Electronic Supplementary Material (ESI) for Nanoscale Advances.

Supporting Information

Tuning of MgO's base characteristics by blending with amphoteric ZnO facilitates the selective glucose isomerization to fructose for bioenergy development

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Mathematical expressions

$$Sugar\ conversion\ (wt.\%) = \frac{(Intial\ wt.\ of\ sugar\ \text{-}\ Remaining\ wt.\ of\ sugar\ after\ completion\ of\ reaction)}{Intial\ wt.\ of\ Sugar} \times 100$$

-------------- (S1)

$$Product\ yield\ (wt.\%) = \frac{Wt.\ of\ product\ formation}{Initial\ wt.\ of\ sugar\ (reactant)} \times 100$$

-------------- (S2)

$$Product\ selectivity\ (wt.\%) = \frac{Wt.\ of\ product\ formation}{Converted\ wt.\ of\ reactant} \times 100$$

-------------- (S3)

Crystal structure parameter calculations using the XRD data:

Lattice strain (ε) of the crystal plane:

$$\varepsilon = \frac{\beta}{4\tan(\theta)}$$

------------- (S4)

Where, β is the full width at half maximum height (FWHM) of the sharp peaks and θ is the measured angle. [1]

Lattice stress (σ) in the lattice plane:

$$\sigma = -4.5 \times 10^{11} \left(\frac{C - C_0}{C_0}\right) \text{N/m}^2$$

------------- (S5)

Where, C is the lattice parameter and C_0 is the bulk value (Å). [1]

Dislocation density (δ):

$$\delta = \frac{1}{D^2}$$

------------- (S6)

Where, D is the crystalline size.[1]

Reaction kinetics

$$Glucose \xrightarrow{rate\ constant,\ \ k} degradation\ products$$

------------- (S7)

Kinetic equation of the first-order reaction

$$ln\left\{\frac{[Glu]_t}{[Glu]_0}\right\} = -\ k_{obs} \times time\ (sec)$$

------------- (S8)

Where, $[Glu]_t$ and $[Glu]_0$ represent the final and initial glucose concentration at time *t*. k_{obs} is the observed rate constant of reaction (disappearance of glucose).

Table S1. XRD data of pristine ZnO and its composites of the (100) plane.

Parameters	ZnO	ZM21	ZM11	ZM12
2θ angle (100) (degree)	31.31	31.56	31.81	31.84
d-spacing	2.85	2.83	2.81	2.80
β-value	0.1743	0.1782	0.2775	0.2755
Crystalline size (nm)	49.44	48.39	31.09	30.86

Table S2. XRD data of pristine ZnO and its composites of the (002) plane.

Parameters	ZnO	ZM21	ZM11	ZM12
2θ angle (002) (degree)	33.97	34.23	34.50	34.57
d-spacing	2.63	2.61	2.59	2.59
β-value	0.1750	0.1887	0.2656	0.2606
Crystalline size (nm)	49.56	46.07	32.71	33.35

Table S3. XRD data of ZnO and its composites of the (101) plane.

Parameters	ZnO	ZM21	ZM11	ZM12
2θ angle (101) (degree)	35.80	36.05	36.32	36.34
d-spacing	2.50	2.48	2.47	2.46
β-value	0.1787	0.1882	0.2697	0.2607
Crystalline size (nm)	48.78	46.37	32.37	33.49

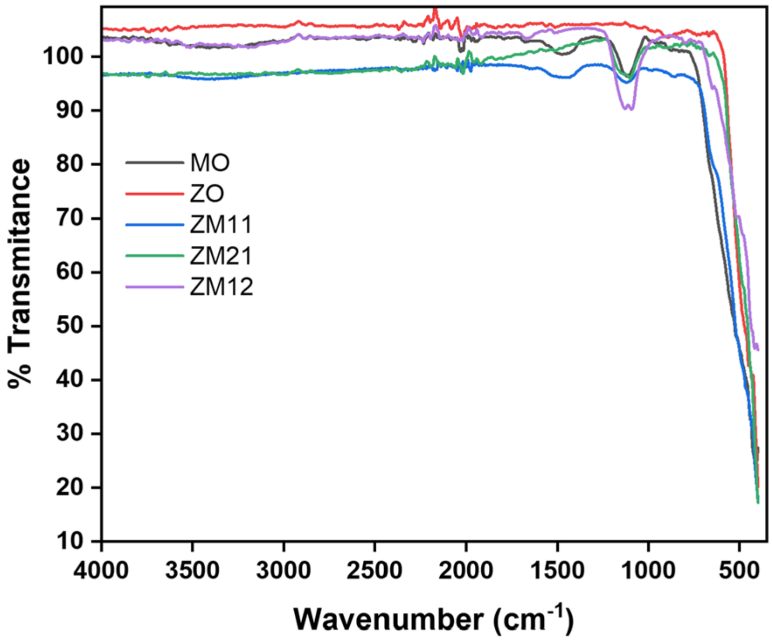


Figure S1. Comparative full-range FTIR spectra of as-synthesized catalysts.

