Insight into the Alkaline Earth Metal Salts Promotion for Alkali-catalyzed Glucose Isomerization

Changqu Lin[1], Yunlin Shi[1], Lulu Xu[1], Zhengyue Wang[1], Lili Zhao[2], Hongli Wu[1, *], Fei Cao[1], Ping Wei[1]

1, College of Biotechnology and Pharmaceutical Engineering, Nanjing Tech University

30 South Puzhu Road, Nanjing, 211816 (P. R. China)

2, Institute of Advanced Synthesis, School of Chemistry and Molecular Engineering, Nanjing Tech University, 30 South Puzhu Road, Nanjing, 211816 (P. R. China)

*Corresponding author Email: hlwu@njtech.edu.cn

MS characterization

Electrospray ionization mass spectrometry (ESI-MS) was performed on an Orbitrap XL mass spectrometer (Thermo Fisher Scientific) with ESI ionization in the positive mode. The reaction solution was measured in the range of m/z 100-300 with the following operating parameters: capillary voltage 3.2 kV, sample cone voltage 40 V, source vaporizer temperature 150 °C, cone gas (N_2) flow 20 L/h, injection volume 5 μL. A collision energy of 20 eV was used for the collision-induced dissociation MS/MS measurement stage. Data acquisition and analyses were performed using Xcalibur software**.**

