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Supplementary Information

Molybdenum sulfide-2D nanosheets offering multiple metallic sites enable different sugar epimerization reactions to rare sugars in water

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Mathematical expressions

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

---------- (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)

Reaction kinetics

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

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

Where, sugar can be glucose and fructose.

Kinetic equation of the first-order reaction

$$ln\left\{\frac{[Sugar]_t}{[Sugar]_0}\right\} = -\ k \times time\ (sec)$$

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

Where, sugar can be glucose and fructose. $[Sugar]_t$ and $[Sugar]_0$ represent the final and initial reactant (sugar) concentration at time *t*. *k* is the observed rate constant of reaction (disappearance of sugar).

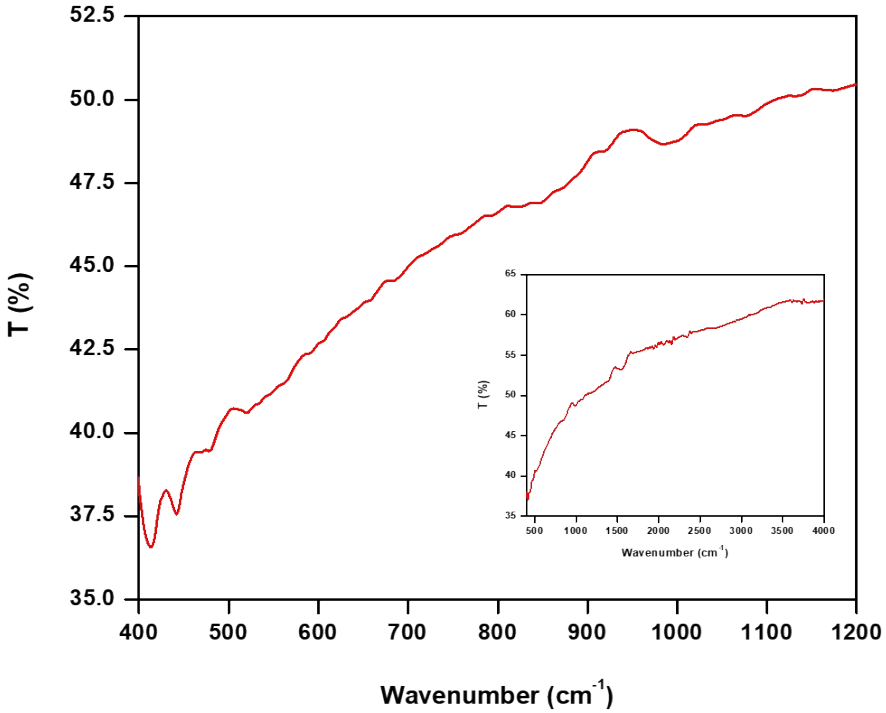

Figure S1: ATR-FTIR spectrum of the as-synthesised MoS_2 nanosheets in the 400-1200 cm^{-1} range. Inset: full spectrum.

Table S1: Comparative XPS analysis data of fresh and recycled catalysts of both epimerization reactions.

S.No.	Catalyst	Molybdenum (%)[a]			Sulphur (%)[a]			Mo[b] (wt.%)
		Mo^{6+}	1T-MoS_2	2H-MoS_2	S^{2-}	S_2^{2-}	S^{6+}	
1	Fresh	8.7	59.6	31.5	70.9	15.2	13.8	--
2	R-MS-1	4.1	51.6	44.2	76.5	23.5	n.a.	< 0.1
3	R-MS-2	3.3	48.6	47.9	74.0	25.9	n.a.	< 0.2

[a]Data calculated from XPS studies; [b]Mo leaching content calculated from ICP-MS studies; R-MS-1 catalyst collected from glucose epimerization reaction; R-MS-2 catalyst collected from fructose epimerization reaction; n.a. not available.