Table S4. XPS analysis data (binding energy) of all synthesized catalysts.

Catalysts	Reference (C 1s)	Zinc (2p)		Magnesium (1s)	Oxygen (1s)
		$2p_{3/2}$	$2p_{1/2}$		
MgO	292.84	n.a	n.a	1312.51	539.08
ZnO	285.90	1022.28	1045.37	n.a	530.99 & 532.90
ZM21	284.51	1021.44	1044.55	1304.29	530.18
ZM11	285.08	1023.11	1045.97	1306.59	534.32
ZM21	284.61	1021.67	1044.79	1304.58	530.01

Note: Binding energy values are given in eV unit.

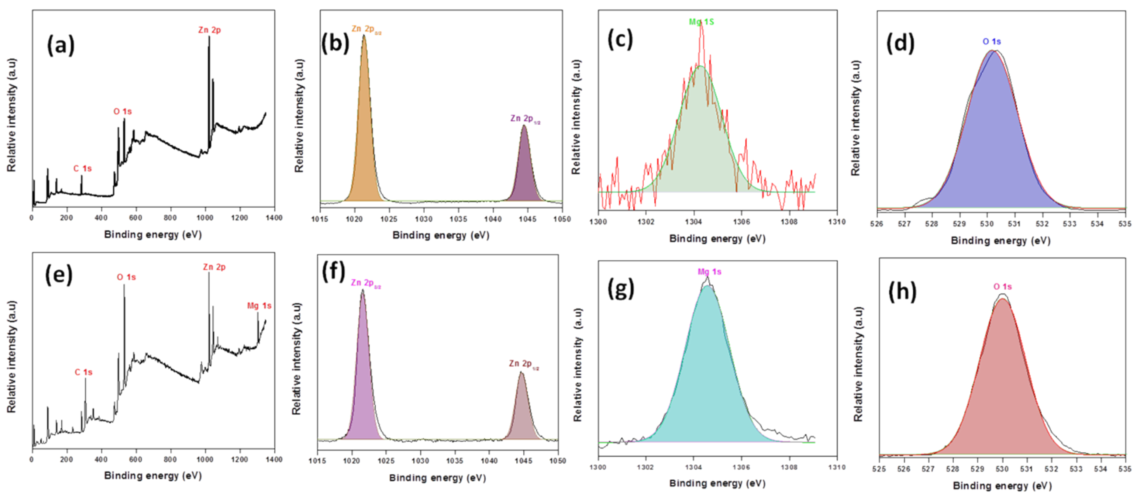
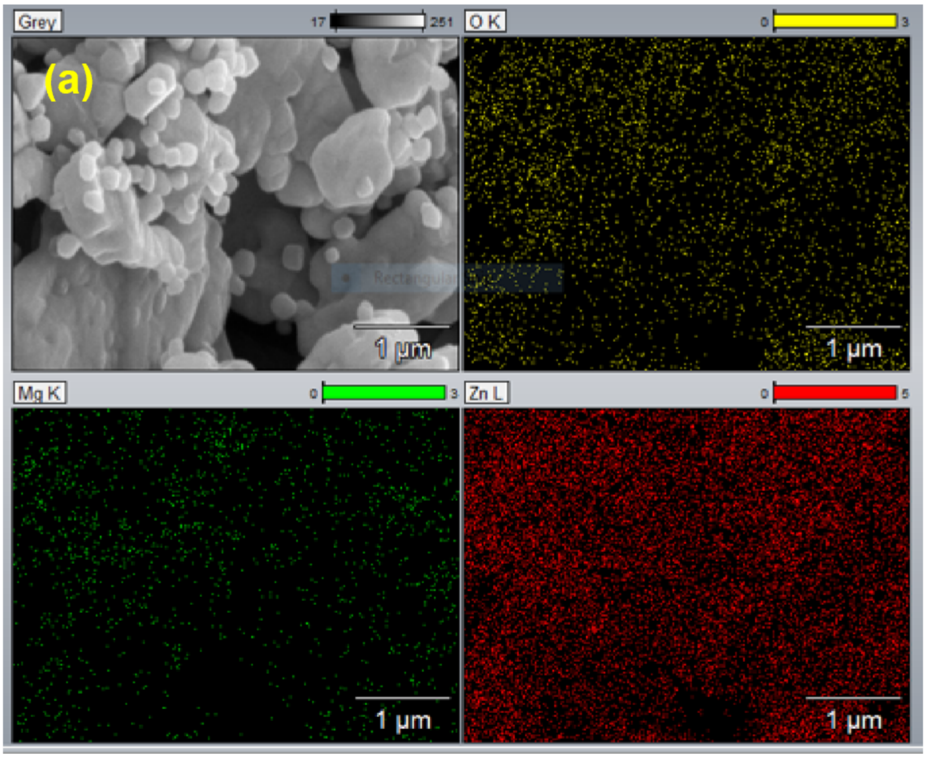