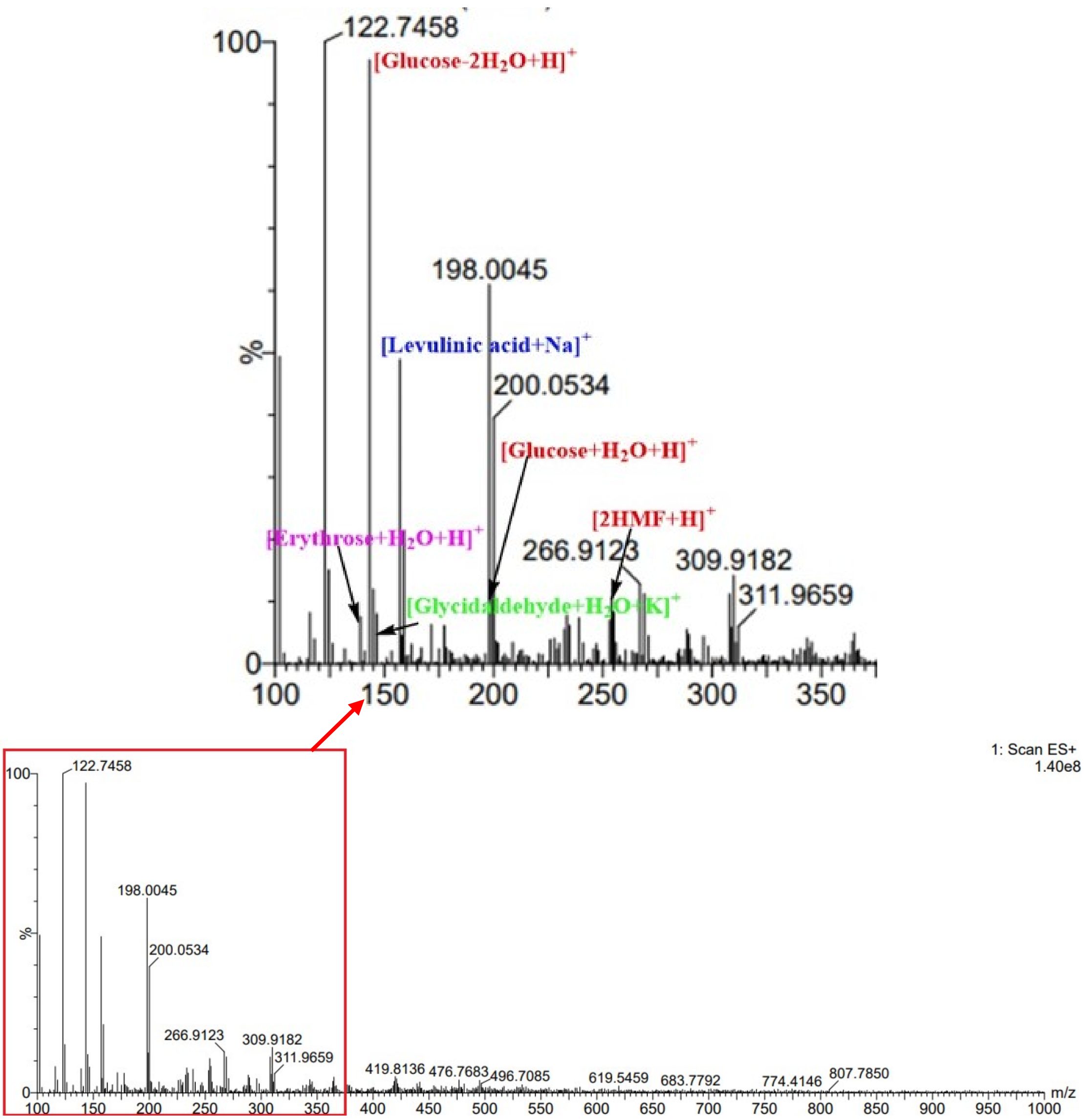


Figure S1 The MS of glucose reaction solution in $Sr(OH)_2$

First-order rate reaction was assumed and the reaction rate could be expressed as follows:

$$\ln\left([\mathrm{Glu}]_t/[\mathrm{Glu}]_0\right) = -kt$$

where $[\mathrm{Glu}]_t$ = glucose concentration at time t with unit of mol/L, $[\mathrm{Glu}]_0$ = initial glucose concentration, k = observed rate constant, and t stands for time in seconds. A linear correlation between $\ln([\mathrm{Glu}]_t/[\mathrm{Glu}]_0)$ and reaction time t was plotted. The k obtained under different temperature was obtained. The results are shown in Figure S2-S5

