acid sites. To know important parameter of the catalysts for the isomerization, TPD measurement and surface area measurement for TiO_2 and ZrO_2 catalysts were conducted. As a result, the reactivity was correlated by the ratio of base to acid sites on the surface. The experimental data was expressed by a simple network model and kinetic parameters in the model were fitted. The kinetic constants concerning fructose formation were linearly proportional to the base/ acid mole ratio of the surface of the catalysts.

INTRODUCTION

Saccharides such as glucose are key compounds for sustainable society because their available amount is huge and they are sustainable carbon sources. One of the most likely resources of saccharide is cellulose. Cellulose can selectively be hydrolyzed efficiently into glucose in an appropriate solvent and in the presence of an appropriate catalyst, for example, cellulose can be hydrolysed into glucose in H_2SO_4 aqueous solution.

5-hydroxymethylfurfural (5-HMF), which is expected as key compounds for sustainable society because it can be converted into useful chemicals, is produced from saccharides such as glucose. To produce 5-HMF from glucose, we consider two-step process; glucose isomerization which needs base catalyst and fructose dehydration which needs acid catalyst. In this work, we study glucose isomerization. The literature reports that alkaline-earth metal carbonate such as CaCO_3 or hydrotalcite ($\text{Mg}_6\text{Al}_2(\text{CO}_3)(\text{OH})_{16}$) can isomerize for lactose effectively [1]. In this work, we used alkaline-earth metal carbonate, CaCO_3 , MgCO_3 , dolomite ($\text{CaMg}(\text{CO}_3)_2$), as catalysts. For comparison, TiO_2 , ZrO_2 and ZrO_2 solid solutions

(CaO or TiO₂ were solubilized in ZrO₂ matrix) were also employed. To know the important parameter for selection of catalyst, simple kinetic analysis was performed.

MATERIALS AND METHODS

All the chemicals were purchased from companies, except for dolomite (CaMg(CO₃)₂) and ZrO₂ solid solutions (CaO or TiO₂ were solubilized in ZrO₂ matrix). These were supplied as special samples. Table 1 shows some physical properties of TiO₂, ZrO₂ and ZrO₂ solid solutions. The amounts of acid and base sites were measured by a temperature programmed desorption (TPD) method. Probe gases for acid and base sites were NH₃ and CO₂ respectively. To measure the TPD, catalysts must be heated up to 1073 K and alkaline earth metal catalysts (CaCO₃, MgCO₃ and dolomite) are not suitable for the measurement due to its low heat resistance.

Table 1 Some physical properties of TiO₂, ZrO₂ and ZrO₂ solid solutions used in this study

Catalyst	BET m ² /g	Amount of acid sites μmol/g	Amount of base sites μmol/g	Density of acid site μmol/m ²	Density of base site μmol/m ²	base / acid mole ratio μmol-base / μmol-acid	Crystal structure
ZrO ₂	110	670	550	6.1	5.0	0.82	monoclinic / tetragonal
TiO ₂	4.7	79	42	16.8	8.9	0.53	anatase
Ca - 4.3 ^a	46.8	410	530	8.8	11.3	1.29	monoclinic
Ca - 14 ^a	54.7	490	570	9.0	10.4	1.16	monoclinic
Ca - 24 ^a	79.2	480	510	6.1	6.4	1.06	monoclinic
Ti - 7.5 ^a	55.4	560	240	10.1	4.3	0.43	monoclinic / tetragonal
Ti - 15 ^a	197.1	400	230	2.0	1.2	0.58	monoclinic / tetragonal

a: number in the catalyst name is mole percentage of metal ion in the ZrO₂ matrix

An aqueous solution (5 g) of glucose (2 wt%) and catalyst (0.1 g) were loaded into the glass reactor. The reactor was heated in a microwave oven [2] to 393 K~433 K for 3~30 min.

Liquid products were analyzed by HPLC and yields were defined on a molar basis.

RESULTS

Without catalyst, fructose selectivity rapidly decreased to 40 % with increasing up to 20 % of glucose conversion. On the other hand, using catalysts, glucose isomerization was improved.