Figure S2. XPS characterization results of ZM21(a-d) and ZM12 (e-h).



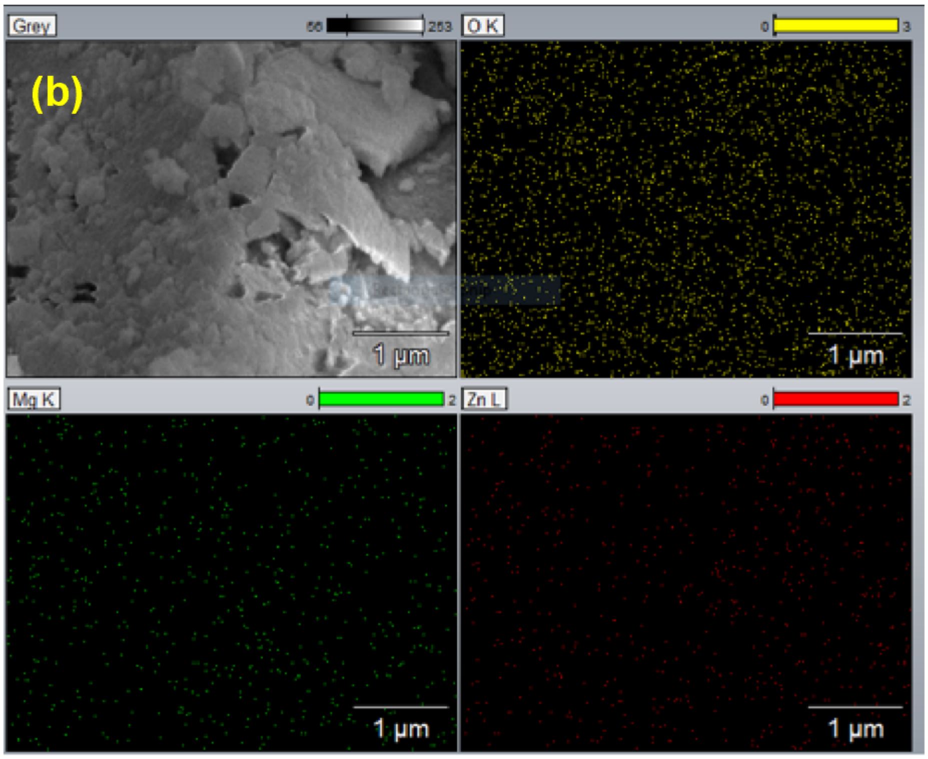


Figure S3. FE-SEM mapping result of ZM21 (a) and ZM12 (b)