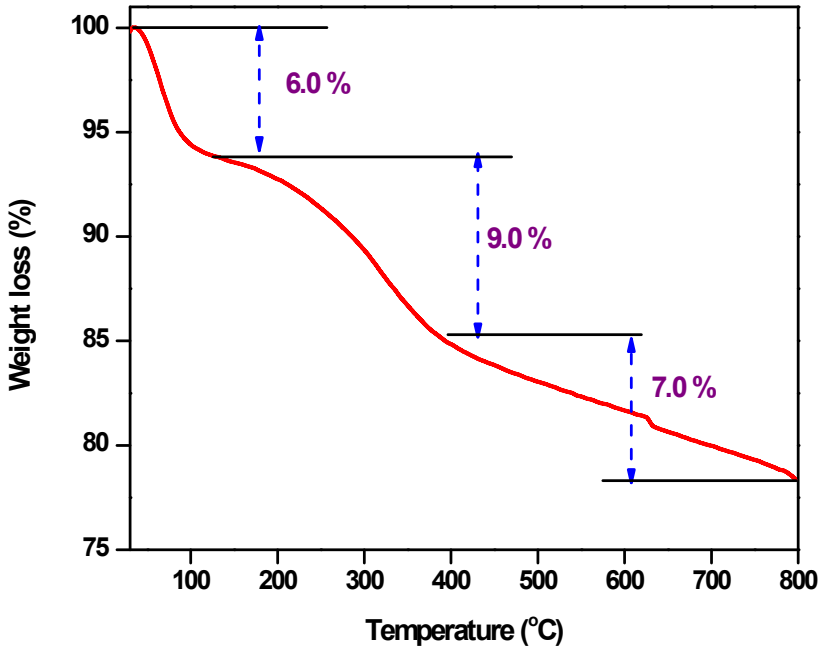

Figure S2: TGA analysis report of the as-synthesized MoS_2 nanosheets.

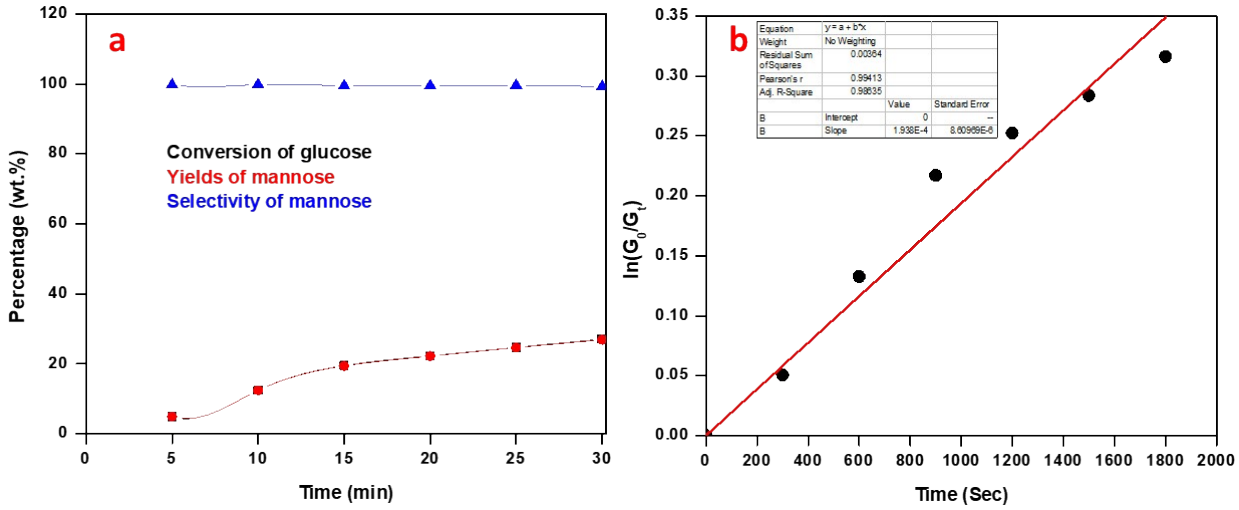

Figure S3: Reaction kinetics of glucose into mannose over MoS_2: (a) kinetic profile (at 100 °C and 10% wt. MoS_2 load on glucose) and (b) ln[Glu_0/Glu_t] *vs*. *t* plot for first-order rate constant determination.

