Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Supporting Information

Revealing the contributions of homogeneous and heterogeneous catalysis for isomerization of D-glucose into D-fructose in the presence of low soluble basic salts

Valérie Toussaint[a,b], and Irina Delidovich[a,b]*

[a]Institute of Chemical, Environmental and Bioscience Engineering, TU Wien, Getreidemarkt 9, 1060 Vienna, Austria.

[b]Chair of Heterogeneous Catalysis and Chemical Technology, Institute for Technical and Macromolecular Chemistry, RWTH Aachen University, Worringerweg 2, 52074 Aachen, Germany.

**E-mail: Irina.delidovich@tuwien.ac.at*

Table of content

1. XRD, Nitrogen Physisorption ……2

2. pH values generated in the presence of the catalysts in 10 wt.% Glc aqueous solution and water 5

3. Kinetic data, pH, and selectivity-conversion curves....6

4. Filtration and contact tests....15

5. Recycling tests 16

6. References 20

1. XRD, Nitrogen Physisorption

XRD

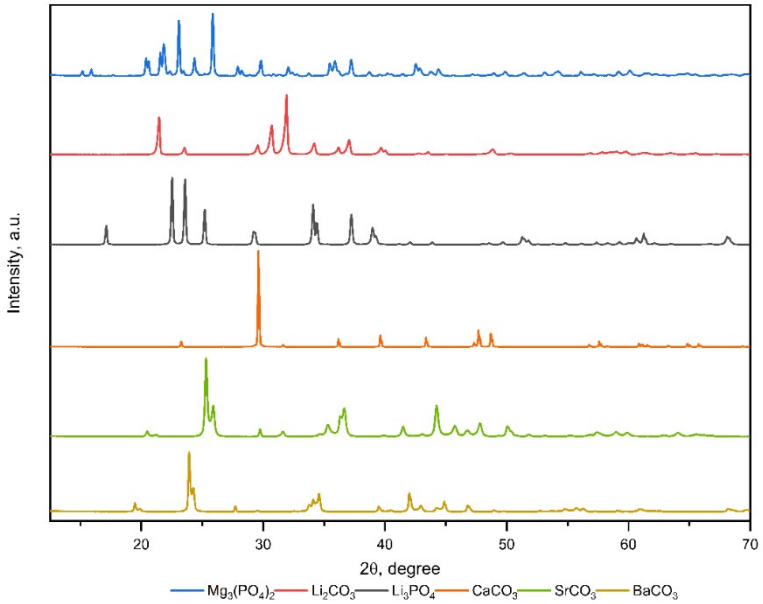


Figure 1S. XRD patterns of $Mg_3(PO_4)_2$ (00-033-0876), Li_2CO_3 (04-008-5839), Li_3PO_4 (00-025-1030), $CaCO_3$ (04-002-9082), $SrCO_3$ (01-074-1491), $BaCO_3$ (00-005-0378). ICDD (International Centre for Diffraction Data) codes are given in parentheses.

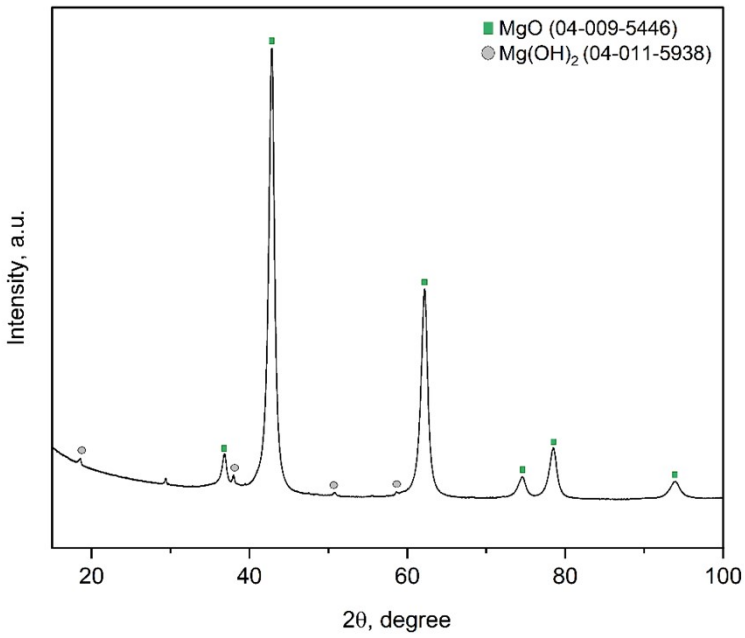


Figure S2. XRD pattern of MgO before catalytic test. ICDD (International Centre for Diffraction Data) codes are given in parentheses.

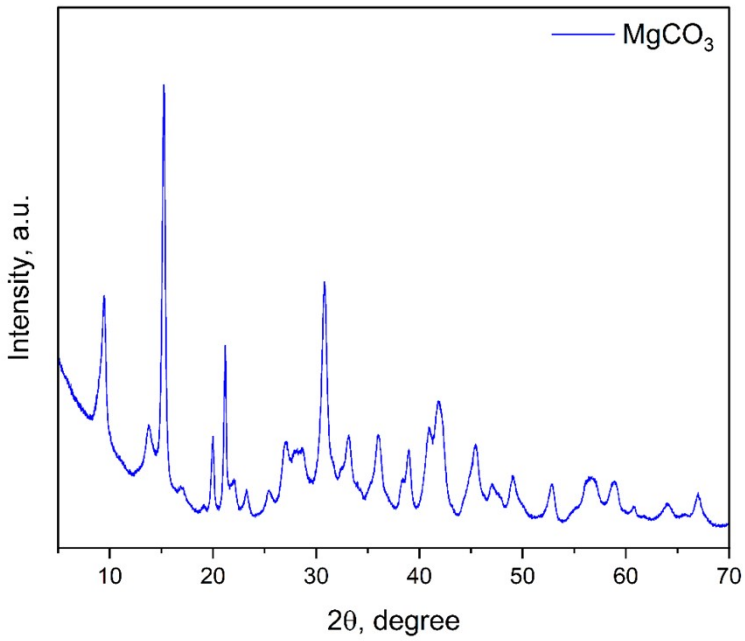


Figure S3. XRD pattern of fresh $MgCO_3$ (04-013-7631). ICDD code is given in parentheses.

N_2 Physisorption

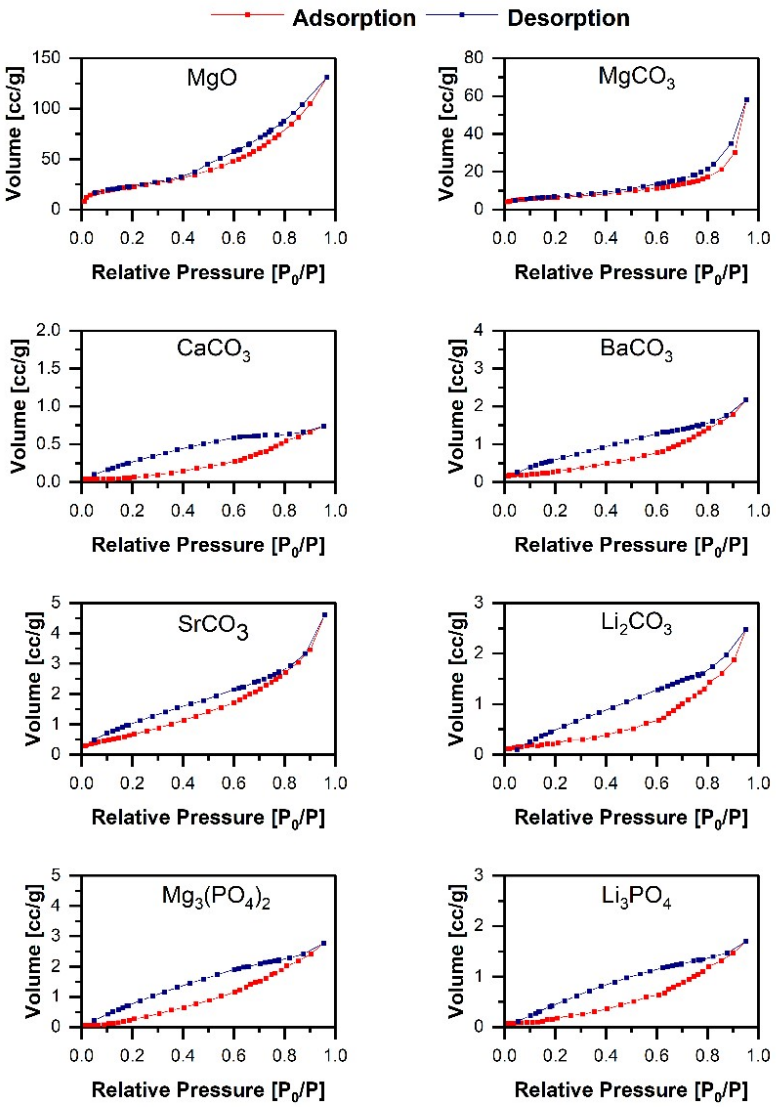


Figure 4S. N_2 physisorption isotherms of the catalysts.