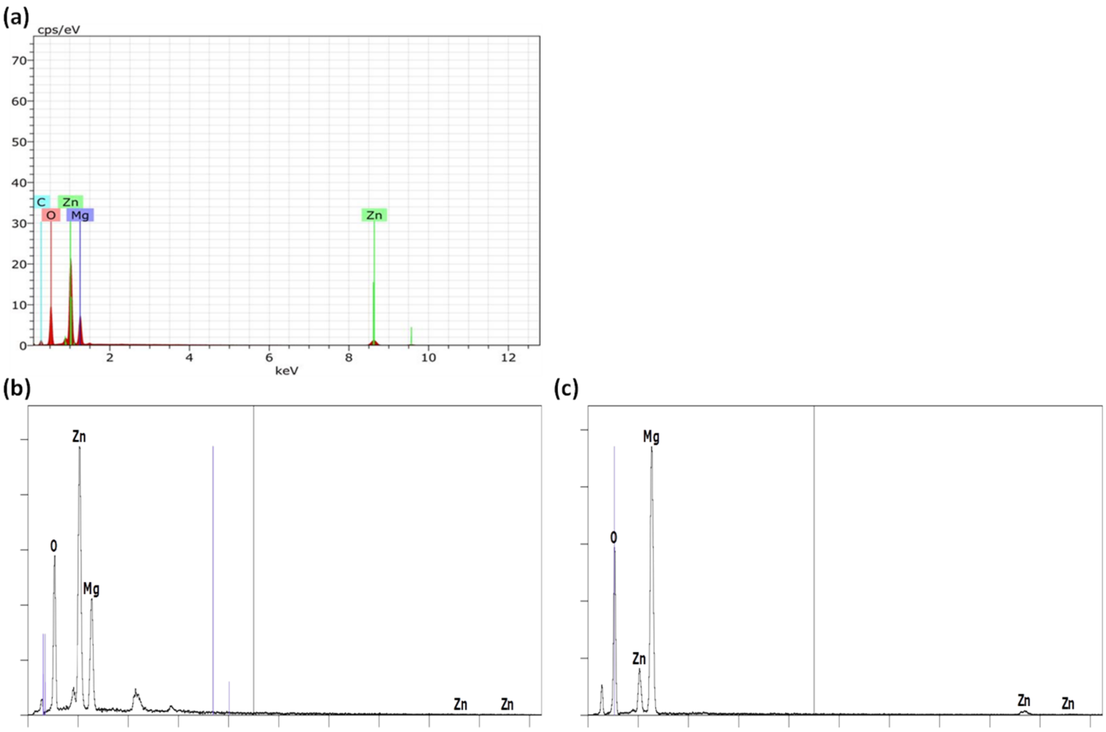


Figure S4. Result of FESEM EDX of ZM11(a), ZM21(b) and ZM12(c).

Catalysts	Wt. ratio of Zn/Mg[a]	Mg (wt. %)[b]	Zn (wt. %)[b]	O (wt. %)[b]
MO	0.0/0.99	-	-	-
ZO	0.98/0.0	-	-	-
ZM11	0.49/0.5	23.0	22.0	55.0
ZM21	0.67/0.32	19.8	59.7	20.5
ZM12	0.33/0.66	45.0	14.1	40.9

Table S5. ICP-MS elemental composition and FESEM EDX analysis result of catalysts.

[a] *ICP-MS;* [b] *FE-SEM-EDX*

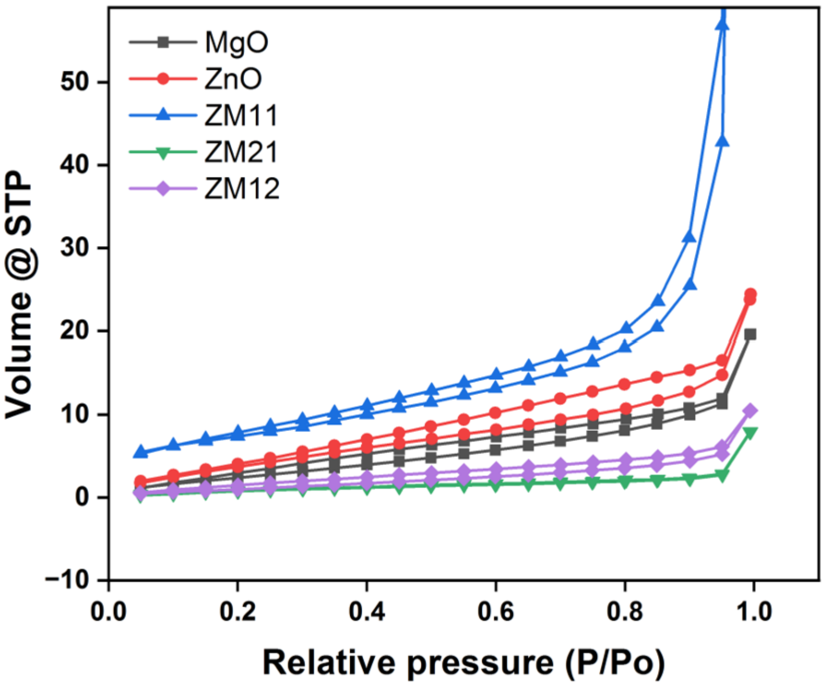


Figure S5. N_2 adsorption-desorption isotherm curve of the as-synthesized catalysts.