Table S2: Product distribution during glucose epimerization over MoS_2 nanosheets with respect to temperature.

Temp (°C)	$Conv_{Glu}$ (%)	$Yield_{Mann}$ (%)	$Yield_{Fruc}$ (%)	Carbon balance (%)	TON	TOF ($\times 10^{-2}$ min^{-1})
80	28.2	27.0	n.d.	95.7	2.70	2.2
90	31.1	27.4	n.d.	88.1	2.74	2.3
100	34.7	29.3	0.5	85.9	2.93	2.4
110	44.0	27.9	0.8	65.2	2.79	2.3
120	55.6	26.0	1.5	49.5	2.60	2.1

Conv-conversion, Glu-glucose, Mann-mannose and Fruc-fructose. Reaction conditions: 10% wt. catalyst to glucose and 120 min in water. N.d.-not detected. TON-turn over number is calculated as moles of reactant consumed per mole of catalyst. TOF-turn over frequency is calculated as moles of reactant consumed per mole of catalyst per unit time.

Table S3: Product distribution during glucose epimerization over MoS_2 nanosheets with time.

Time (min)	$Conv_{Glu}$ (%)	$Yield_{Mann}$ (%)	$Yield_{Fruc}$ (%)	Carbon balance (%)	TON	TOF ($\times 10^{-2}$ min^{-1})
30	27.0	26.9	n.d.	99.6	2.69	8.9
60	31.1	27.2	n.d.	87.4	2.72	4.5
90	33.2	28.8	0.1	87.0	2.88	3.2
120	34.7	29.3	0.5	85.9	2.93	2.4
150	35.8	27.9	0.5	79.3	2.79	1.8
180	39.7	27.4	0.5	70.2	2.74	1.5
210	42.0	27.2	0.5	65.9	2.72	1.3
240	43.5	26.8	0.5	62.7	2.68	1.1

Conv-conversion, Glu-glucose, Mann-mannose and Fruc-fructose. Reaction conditions: 100 °C, 10% wt. catalyst to glucose in water. N.d.-not detected. TON-turn over number is calculated as moles of reactant consumed per mole of catalyst. TOF-turn over frequency is calculated as moles of reactant consumed per mole of catalyst per unit time.

Table S4: Product distribution during glucose epimerization over MoS_2 nanosheets under varying catalyst load conditions.

Cat. loading (wt. %)	$Conv_{Glu}$ (%)	$Yield_{Mann}$ (%)	$Yield_{Fruc}$ (%)	Carbon balance (%)	TON	TOF ($\times 10^{-2}$ min^{-1})
5.0	34.4	28.2	n.d.	81.9	2.82	2.3
10.0	34.7	29.3	0.5	85.9	2.93	2.4
15.0	37.4	28.8	0.8	79.1	2.88	2.4
20.0	41.7	28.5	1.2	71.2	2.85	2.3

Conv-conversion, Glu-glucose, Mann-mannose and Fruc-fructose. Reaction conditions: 100 °C and 120 min in water. N.d.-not detected. TON-turn over number is calculated as moles of reactant consumed per mole of catalyst. TOF-turn over frequency is calculated as moles of reactant consumed per mole of catalyst per unit time.

Table S5. Product distribution during glucose epimerization over MoS_2 nanosheets in different solvent mediums.

Solvent	$Conv_{Glu}$ (%)	$Yield_{Mann}$ (%)	$Yield_{Fruc}$ (%)	Carbon balance (%)	TON	TOF ($\times 10^{-2}$ min^{-1})
MeOH	38.8	25.5	0.8	67.8	2.55	2.1
EtOH	34.2	25.3	n.d.	74.0	2.53	2.1
IPA	44.4	19.3	n.d.	43.4	1.93	1.6
Water	34.7	29.3	0.5	85.9	2.93	2.4

Conv-conversion, Glu-glucose, Mann-mannose and Fruc-fructose. Reaction conditions: 100 °C, 5% wt. catalyst load on glucose and 120 min. N.d.-not detected and IPA-iso propyl alcohol. TON-turn over number is calculated as moles of reactant consumed per mole of catalyst. TOF-turn over frequency is calculated as moles of reactant consumed per mole of catalyst per unit time.