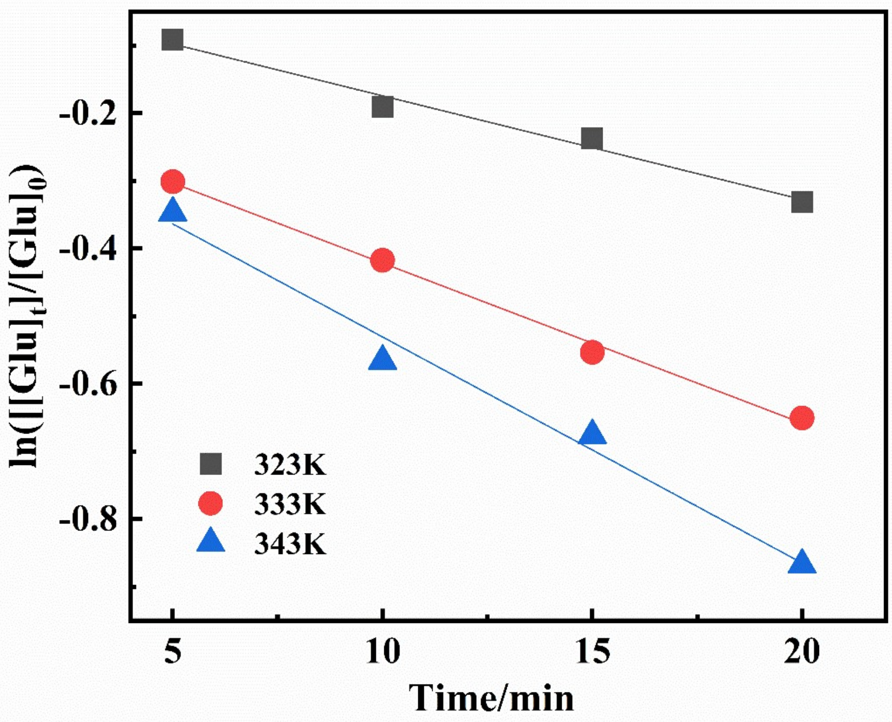


Figure S2 First order kinetic fit for the conversion of fructose in $Sr(OH)_2$

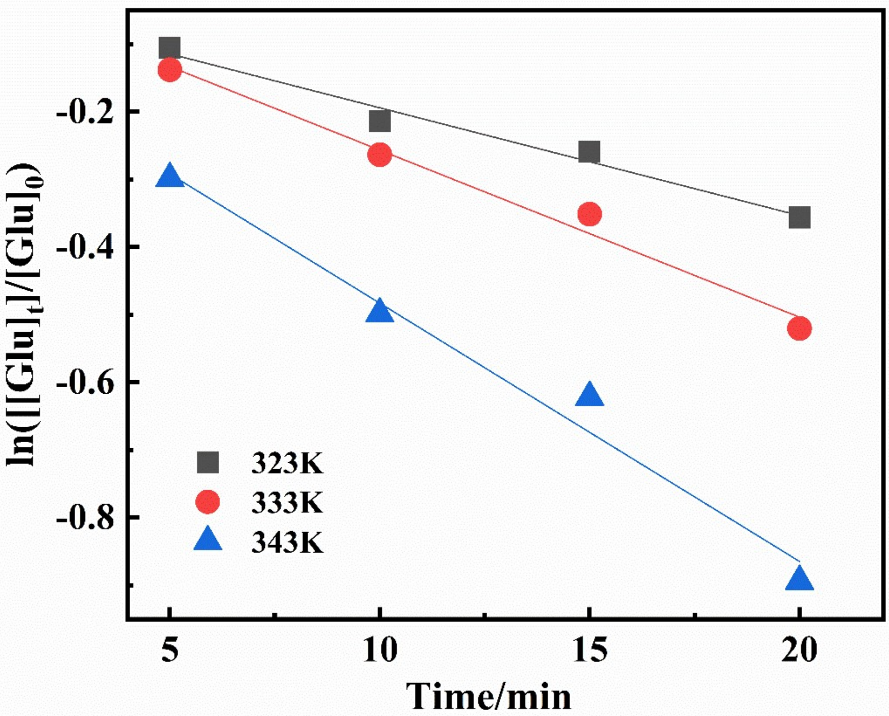


Figure S3 First order kinetic fit for the conversion of glucose in $Sr(OH)_2$.