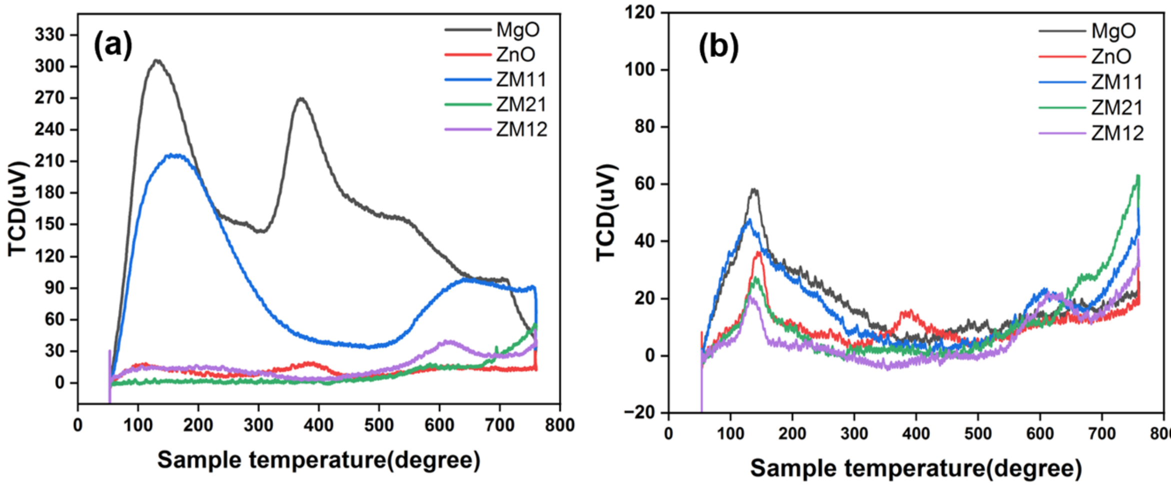


Figure S6. (a) CO_2-TPD and (b) NH_3-TPD response curves of the as-synthesized catalysts via chemisorption.

Table S6. Formed products of the glucose isomerization at 100 °C in water after 90 min at 12.5% catalyst load.

Catalysts	Residual glucose (%)	Fructose yield (%)	Mannose yield (%)	Allulose yield (%)
MO	47.23	29.75	2.65	0.8
ZO	97.16	1.92	n.d.	n.d.
ZM11	62.22	31.29	2.49	1.21
ZM21	94.22	3.13	n.d	1.129
ZM12	68.29	25.29	1.77	0.63

n.d- not detected.

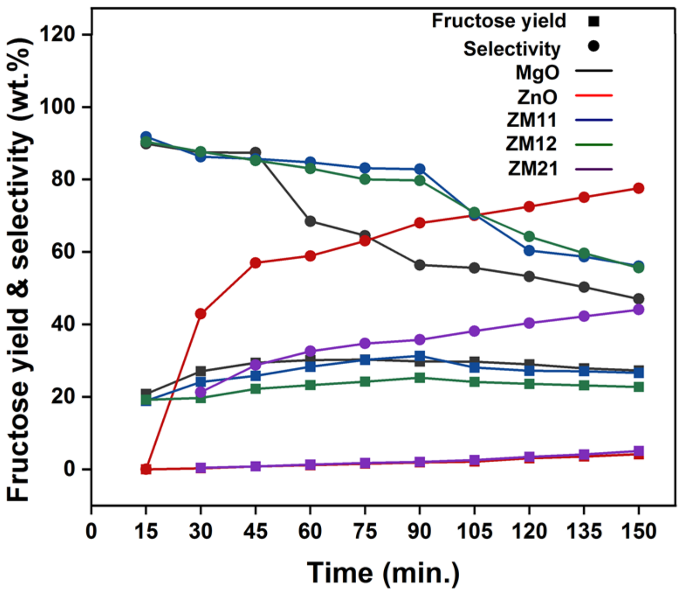


Figure S7. Glucose isomerization profile of different catalysts in water at 100 °C and 12.5% catalyst load on glucose up to 150 min.