In the case of addition of the solid catalysts, regardless of the kind of catalyst, glucose conversion and fructose selectivity were improved. **Figure 1** shows the

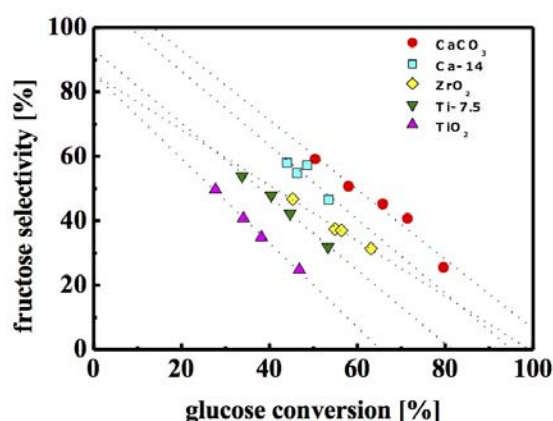


Figure 1 Relationship between glucose conversion and fructose selectivity at 433 K, 3~30 min

typical trend of the relationship between glucose conversion and fructose selectivity. In any case, by increasing glucose conversion, fructose selectivity decreased. In this figure, the plot located on right-up side is favorable. As shown in **Fig. 1**, CaCO_3 is better and TiO_2 is worse. Please notice that the better catalyst among TiO_2 and ZrO_2 catalysts including the solid solutions has high base/acid mole ratio, while worse catalyst has low (see in Table 1, Ca-14: 1.16, TiO_2 : 0.53).

Figure 2 shows the relationship between glucose conversion and fructose selectivity for calcite (**Fig. 2-a**) and dolomite (**Fig. 2-b**) at 393 K~ 433 K for 3~30 min. As shown in **Fig. 2**, for calcite and dolomite, the location of the plots on the graph at the relationship between glucose conversion and fructose selectivity were located at high fructose selectivity area (dolomite: 89% at 41% glucose conversion at 393 K for 30min, CaCO_3 : 96% at 34% glucose conversion at 393 K for 30 min). It must be noticed that fructose selectivity increased with increasing glucose conversion in the case of calcite at 393 K (at lower glucose conversion), as shown in **Fig. 2-a**. This might indicate that an intermediate of the isomerization probably exit in addition to the direct route of glucose into fructose.

To know the catalytic activity, the correlation between physical properties of catalysts and reactivity (fructose selectivity at a glucose conversion) was evaluated based on a simple reaction network model, as shown in **Figure 3**. As shown in this figure, based on the experimental results mentioned just above, there are three reaction routes: glucose and fructose are directly isomerized each other and an intermediate of the isomerization is also considerable. In the figure, rate constant of each pathway are described on each allow. By fitting the experimental results with the reaction network model, the rate constants were obtained. For the correlation of the physical properties and the reactivity, the acid/base mole ratio (as seen in **Table 1**) of the catalyst and the fructose formation/disappearance ratio, which are defined by Eqs. 1 and 2 as