Table 1S. Specific surface areas S_{BET} and total pore volumes of the catalysts determined by N_2 physisorption.

Entry	Catalyst	S_{BET} [m^2/g]	Total Pore Volume [cc/g]
1	MgO	82	$2.03 \cdot 10^{-1}$
2	$SrCO_3$	3	$7.13 \cdot 10^{-3}$
3	$BaCO_3$	1	$3.35 \cdot 10^{-3}$
4	$CaCO_3$	0.2	$1.14 \cdot 10^{-3}$
5	$MgCO_3$	23	$9.00 \cdot 10^{-2}$
6	Li_2CO_3	0.8	$3.84 \cdot 10^{-3}$
7	Li_3PO_4	0.8	$2.63 \cdot 10^{-3}$
8	$Mg_3(PO_4)_2$	5	$4.28 \cdot 10^{-3}$

2. pH values generated in the presence of the catalysts in 10 wt.% Glc aqueous solution and water

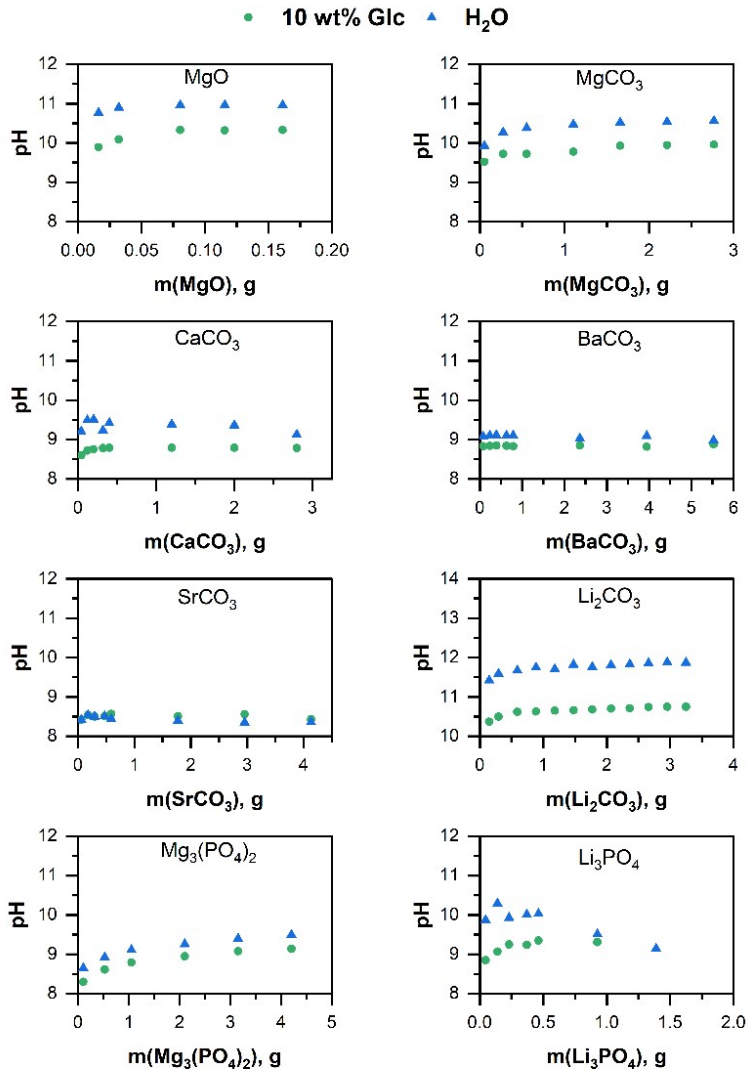


Figure 5S. pH of 10 wt.% aqueous Glc solution (green circles) and water (blue triangles) upon variation of solid-to-liquid ratio. Reaction conditions: 500 rpm, 40 mL of water or Glc solution, room temperature.

Table 2S. A list of conducted experiments including catalysts, their solubility product constants [1], catalyst loadings, and temperatures. 40 mL 10 wt.% Glc solution, 500 rpm, pH_0 was measured directly prior to the reaction.

Entry	Catalyst	T, °C	pH_0	Loading, $g \cdot mL^{-1}$	Solubility product constant (K_{sp})
1	Li_2CO_3	60	10.6	0.022	$8.15 \cdot 10^{-4}$
2	Li_2CO_3	80	10.5	0.022	
3	MgO	40	10.2	0.054	
4	MgO	60	10.2	0.004	$5.61 \cdot 10^{-12}$
5	MgO	80	10.2	0.004	
6	$MgCO_3$	60	9.7	0.042	/
7	$MgCO_3$	80	9.8	0.042	
8	Li_3PO_4	60	9.7	0.0116	$2.37 \cdot 10^{-11}$
9	Li_3PO_4	80	9.7	0.0116	
10	$SrCO_3$	80	8.1	0.007	$5.60 \cdot 10^{-9}$
11	$BaCO_3$	80	8.1	0.010	$2.58 \cdot 10^{-9}$
12	$Mg_3(PO_4)_2$	80	7.9	0.053	$1.04 \cdot 10^{-24}$
13	$CaCO_3$	80	7.8	0.010	$3.36 \cdot 10^{-9}$

3. Kinetic data, pH, and selectivity-conversion curves

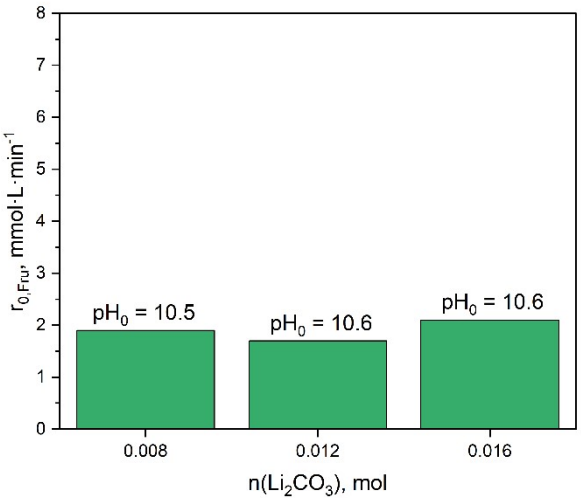


Figure 6S. Initial reaction rates r_0 in the presence of Li_2CO_3 for various catalyst loadings. Reaction conditions: 40 mL, 10 wt.% Glc aqueous solution, 500 rpm, 60°C.