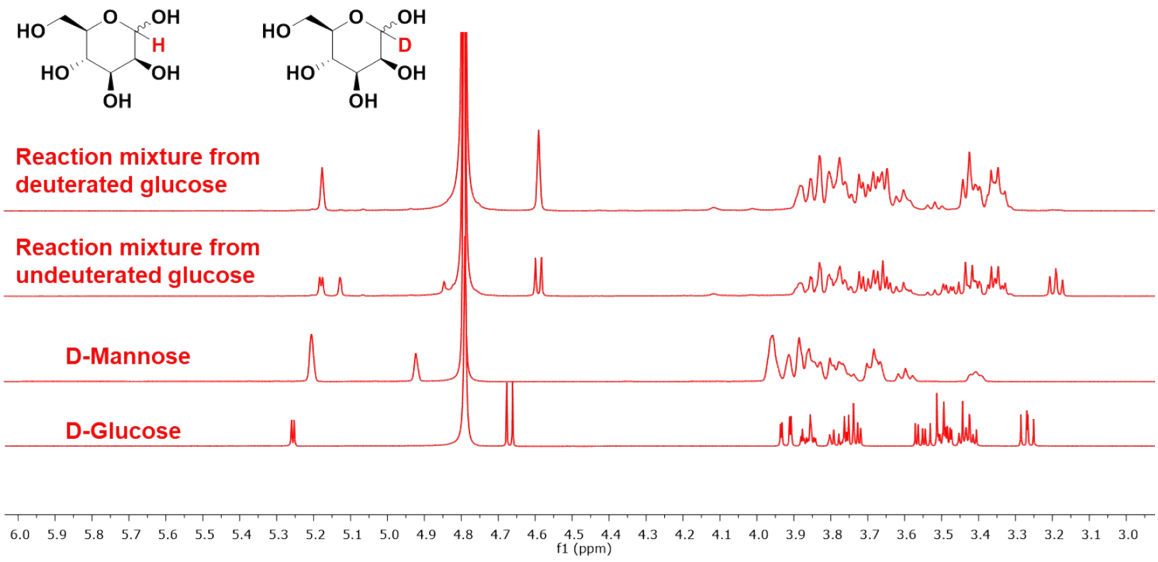

Figure S4: Comparative ^{1}H-NMR spectra of post-reaction mixtures obtained using labelled and unlabelled glucose (at C2) as a substrate in D_2O and reference sugars.

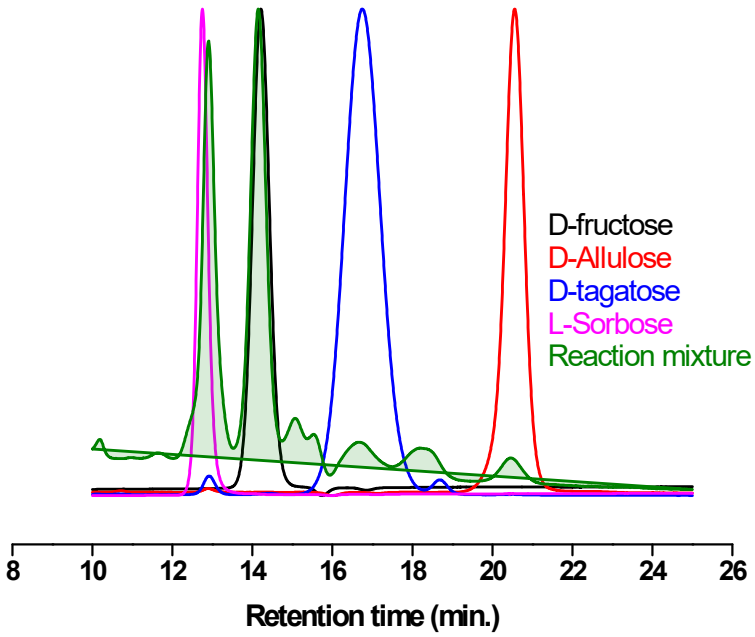

Figure S5: Comparative HPLC chromatograms of reference sugars and the post-reaction mixture of fructose epimerization into L-sorbose under optimum conditions.