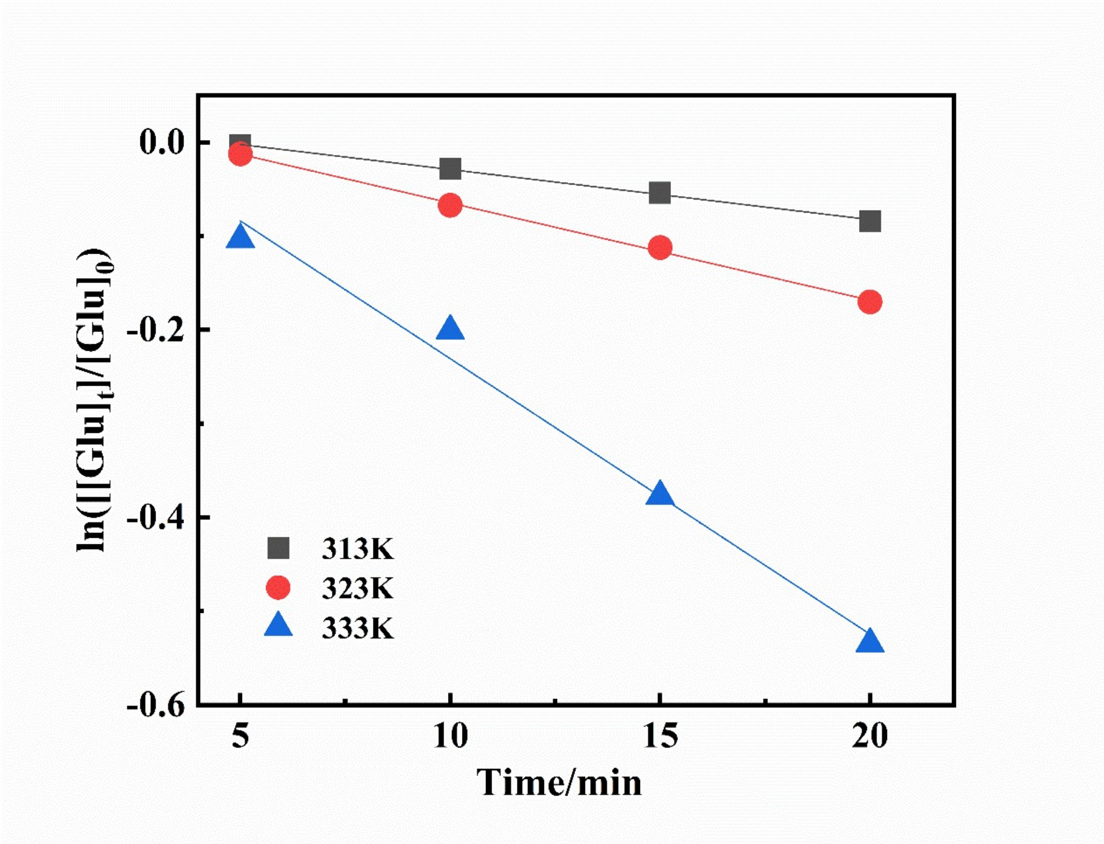


Figure S4 First order kinetic fit for the conversion of fructose in $CaCl_2$-$Sr(OH)_2$

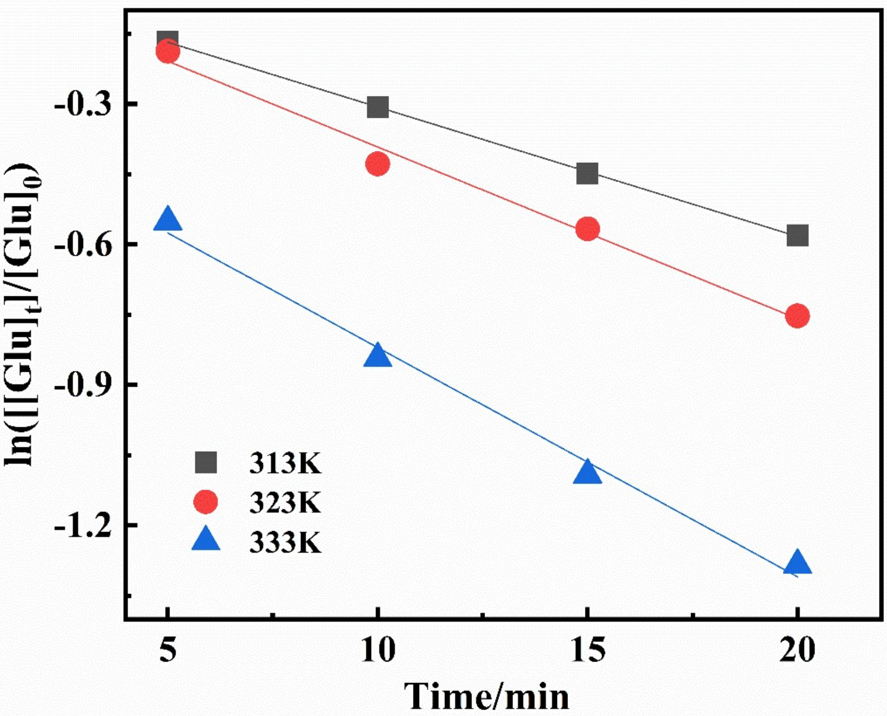
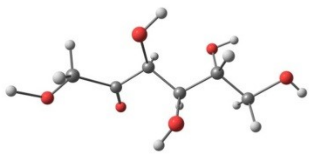


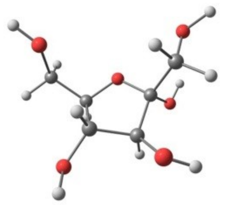
Figure S5 First order kinetic fit for the conversion of glucose in $CaCl_2$-$Sr(OH)_2$

Table S1 The optimized structures, energy differences (ΔG in hartree) for $C_6H_{12}O_6$, α-D-Fructofuranose, β-D-Fructofuranose and β-D-Fructopyranose at the B3LYP/AUG-cc-pVDZ level.