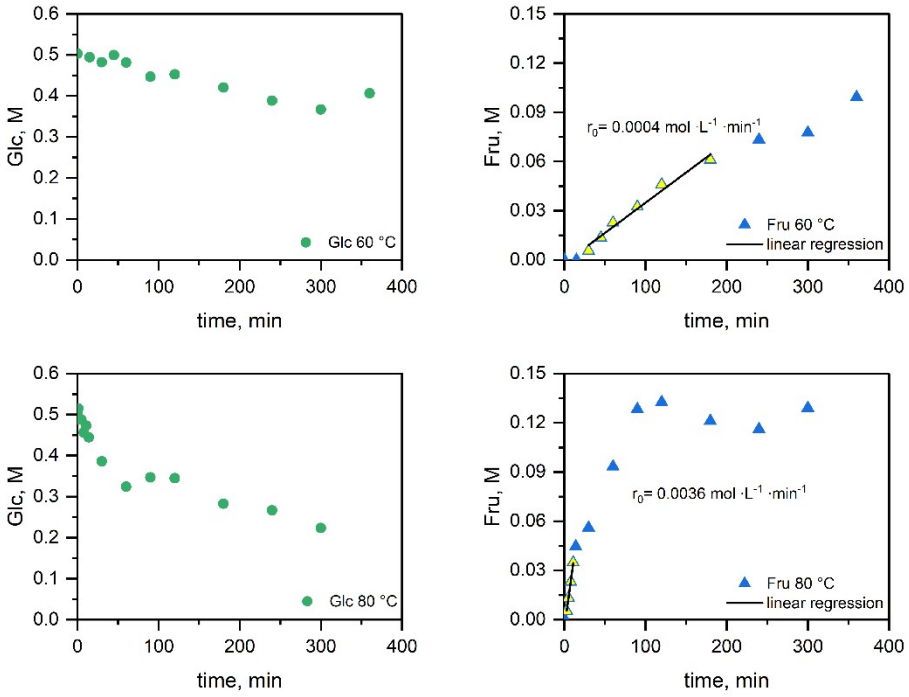


Figure 7S. Concentrations of Glc (green circles) and Fru (blue triangles) during the conversion of D-glucose in the presence of MgO at 60 and 80 °C. Reaction conditions: 40 mL 10 wt.% Glc aqueous solution, 4 mmol MgO, 500 rpm, 60 and 80°C.

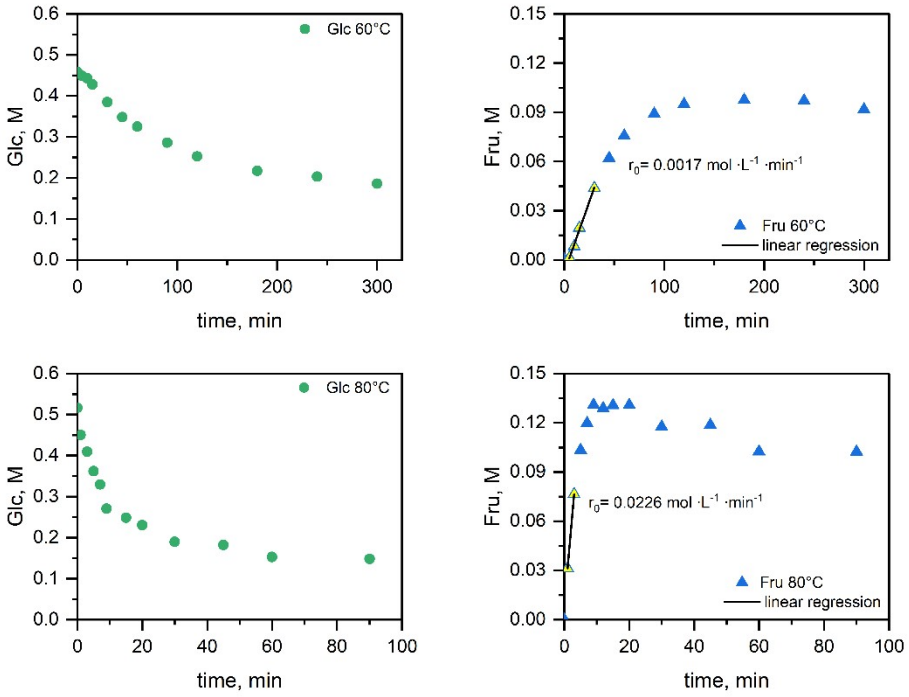


Figure 8S. Concentrations of Glc (green circles) and Fru (blue triangles) during the conversion of D-glucose in the presence of Li_2CO_3 at 60 and 80°C. Reaction conditions: 40 mL 10 wt.% Glc aqueous solution, 12 mmol Li_2CO_3, 500 rpm, 60 and 80°C.

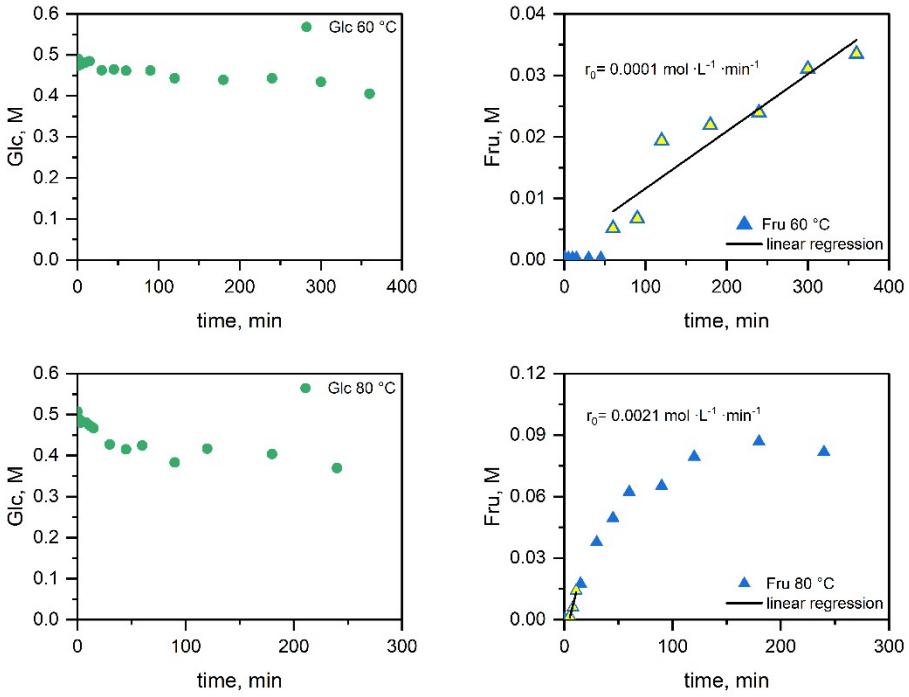


Figure 9S. Concentrations of Glc (green circles) and Fru (blue triangles) during the conversion of D-glucose in the presence of Li_3PO_4 at 60 and 80 °C. Reaction conditions: 40 mL 10 wt.% Glc aqueous solution, 4 mmol Li_3PO_4, 500 rpm, 60 and 80°C.

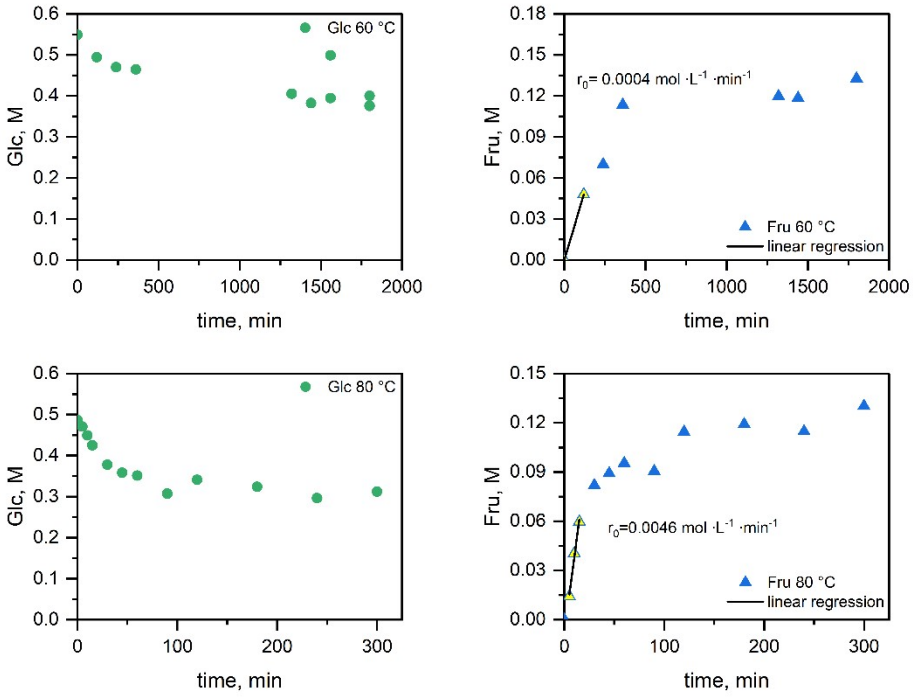


Figure 10S. Concentrations of Glc (green circles) and Fru (blue triangles) during the conversion of D-glucose in the presence of $MgCO_3$ at 60 and 80 °C. Reaction conditions: 40 mL 10 wt.% Glc aqueous solution, 4 mmol $MgCO_3$, 500 rpm, 60 and 80°C.