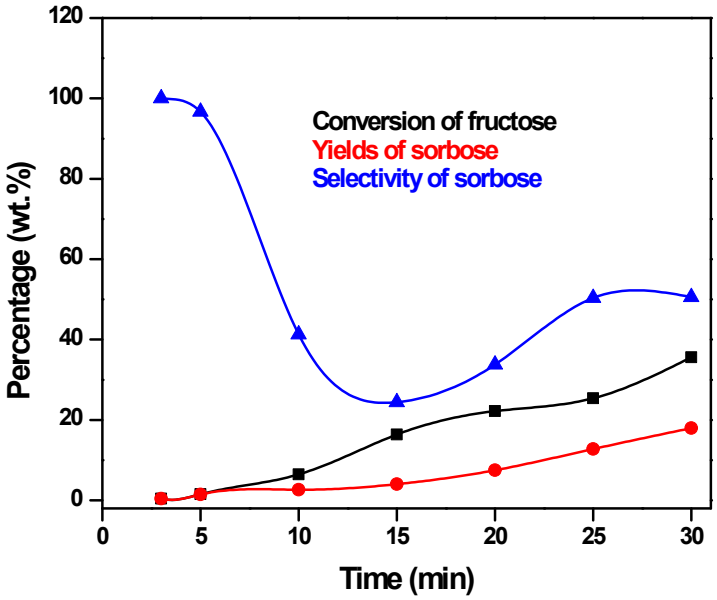

Figure S6: Kinetic profile of fructose to L-sorbose epimerization up to 30 minutes (at 130 °C and 20% wt. MoS_2 on fructose) in water.

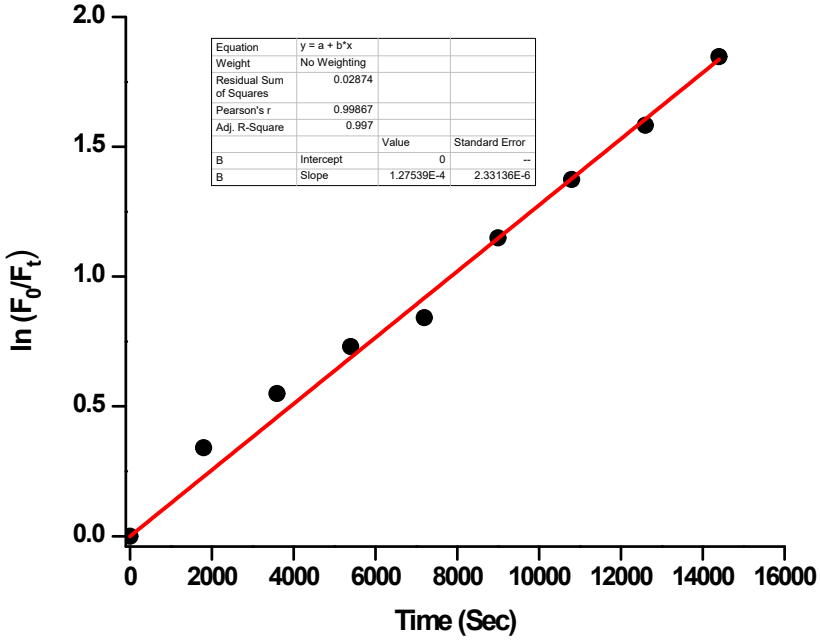

Figure S7: Plot of ln[Fru_0/Fru_t] *vs*. *t* for first-order rate constant determination.

Table S6: Product distribution during fructose epimerization over MoS_2 nanosheets under varying catalyst load conditions.