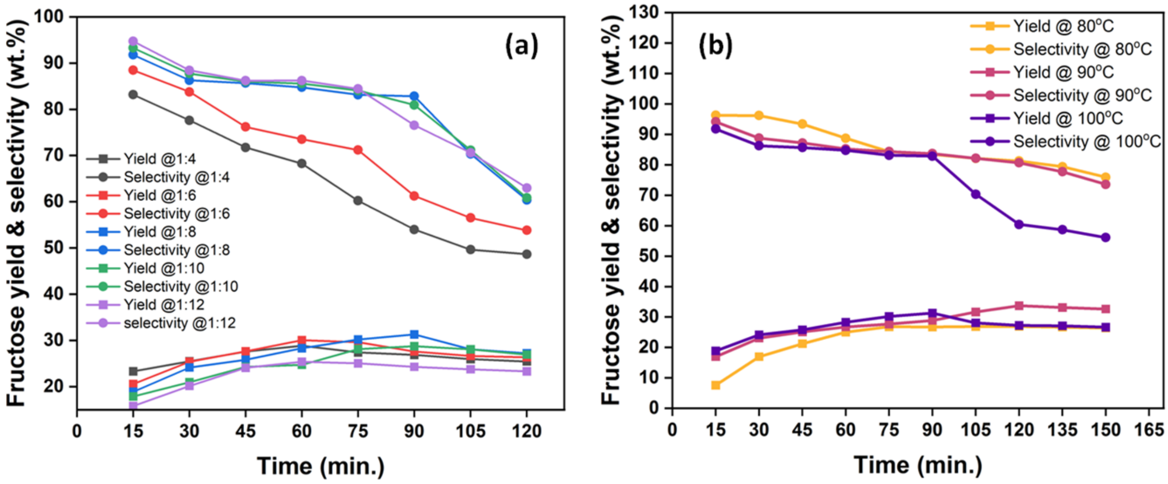


Figure S8. Glucose isomerization profile of ZM11 in water: (a) under different catalyst load conditions at 100 °C up to 120 min, and (b) under different temperature conditions at 12.5% (1:8) catalyst load up to 150 min.

Table S7. Carbon balance result of glucose isomerization to fructose over ZnO/MgO under different operating conditions.

Different catalyst (100 °C in water for 90 min, catalyst:substrate-1:8)	Carbon balance	Different catalyst loading (100 °C for 90 min in water)	Carbon balance	Different Temp. (120 min, catalyst:substrate-1:8)	Carbon balance
MgO	63.02	1:4	64.18	100	70.13
ZnO	67.97	1:6	70.48	90	90.75
ZM11	93.14	1:8	92.65	80	91.63
ZM21	73.86	1:10	90.28	-	-
ZM12	87.20	1:12	83.48	-	-

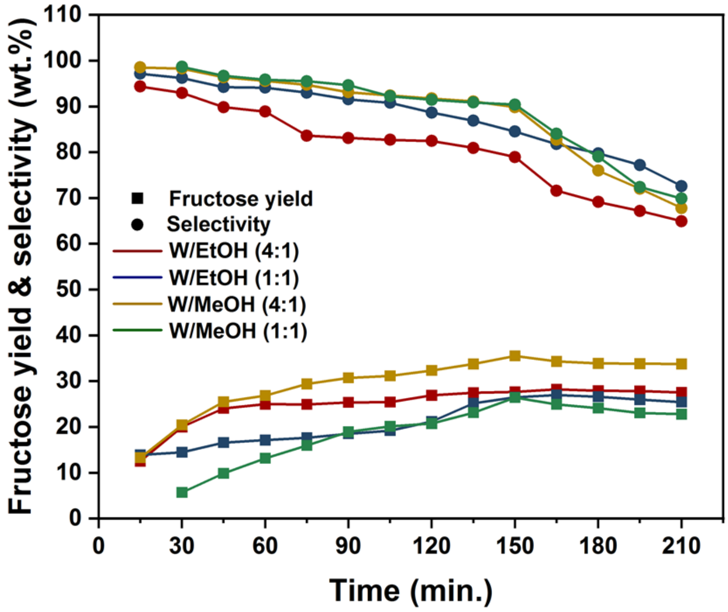


Figure S9. Glucose isomerization profile of ZM11in different reaction mediums (water/alcohol) at 90 °C and 12.5% catalyst load on glucose up to 210 min.