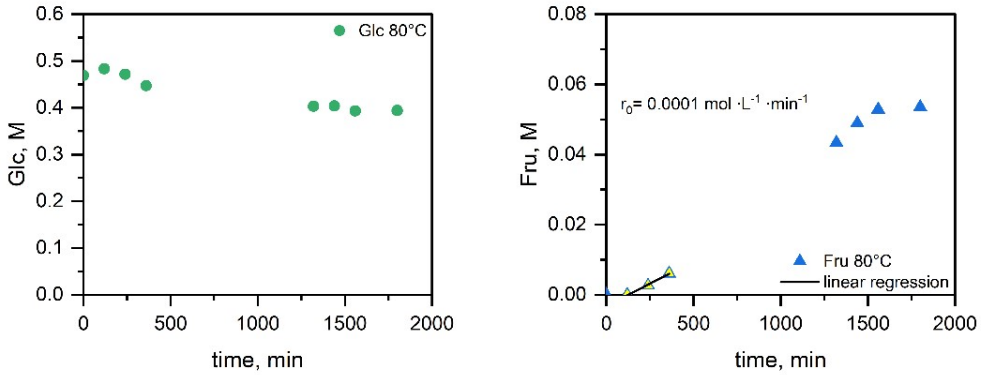


Figure 11S. Concentrations of Glc (green circles) and Fru (blue triangles) during the conversion of D-glucose in the presence of $CaCO_3$ at 80 °C. Reaction conditions: 40 mL 10 wt.% Glc aqueous solution, 4 mmol $CaCO_3$, 500 rpm, 80°C.

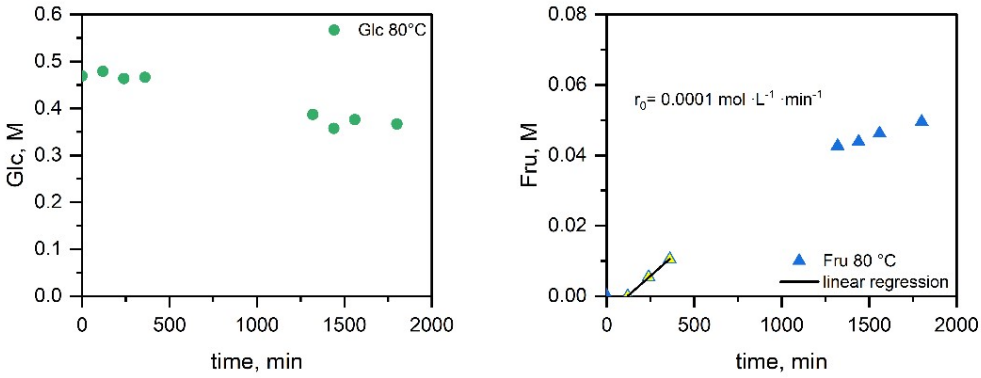


Figure 12S. Concentrations of Glc (green circles) and Fru (blue triangles) during the conversion of D-glucose in the presence of $SrCO_3$ at 80 °C. Reaction conditions: 40 mL 10 wt.% Glc aqueous solution, 4 mmol $SrCO_3$, 500 rpm, 80°C.

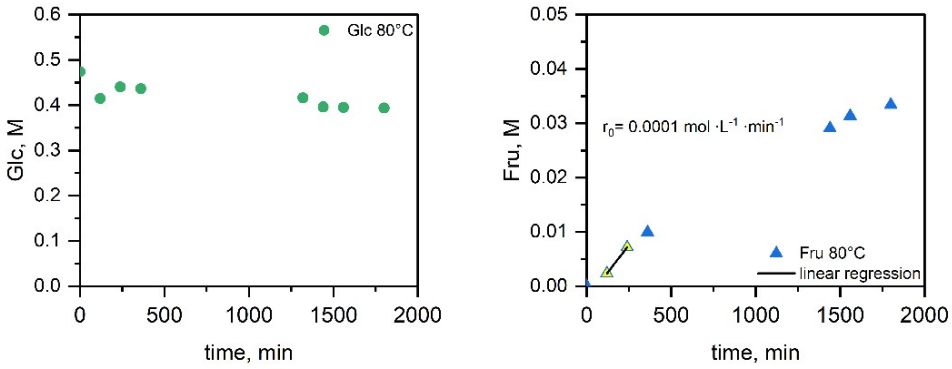


Figure 13S. Concentrations of Glc (green circles) and Fru (blue triangles) during the conversion of D-glucose in the presence of $BaCO_3$ at 80°C. Reaction conditions: 40 mL 10 wt.% Glc aqueous solution, 4 mmol $BaCO_3$, 500 rpm, 80°C.

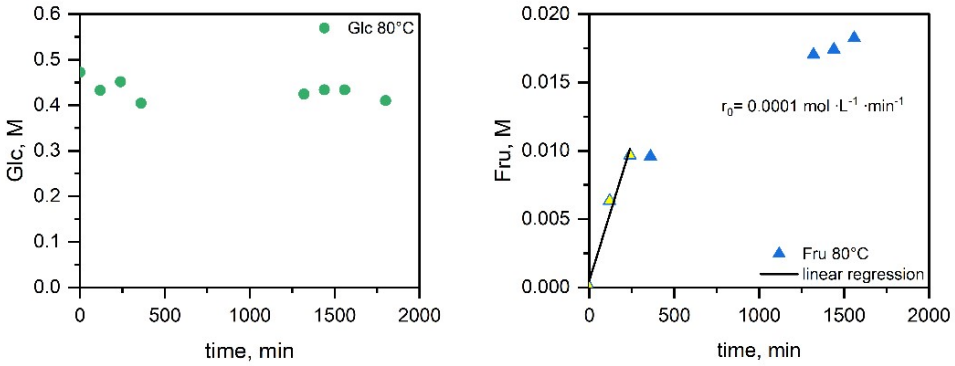


Figure 14S. Concentrations of Glc (green circles) and Fru (blue triangles) during the conversion of D-glucose in the presence of $Mg_3(PO_4)_2$ at 80 °C. Reaction conditions: 40 mL 10 wt.% Glc aqueous solution, 4 mmol $Mg_3(PO_4)_2$, 500 rpm, 80°C.

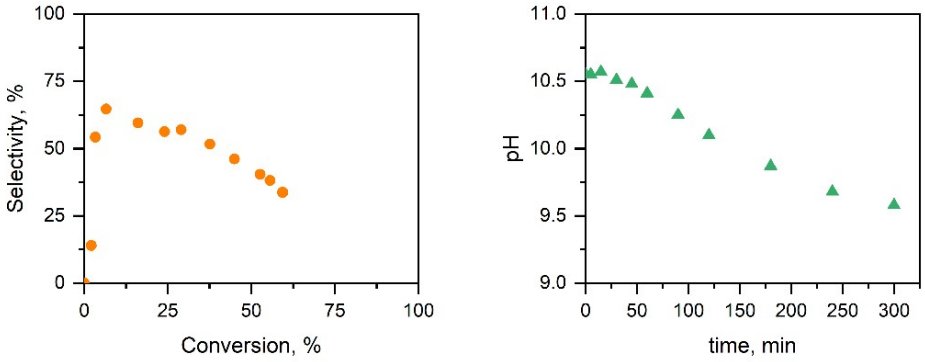


Figure 15S. Selectivity-conversion curve (orange circles) and pH of the solution (green triangles) as a function of time during the isomerization reaction in the presence of Li_2CO_3 at 60°C. Reaction conditions: 40 mL 10 wt.% Glc aqueous solution, 12 mmol Li_2CO_3, 500 rpm, 60°C.