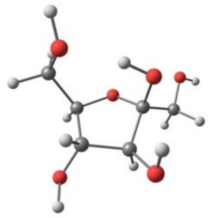
	$C_6H_{12}O_6$	α-D-Fructofuranose	β-D-Fructofuranose	β-D-Fructopyranose
ΔG	-687.2045314	-687.2039814	-687.206687	-687.207196



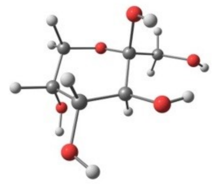
$C_6H_{12}O_6$



α-D-Fructofuranose



β-D-Fructofuranose



β-D-Fructopyranose

Table S2 The isomers, energy differences (ΔG in hartree) for Ca^{2+}+β-D-Fructofuranose at the B3LYP/ BSI level.

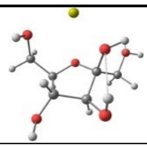
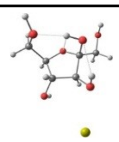
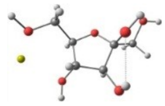
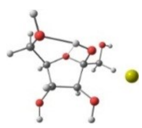
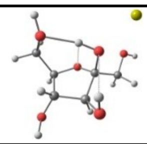
					
Ca^{2+}+β-D-Fructofuranose	Iso-1	Iso-2	Iso-3	Iso-4	Iso-5
ΔG	-1364.751674	-1364.748888	-1364.746115	-1364.747458	-1364.748522

Table S3 The isomers, energy differences (ΔG in hartree) for Ca^{2+}+α-D-Fructofuranose at the B3LYP/ BSI level.

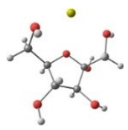
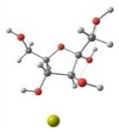
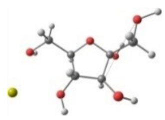
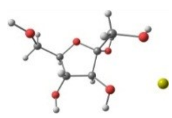
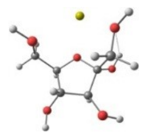
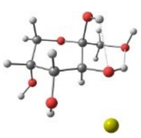
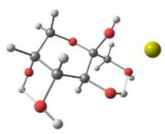
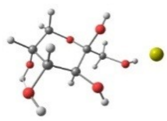
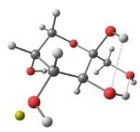
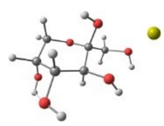
					
Ca^{2+}+α-D-Fructofuranose	Iso-1	Iso-2	Iso-3	Iso-4	Iso-5
ΔG	-1364.748074	-1364.744576	-1364.745985	-1364.744735	-1364.747669

Table S4 The isomers, energy differences (ΔG in hartree) for Ca^{2+}+β-D-Fructopyranose at the B3LYP/BSI level.

					
Ca^{2+}+β-D-Fructopyranose	Iso-1	Iso-2	Iso-3	Iso-4	Iso-5
ΔG	-1364.750756	-1364.750434	-1364.750433	-1364.749652	-1364.74802

$C_6H_{12}O_6 + CaCl_2 = C_6H_{12}O_6CaCl_2$

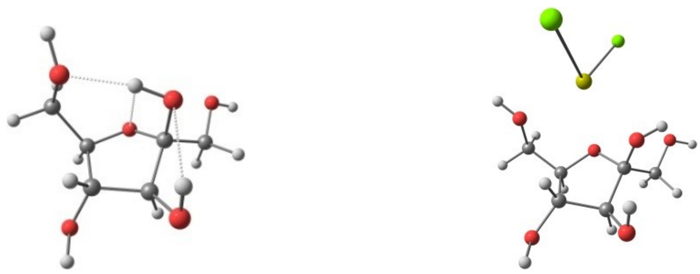


Table S5 Reaction formula and reaction energy(kcal/mol).