MoS_2 load (%)	$Conv_{Fruc}$ (%)	$Yield_{Sorb}$ (%)	$Yield_{Taga}$ (%)	$Yield_{Allu}$ (%)	$Yield_{HMF}$ (%)	Carbon balance (%)	TON	TOF ($\times 10^{-2}$ min^{-1})
5	34.2	15.9	0.5	0.5	1.2	54.7	0.79	0.66
10	41.7	21.1	1.7	1.0	2.7	66.8	1.05	0.87
15	51.3	21.7	1.6	0.8	3.2	56.3	1.08	0.90
20	56.4	22.0	1.3	0.7	4.1	53.4	1.10	0.91

Conv-conversion, Fruc-fructose, Sorb-sorbose, Allu-allulose and Taga-tagatose. Reaction conditions: 100 °C and 120 min in water. N.d.-not detected. TON-turn over number is calculated as moles of reactant consumed per mole of catalyst. TOF-turn over frequency is calculated as moles of reactant consumed per mole of catalyst per unit time.

Table S7: Product distribution during fructose epimerization over MoS_2 nanosheets with respect to temperature.

Temp (°C)	$Conv_{Fruc}$ (%)	$Yield_{Sorb}$ (%)	$Yield_{Taga}$ (%)	$Yield_{Allu}$ (%)	$Yield_{HMF}$ (%)	Carbon balance (%)	TON	TOF ($\times 10^{-2}$ min^{-1})
80	21.7	8.3	0.2	n.d.	1.2	47.4	0.41	0.34
90	25.0	9.7	0.5	n.d.	1.7	50.9	0.48	0.40
100	41.7	21.1	0.9	0.1	2.2	60.9	1.05	0.87
110	43.9	21.7	1.1	0.2	2.3	60.2	1.08	0.90
120	45.3	22.1	1.3	0.6	2.5	61.2	1.10	0.92
130	52.3	26.3	1.7	1.0	2.7	63.2	1.31	1.09
140	63.1	25.9	1.8	0.9	3.2	52.9	1.29	1.07
150	73.9	21.9	2.6	1.6	4.8	45.0	1.09	0.90

Conv-conversion, Fruc-fructose, Sorb-sorbose Allu-allulose and Taga-tagatose. Reaction conditions: 10% wt. catalyst to fructose for 120 mins in water. N.d.-not detected. TON-turn over number is calculated as moles of reactant consumed per mole of catalyst. TOF-turn over frequency is calculated as moles of reactant consumed per mole of catalyst per unit time.

Table S8: Product distribution during fructose epimerization over MoS_2 nanosheets with time.

Time (min)	$Conv_{Fruc}$ (%)	$Yield_{Sorb}$ (%)	$Yield_{Taga}$ (%)	$Yield_{Allu}$ (%)	$Yield_{HMF}$ (%)	Carbon balance (%)	TON	TOF ($\times 10^{-2}$ min^{-1})
30	35.6	18.0	0.9	n.d.	n.d.	53.0	0.90	3.0
60	45.6	22.8	1.4	0.5	2.5	62.3	1.14	1.9
90	51.8	25.9	1.7	0.8	3.5	64.9	1.29	1.4
120	52.3	26.3	1.8	1.0	2.7	63.3	1.31	1.0
150	68.3	23.4	2.4	1.2	4.0	48.3	1.17	0.8
180	74.6	21.3	2.9	1.0	5.8	45.4	1.06	0.6
210	79.4	18.7	2.6	1.1	6.0	39.5	0.93	0.4
240	84.2	15.4	2.4	1.2	6.1	33.4	0.77	0.3

Conv-conversion, Fruc-fructose, Sorb-sorbose Allu-allulose and Taga-tagatose. Reaction conditions: 130 °C, 10% wt. catalyst to fructose in water. N.d.-not detected. TON-turn over number is calculated as moles of reactant consumed per mole of catalyst. TOF-turn over frequency is calculated as moles of reactant consumed per mole of catalyst per unit time.

Table S9: Product distribution during fructose epimerization over MoS_2 nanosheets in different solvent mediums.