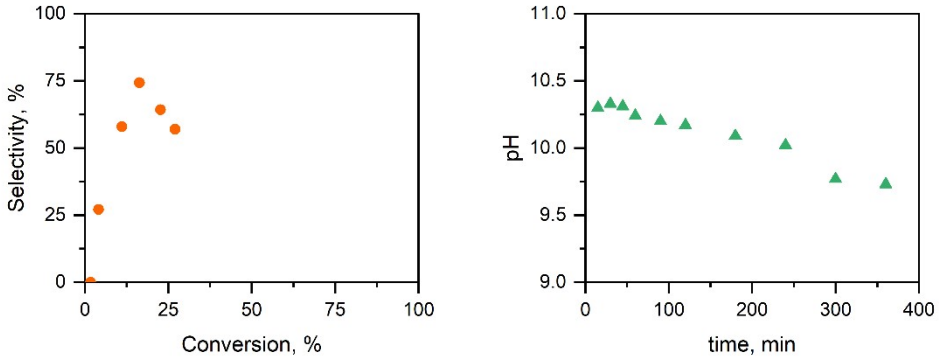


Figure 16S. Selectivity-conversion curve (orange circles) and pH of the solution (green triangles) during the isomerization reaction in the presence of MgO at 60°C. Reaction conditions: 40 ml 10 wt.% Glc aqueous solution, 4 mmol MgO, 500 rpm, 60°C.

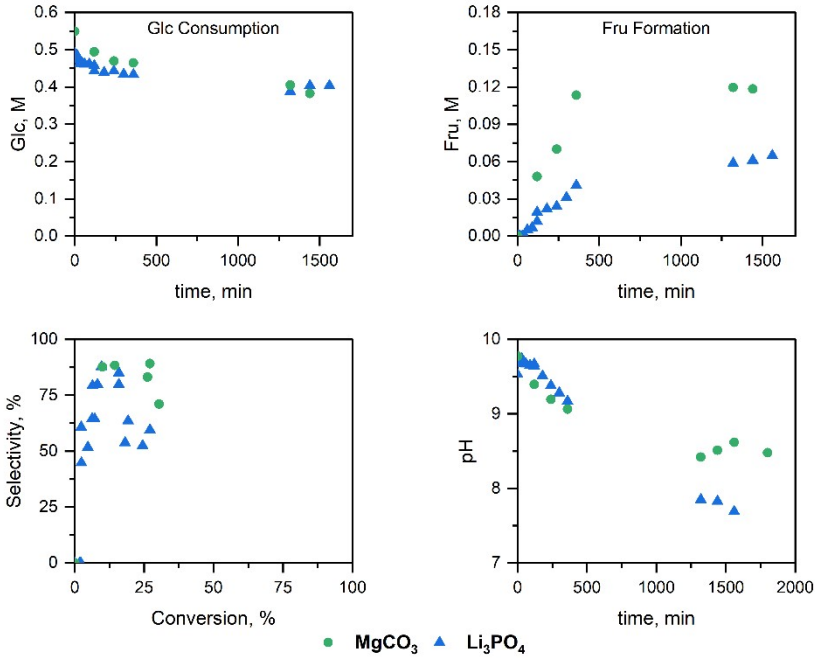


Figure S17. Selectivity-conversion curves and pH values during the conversion of D-glucose in the presence of $MgCO_3$ (green circles) and Li_3PO_4 (blue triangles) at 60°C. Reaction conditions: 40 mL 10wt.% Glc aqueous solution, 4 mmol $MgCO_3$, 4 mmol Li_3PO_4, 500 rpm, 60°C.

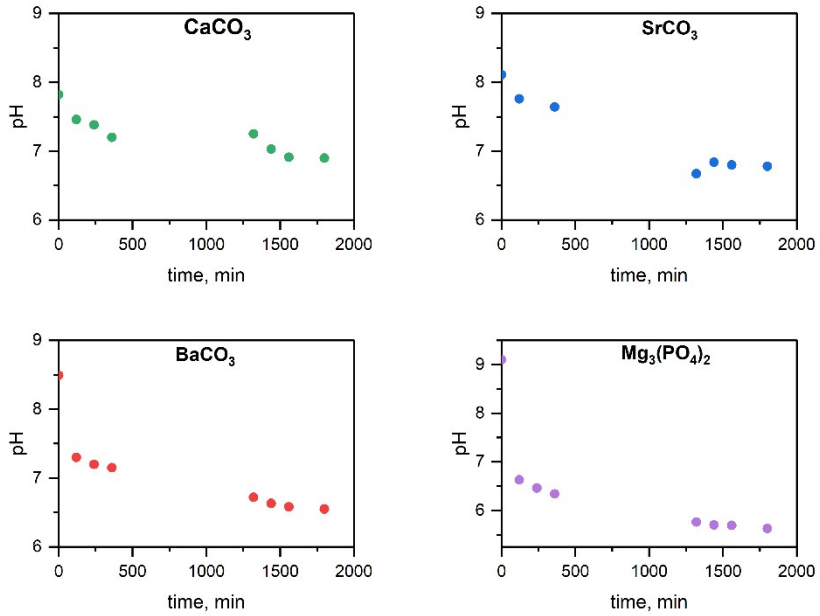


Figure 18S. pH of the solution as a function of time during the isomerization reaction in the presence of $CaCO_3$ (green), $SrCO_3$ (blue), $BaCO_3$ (red), and $Mg_3(PO_4)_2$ (violet) at 80°C. Reaction conditions: 40 mL 10 wt.% Glc aqueous solution, 4 mmol $CaCO_3$, 4 mmol $SrCO_3$, 4 mmol $BaCO_3$, and 8 mmol $Mg_3(PO_4)_2$,500 rpm, 80°C.

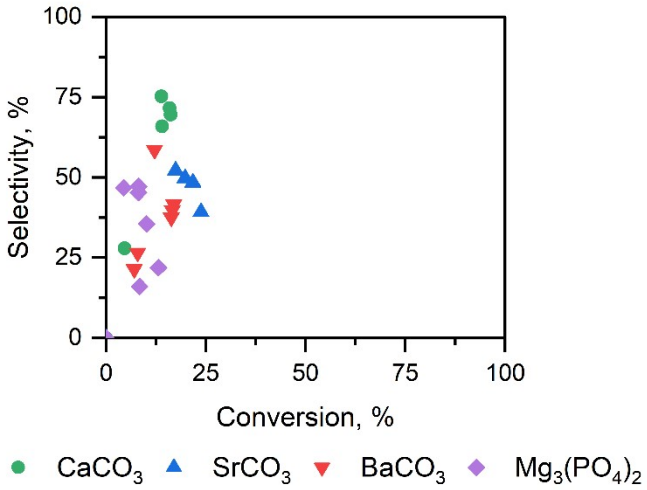


Figure 19S. Selectivity-conversion curves of the isomerization reaction in presence of $CaCO_3$, $SrCO_3$, $BaCO_3$, and $Mg_3(PO_4)_2$ at 80°C. Reaction conditions: 40 mL 10 wt.% Glc aqueous solution, 4 mmol $CaCO_3$, 4 mmol $SrCO_3$, 4 mmol $BaCO_3$, or 8 mmol $Mg_3(PO_4)_2$, 500 rpm, 80°C.

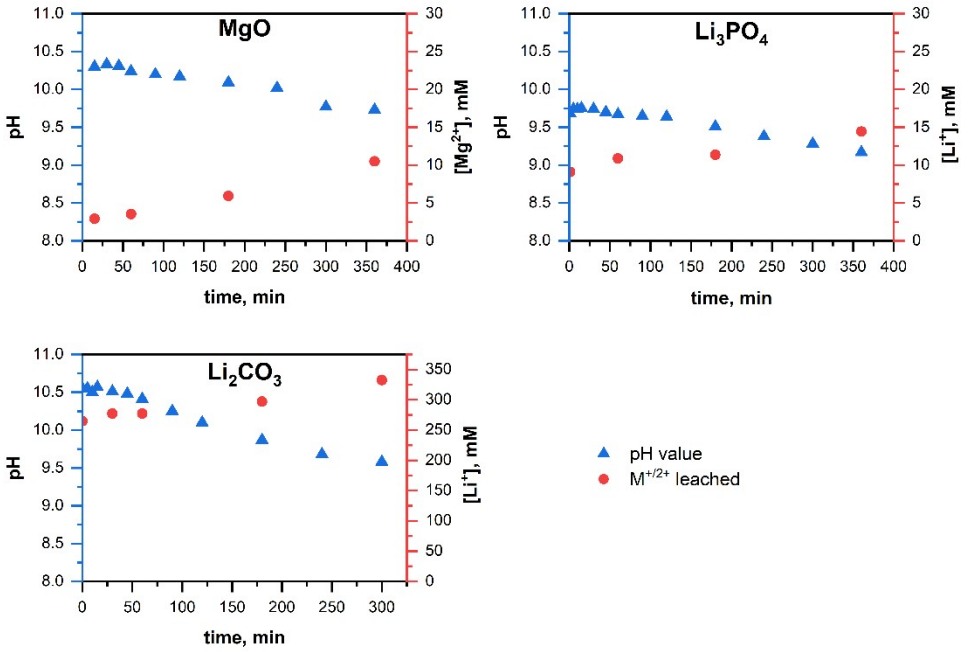


Figure 20S. pH values (blue triangles) and concentrations of leached metals over the course of the isomerization (red circles). Reaction conditions: 40 mL 10 wt.% Glc aqueous solution, 4 mmol MgO, 4 mmol Li_3PO_4, 12 mmol Li_2CO_3, 500 rpm, 60°C.