	$C_6H_{12}O_6 + CaCl_2$	$C_6H_{12}O_6CaCl_2$
ΔE	0	-12.0
ΔH	0	-12.0
ΔG	0	-0.3

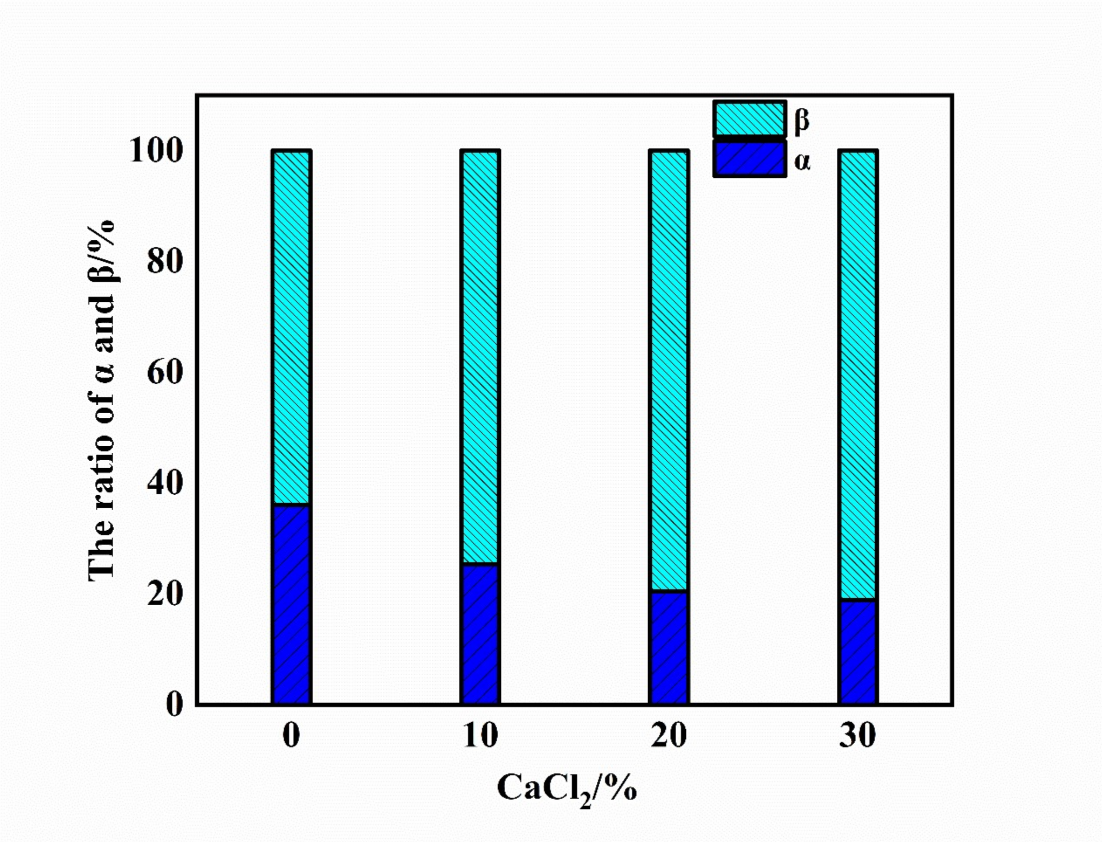


Figure S6 The ratio of α- and β-glucopyranose at 60°C for 5min in NaOH-$CaCl_2$ solution