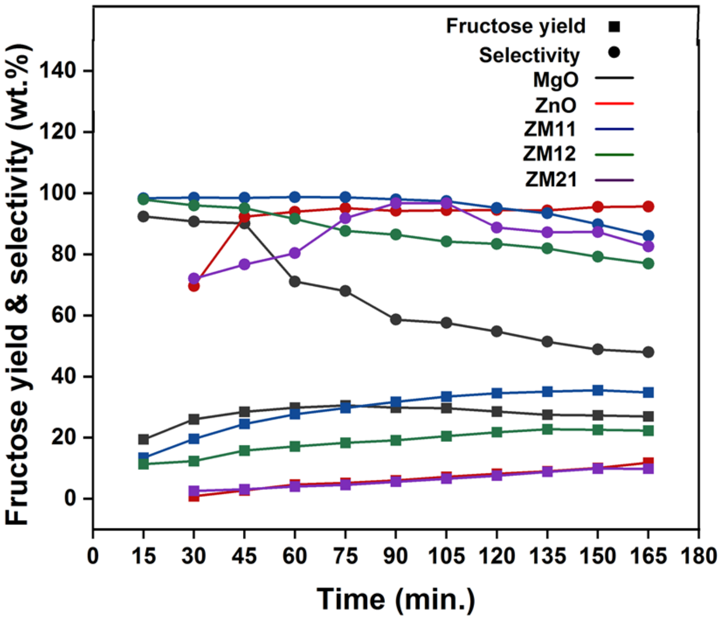


Figure S10. Glucose isomerization profile of different catalysts in 4:1 vol. W/MeOH medium at 90 °C and 12.5% catalyst load on glucose up to 165 min.

Table S8. Carbon balance result of glucose isomerization to fructose over ZnO/MgO in different solvent medium.

Different solvent (at 90 °C, 150 min, catalyst:substrate-1:8)	Carbon balance	Different catalyst in W/MeOH (4:1) at 90 °C for 150 min	Carbon balance
Water	54.70	MgO	61.94
W/EtOH (4:1)	86.00	ZnO	95.40
W/MeOH (4:1)	95.92	ZM11	95.92
-	-	ZM21	84.05
-	-	ZM12	87.29

Table S9. Formed products of the glucose isomerization at 90 °C in W/MeOH(4:1) after 150 min at 12.5% catalyst load.

Catalysts	Residual glucose (%)	Fructose yield (%)	Mannose yield (%)	Allulose yield (%)
MO	44.07	27.335	4.91	2.41
ZO	89.4	10.12	n.d.	n.d.
ZM11	60.48	35.5	0.81	n.d.
ZM21	88.71	9.86	n.d.	n.d.
ZM12	71.53	22.54	0.45	0.94

n.d- not detected.

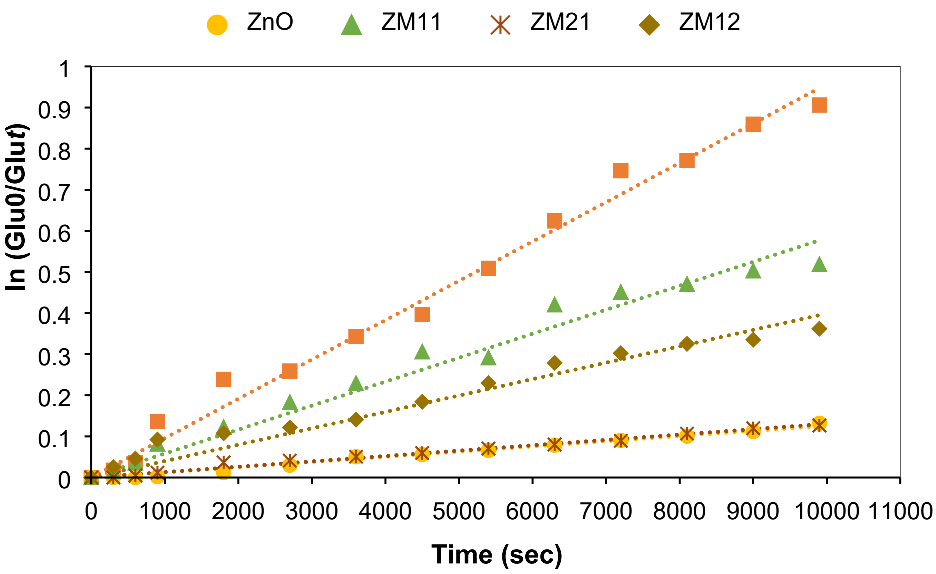


Figure S11. First-order kinetics of glucose isomerization over pristine and composite metal oxide catalysts in optimum solvent (W/MeOH) at 90 °C and 12.5% wt. catalyst load up to 165 min.