Temp (°C)	$Conv_{Fruc}$ (%)	$Yield_{Sorb}$ (%)	$Yield_{Taga}$ (%)	$Yield_{Allu}$ (%)	$Yield_{HMF}$ (%)	Carbon balance (%)	TON	TOF ($\times 10^{-2}$ min^{-1})
MeOH	26.2	9.0	0.1	n.d.	2.2	47.3	0.45	0.37
EtOH	31.7	6.9	n.d.	n.d.	2.0	31.2	0.34	0.28
W: M[a]	28.7	14.3	n.d.	0.3	2.1	61.8	0.72	0.59
W: E[b]	29.8	11.3	n.d.	0.2	1.5	46.1	0.56	0.47
Water	52.3	26.3	1.7	1.0	2.7	63.1	1.32	1.09

Conv-conversion, Fruc-fructose, Sorb-sorbose Allu-allulose and Taga-tagatose. Reaction conditions: 130 °C, 10% wt. catalyst to fructose and 120 min. N.d.-not detected. [a]Water:Methanol (1:1 v/v) and [b]Water:Ethanol (1:1 v/v). TON-turn over number is calculated as moles of reactant consumed per mole of catalyst. TOF-turn over frequency is calculated as moles of reactant consumed per mole of catalyst per unit time.

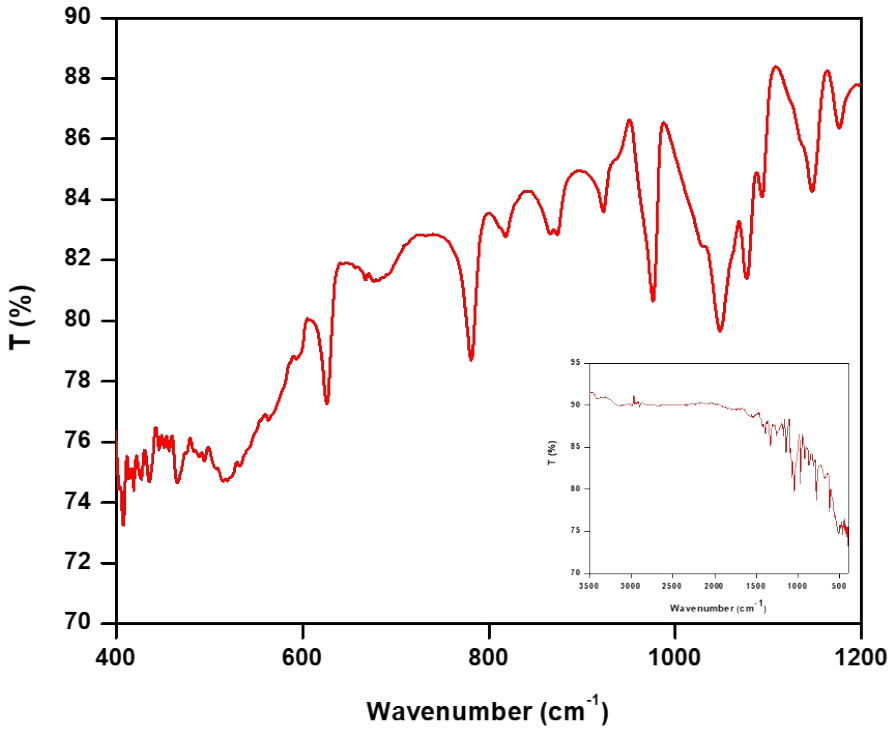

Figure S8: In-situ ATR-FTIR spectrum of fructose to sorbose epimerisation reaction with MoS_2 nanosheet in the 400-1200 cm^{-1} range. Inset: full spectrum. (Reaction conditions: 20 wt.% catalyst loading on sugar, 1 h. 130 ^oC in water).