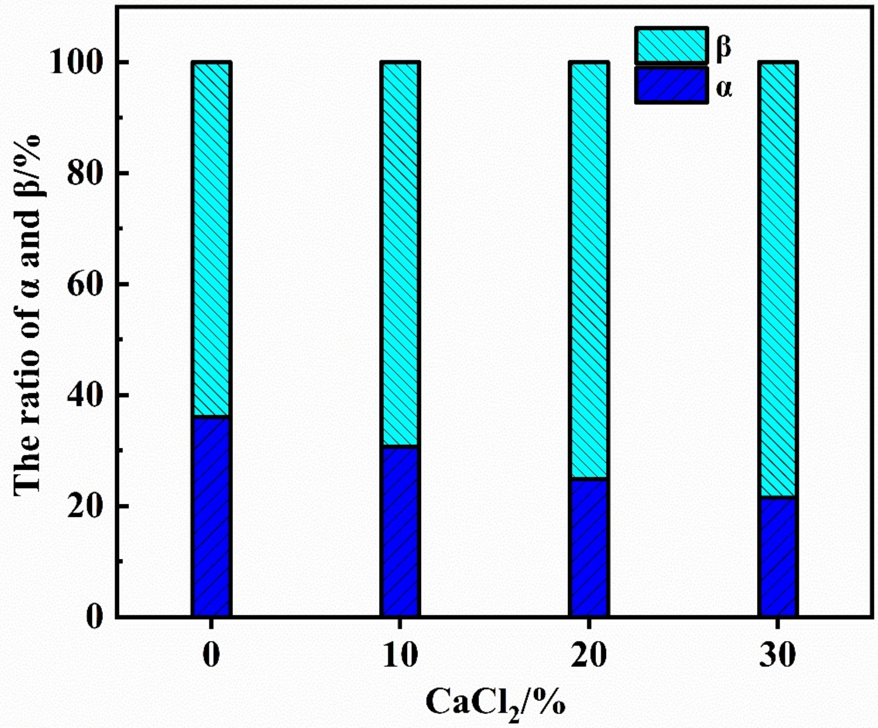


Figure S7 The ratio of α- and β-glucopyranose at 60°C for 5min in LiOH-$CaCl_2$ solution