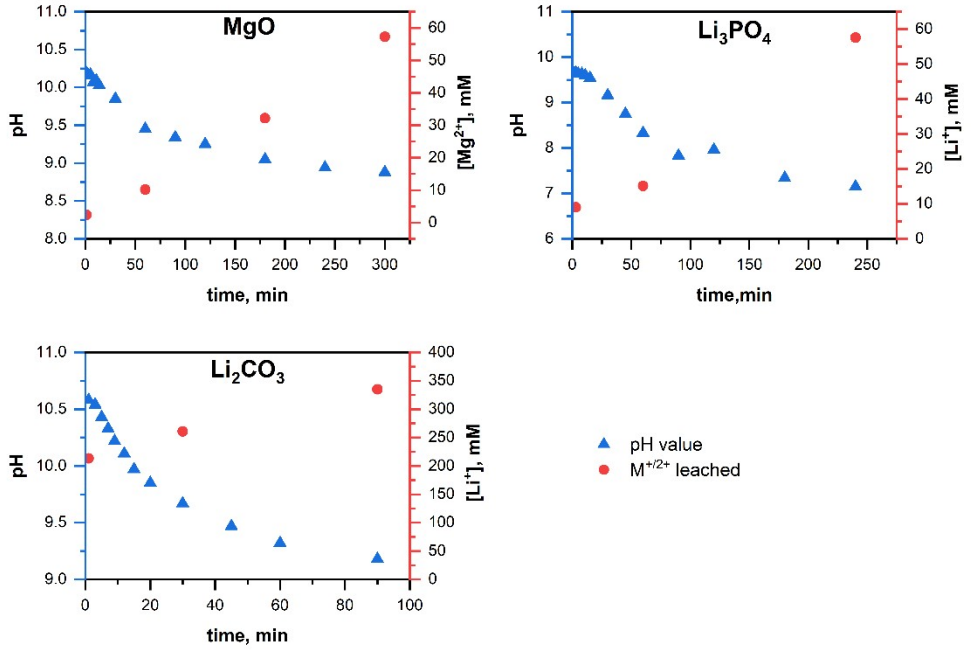


Figure 21S. pH values (blue triangles) and concentrations (red circles) of leached metals over the course of the isomerization. Reaction conditions: 40 mL 10 wt.% Glc aqueous solution, 4 mmol MgO, 4 mmol, Li_3PO_4, or 12 mmol Li_2CO_3, 500 rpm, 80°C.

4. Filtration and contact tests

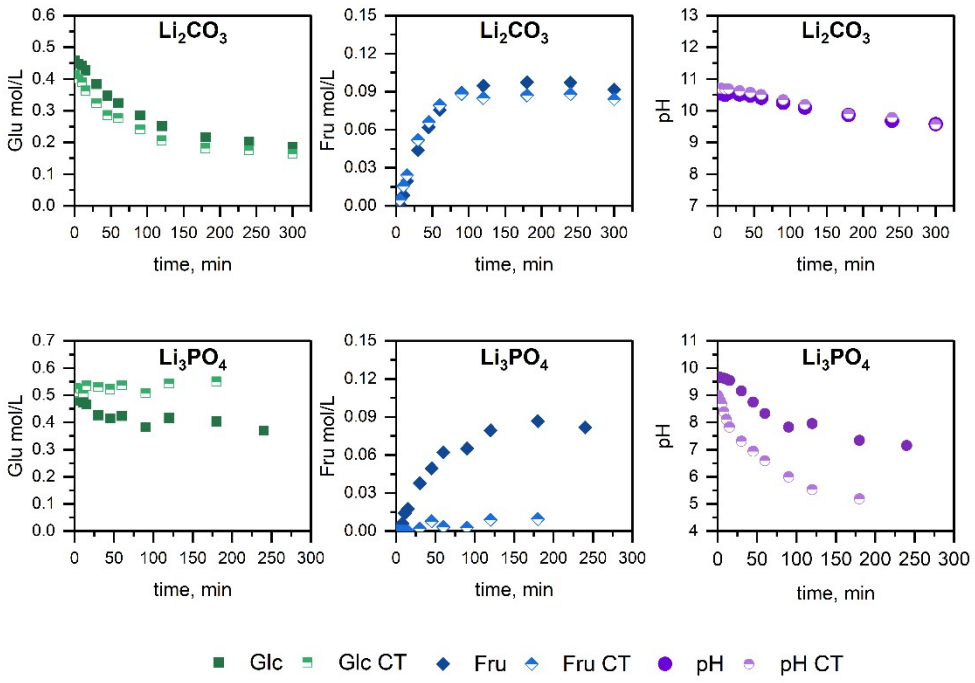


Figure 22S. Resutst of the contact tests in the presence of Li_3PO_4 and Li_2CO_3. Reaction conditions: 40 mL 10 wt.% Glc solution, 4 mmol Li_3PO_4 (80°C), 12 mmol Li_2CO_3 (60°C), 500 rpm.