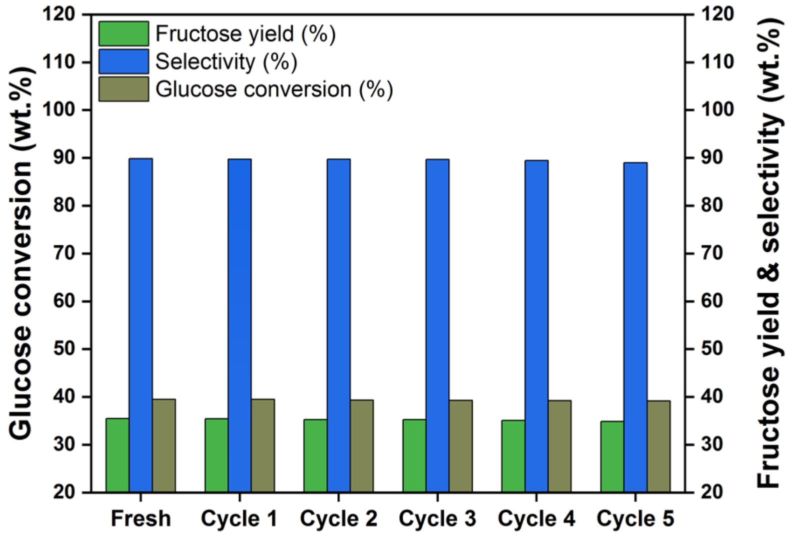


Figure S12. Recyclability result of ZM11 in W/MeOH(4:1)medium under optimum conditions.

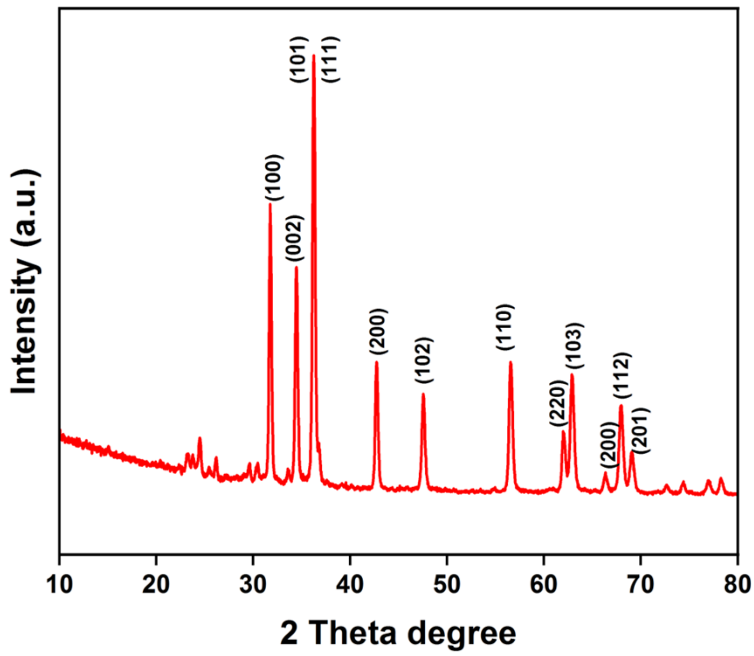


Figure S13. XRD characterization result of ZM11 after 5 recycles under optimum conditions.

Table S10. Green metrics calculation of the MZ11 catalyzed glucose isomerization in W/MeOH.

Sl. No.	Green metrics*	Ideal value	Process: glucose isomerization over ZM11
1.	Environmental factor (E-factor)	0.0	1.67
2.	Process mass intensity (MI)	1.0	2.67
3.	Carbon efficiency (CE, %)	100.0	37.44
4.	Atom economy (AE, %)	100.0	100.0

***Calculations:**

$$Environmental\ (E)\ factor = \frac{Wt.\ total\ waste\ formed}{Wt.\ total\ product\ formed}$$

$$Process\ mass\ intensity\ (MI) = \frac{Mass\ of\ reactant\ supplied}{Mass\ of\ product(s)\ formed}$$

$$Carbon\ efficiency = \frac{Moles\ of\ carbon\ in\ product(s)}{Moles\ of\ carbon\ in\ reactant} \times 100$$

$$Atom\ economy = \frac{Mol.wt.\ of\ product(s)}{Total\ mol.wt.\ of\ reactant} \times 100$$

Reference:

1. Abed, C., Ali, M. B., Addad, A., & Elhouichet, H. (2019). Growth, structural and optical properties of ZnO-ZnMgO-MgO nanocomposites and their photocatalytic activity under sunlight irradiation. *Materials Research Bulletin*, 110, 230-238.