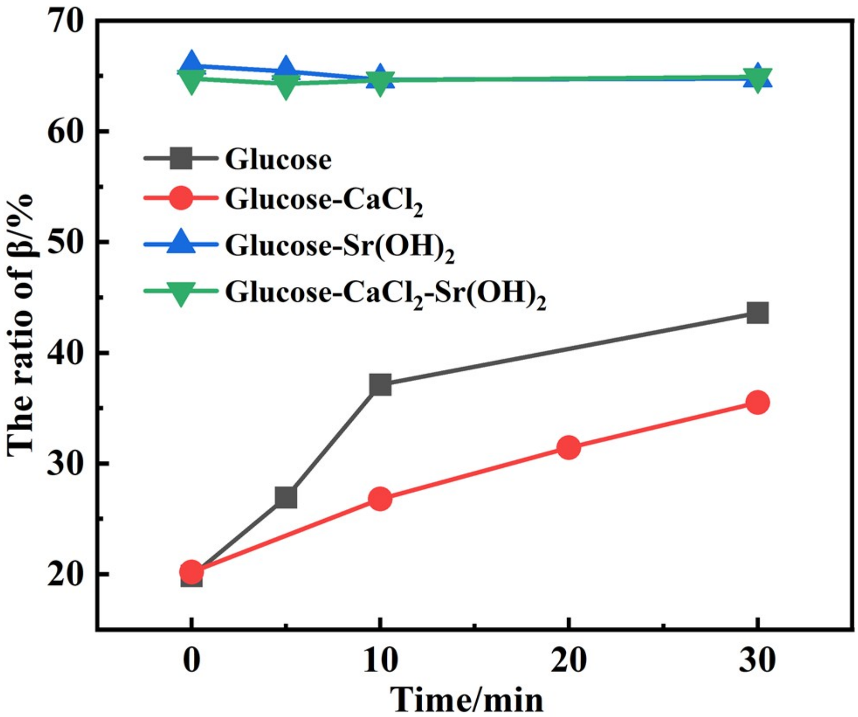


Figure S8 The ratio of β-glucopyranose at room temperature with the time

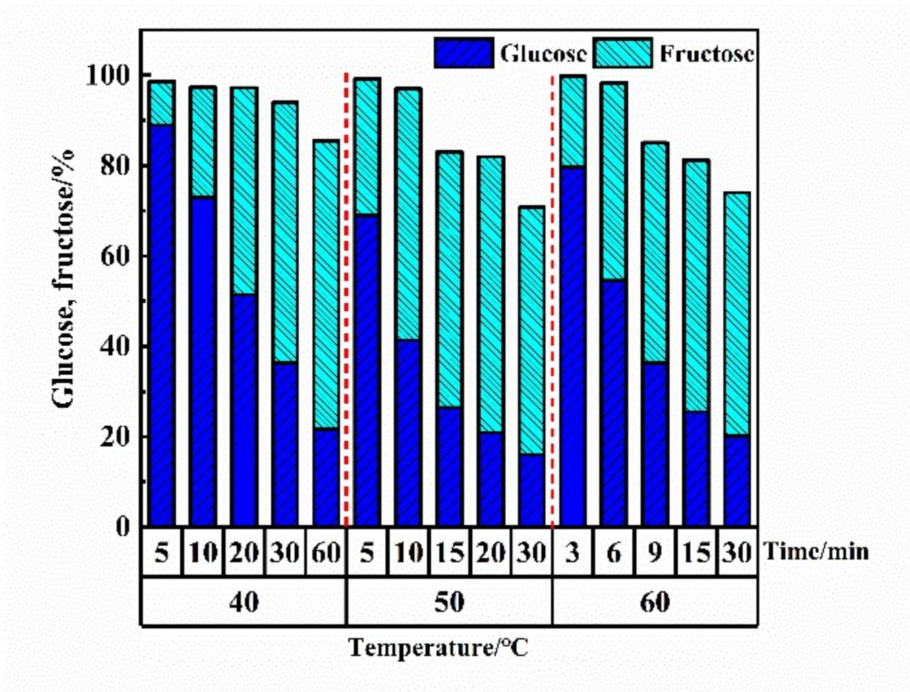


Figure S9 Effect of reaction temperature and reaction time on glucose isomerization in 0.5 g·mL^{-1}$CaCl_2$-0.008 g·mL^{-1} NaOH.

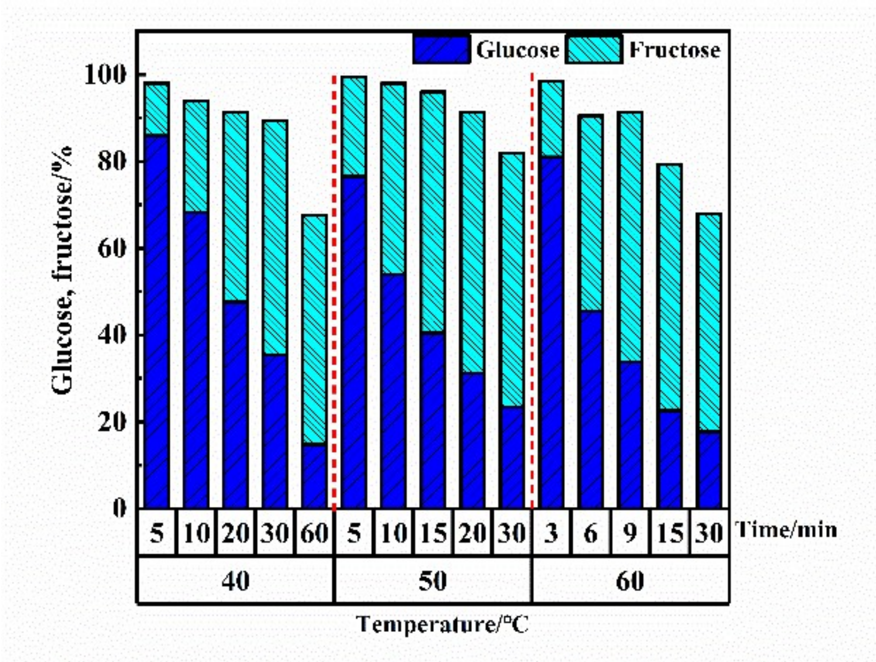


Figure S10 Effect of reaction temperature and reaction time on glucose isomerization in 0.5 g·mL^{-1}$CaCl_2$-0.0048 g·mL^{-1} LiOH.