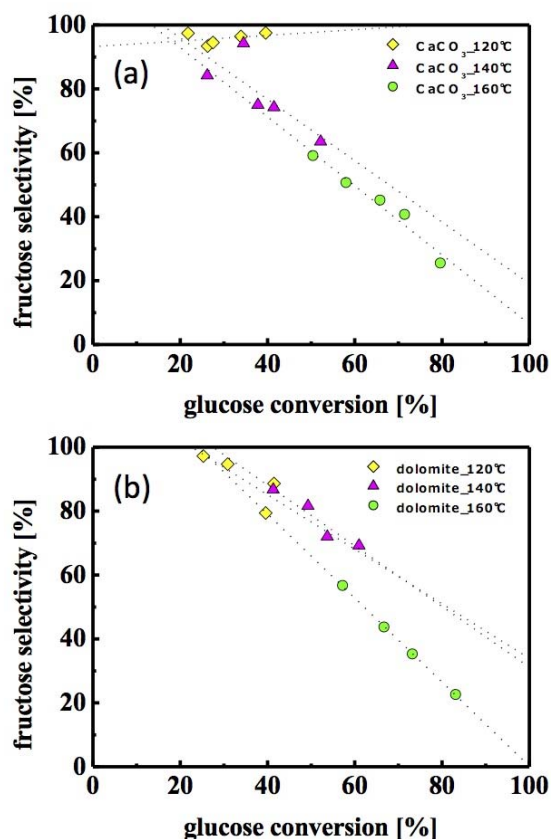


Figure 2 Relationship between glucose conversion and fructose selectivity in the presence of calcite (a) and dolomite (b) at 393 K~ 433 K, 3~30 min

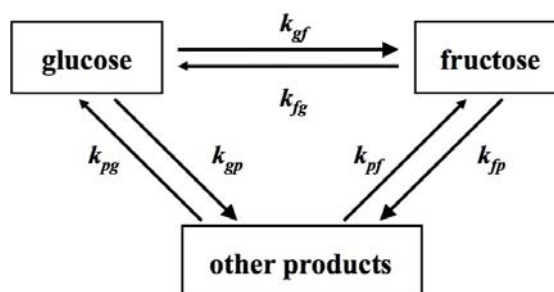


Figure 3 Simple reaction network model for glucose isomerization

shown below, were employed:

$$\text{Base/Acid mole ratio} = \frac{\text{Mole of base sites}}{\text{Mole of acid sites}} \quad (1)$$

$$\text{Fructose formation/disappearance ratio} = \frac{k_{gf} + k_{pf}}{k_{fg} + k_{fp}} \quad (2)$$

Figure 4 shows the correlation between the base/acid mole ratio and fructose formation/disappearance ratio at 433 K for ZrO₂, TiO₂, Ca-4.3, Ca-14, Ca-24, Ti-7.5 and Ti-15. As shown in this figure, high ratio of base sites on the catalysts enhanced fructose formation over its disappearance. By using the correlation, base/acid mole ratio on dolomite was estimated to be 10. To enhance the catalytic activity for glucose isomerization into fructose, the ratio of base site to acid site must be exceeded.

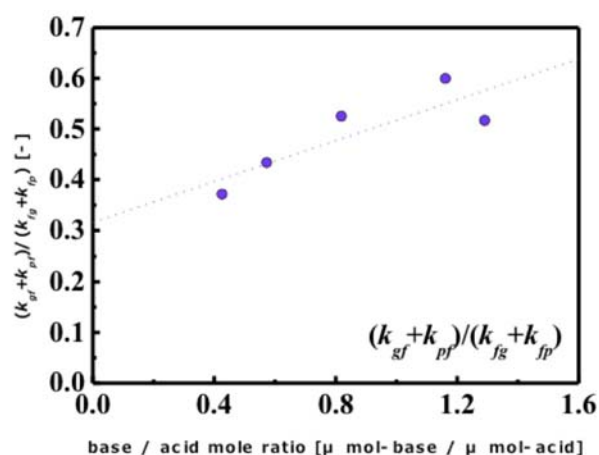


Figure 4 Correlation between base/acid mole ratio and fructose formation/disappearance ratio (433 K for ZrO₂, TiO₂, Ca-4.3, Ca-14, Ca-24, Ti-7.5 and Ti-15)

CONCLUSION

The effect of solid base catalysts (CaCO₃, MgCO₃, dolomite, TiO₂, ZrO₂ and ZrO₂ solid solutions) on isomerization of glucose to fructose in water was examined with microwave-assisted heating. All catalysts promoted isomerization and for alkaline-earth metal carboxides (CaCO₃, MgCO₃ and dolomite), glucose conversion was over 50% and fructose yields were around 30%. The correlation between the surface properties of metal oxides (TiO₂, ZrO₂ and ZrO₂ solid solutions) and reactivity revealed that base/acid mole ratio on the catalyst might be strongly related to the catalytic activity for glucose isomerization. From the correlation, the base/acid mole ratio on the dolomite would be 10 and this high base/acid ratio caused the high fructose selectivity.

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