5. Recycling tests

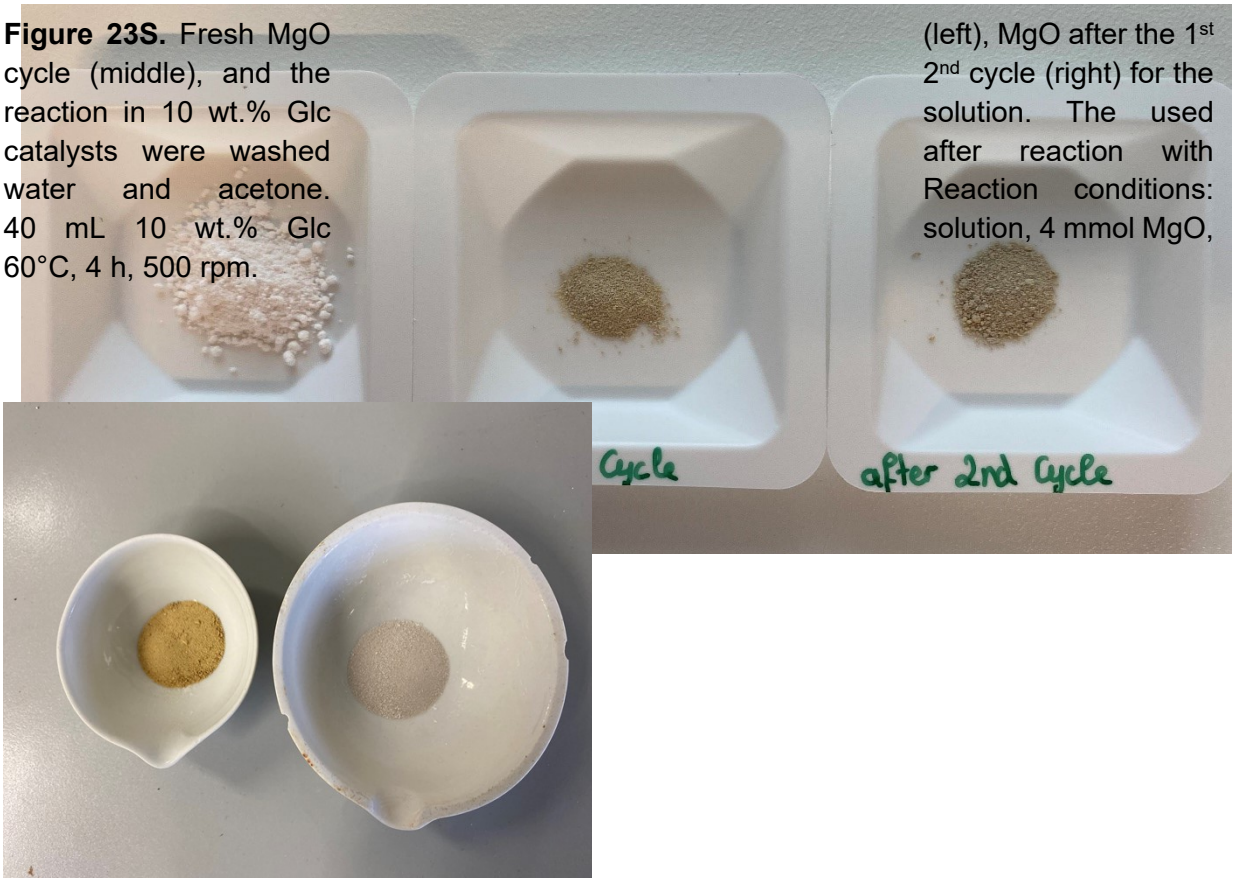
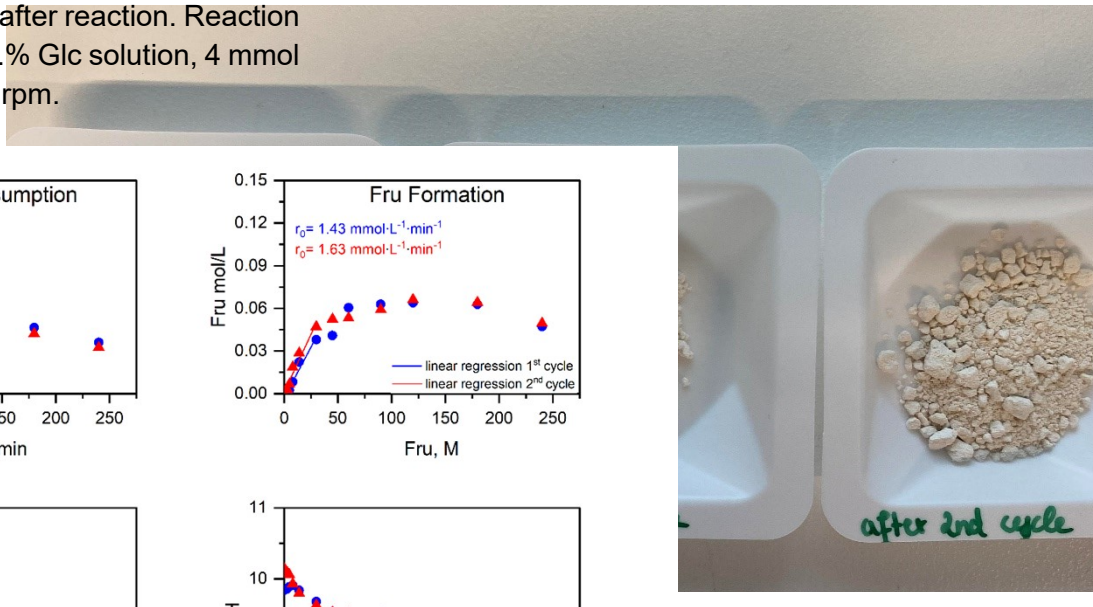


Figure 23S. Fresh MgO (left), MgO after the 1st cycle (middle), and the 2nd cycle (right) for the reaction in 10 wt.% Glc solution. The used catalysts were washed after reaction with water and acetone. Reaction conditions: 40 mL 10 wt.% Glc solution, 4 mmol MgO, 60°C, 4 h, 500 rpm.

Figure 24S. MgO after the 1st cycle washed with water and acetone (left) after calcination (right) Reaction conditions: 40 mL 10 wt.% Glc solution, 25 mmol MgO, 80°C, 4 h, 500 rpm.

Figure 25S. Fresh $MgCO_3$ (left), $MgCO_3$ after the 1st cycle (middle), and the 2nd cycle (right) for the reaction in 10 wt.% Glc solution washed with water and acetone after reaction. Reaction conditions: 40 mL 10 wt.% Glc solution, 4 mmol $MgCO_3$, 80°C, 4 h, 500 rpm.



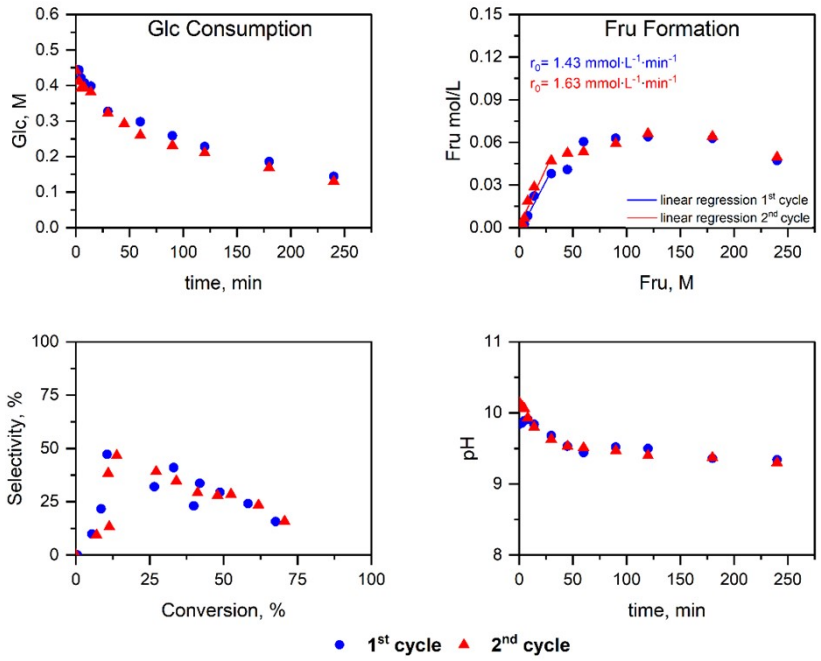


Figure 26S. Concentration-time curves, selectivity-conversion curves and pH values during the isomerization in the presence of MgO. Reaction condition: 40 mL 10 wt.% Glc solution, 25 mmol MgO, 4 h, 500 rpm, 80°C, calcination after 1st cycle for 3 h at 500°C (5 K·min^{-1}).

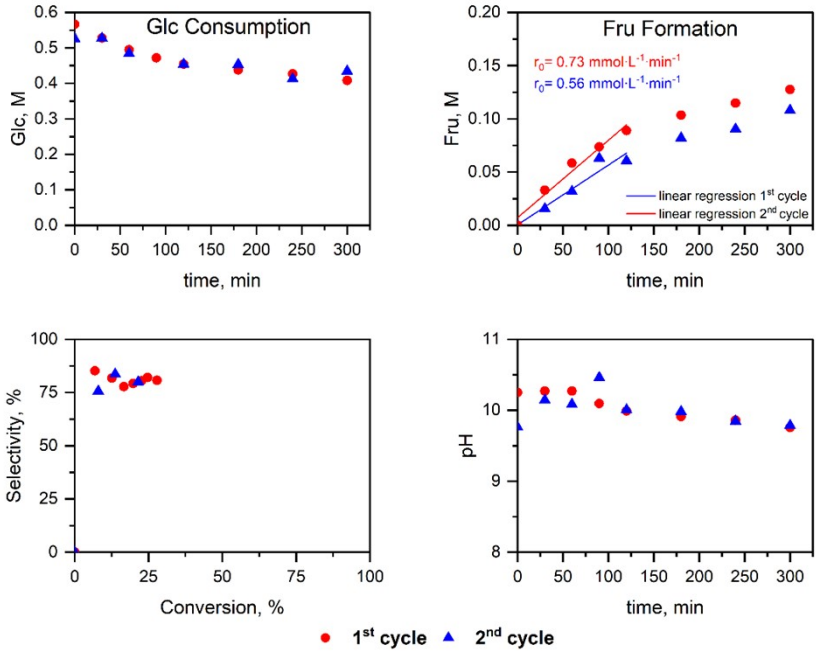


Figure 27S. Concentration-time curves, selectivity-conversion curves, and pH values of the isomerization in the presence of MgO. Reaction condition: 40 mL 10 wt.% Glc solution, 4 mmol MgO, 5 h, 500 rpm, 60°C, washed with water and acetone after the 1st cycle.

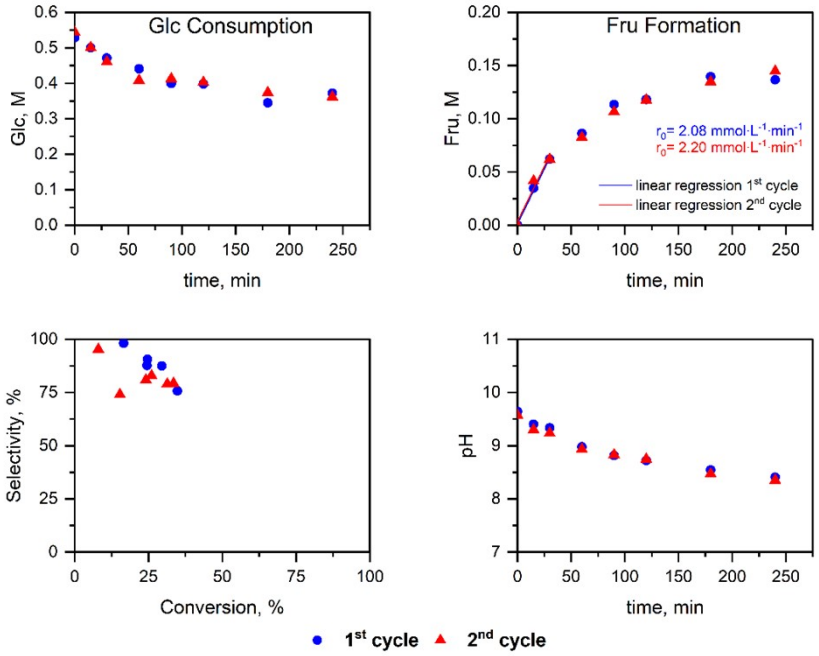


Figure 28S. Concentration-time curves, selectivity-conversion curves and pH values of the isomerization in the presence $MgCO_3$. Reaction condition: 40 mL 10 wt.% Glc solution, 4 mmol $MgCO_3$, 4 h, 500 rpm, 80°C.

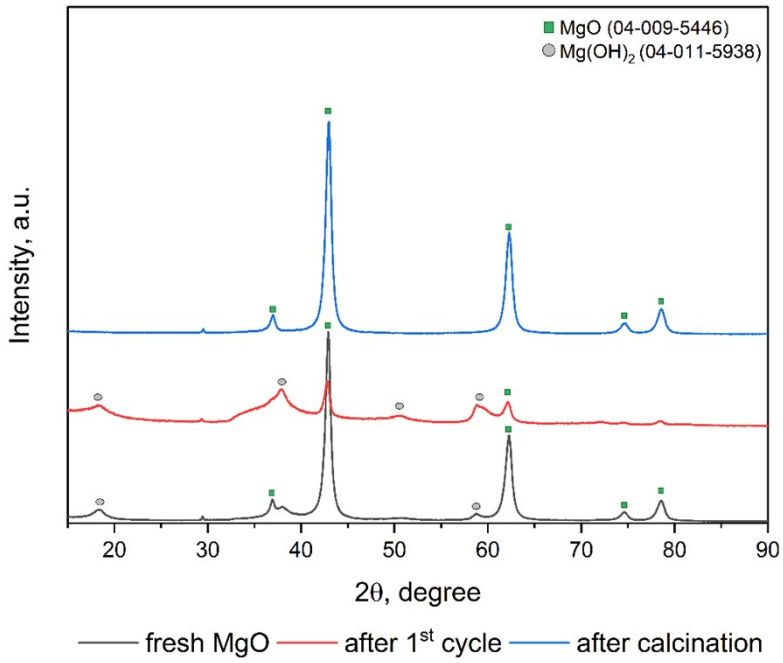


Figure S29. XRD patterns of fresh MgO (black), after the 1st cycle (red) and after calcination (blue). Reaction conditions: 40 mL 10 wt.% Glc solution, 4 mmol MgO, 4 h, 500 rpm, 60°C, after reaction washing with water and acetone + calcination for 3 h at 500°C (5 K·min^{-1}). ICDD (International Centre for Diffraction Data) codes are given in parentheses.

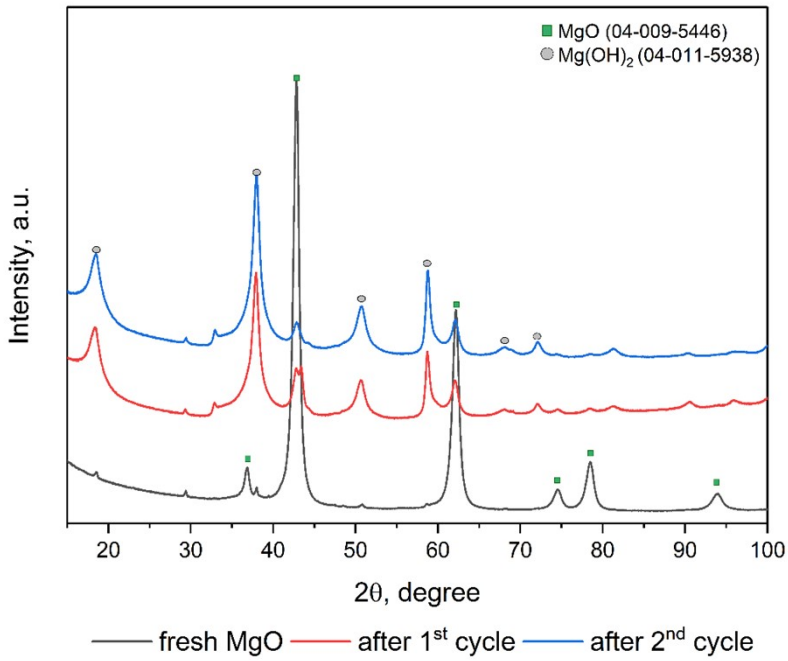


Figure S30. XRD patterns of MgO before catalysis (fresh, black), after the 1st cycle (red) and after the 2nd cycle (blue). Reaction conditions: 40 mL 10 wt.% Glc solution, 4 mmol MgO, 4 h, 500 rpm, 60°C. The catalyst was washed after reaction with water and acetone. ICDD (International Centre for Diffraction Data) codes are given in parentheses.

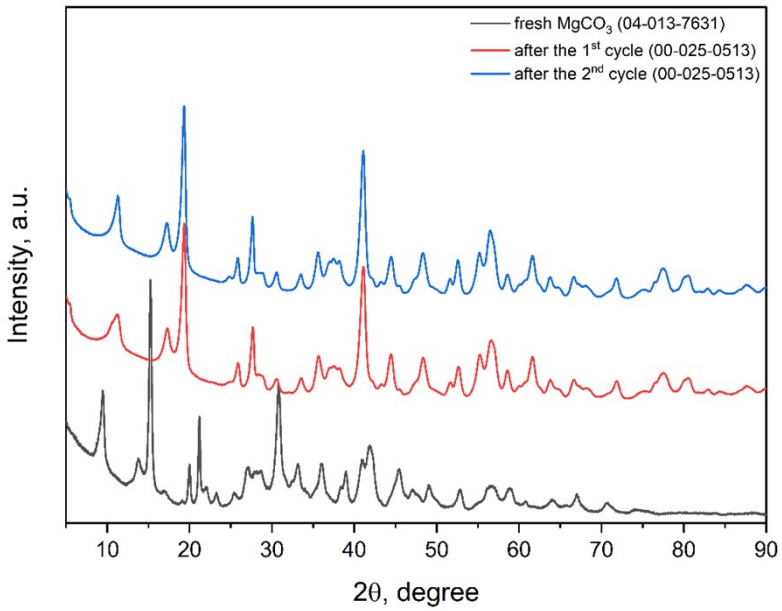


Figure S31. XRD patterns of $MgCO_3$ before catalysis (fresh, black), after the 1st cycle (red) and after the 2nd cycle (blue). Reaction conditions: 40 mL 10 wt.% Glc solution, 4 mmol $MgCO_3$, 4 h, 500 rpm, 60°C. The catalyst was washed after reaction with water and acetone. ICDD (International Centre for Diffraction Data) codes are given in parentheses.

6. References

[1] S. Yalkowsky, Y. He, J. Parijat, Handbook of Aqueous Solubility Data, CRC Press, Taylor & Francis, London, UK., 2016.