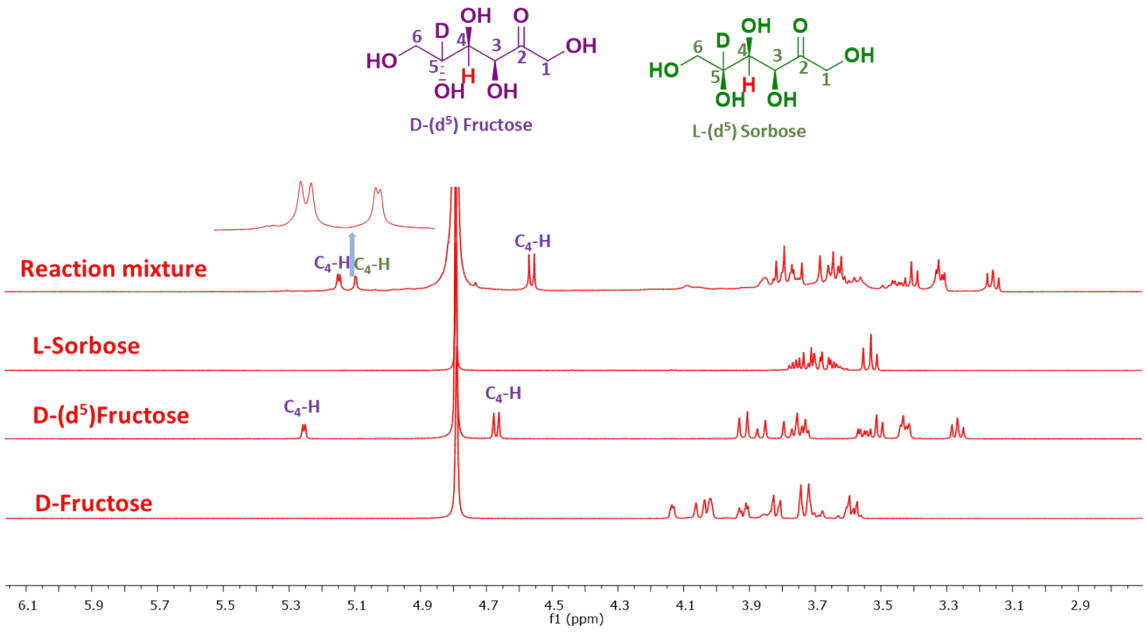

Figure S9: Comparative ^{1}H-NMR spectra of post-reaction mixtures obtained when using labelled and unlabelled glucose (at C2) as a substrate in D_2O along with reference sugars.

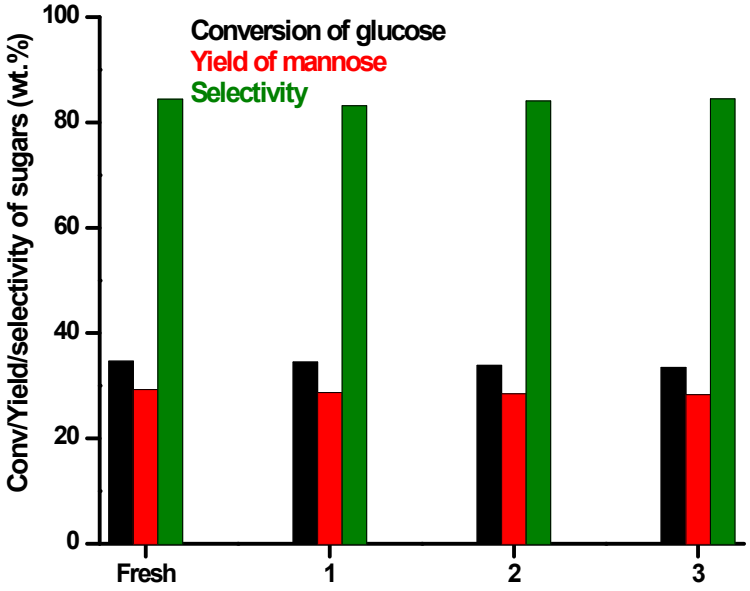

Figure S10: Result of catalyst recycling during glucose into mannose epimerization under optimum conditions. (Reaction condition: solvent-water, temperature 100 ºC, concentration of glucose 50 mg, time 2 h, catalyst dosage 5 mg).

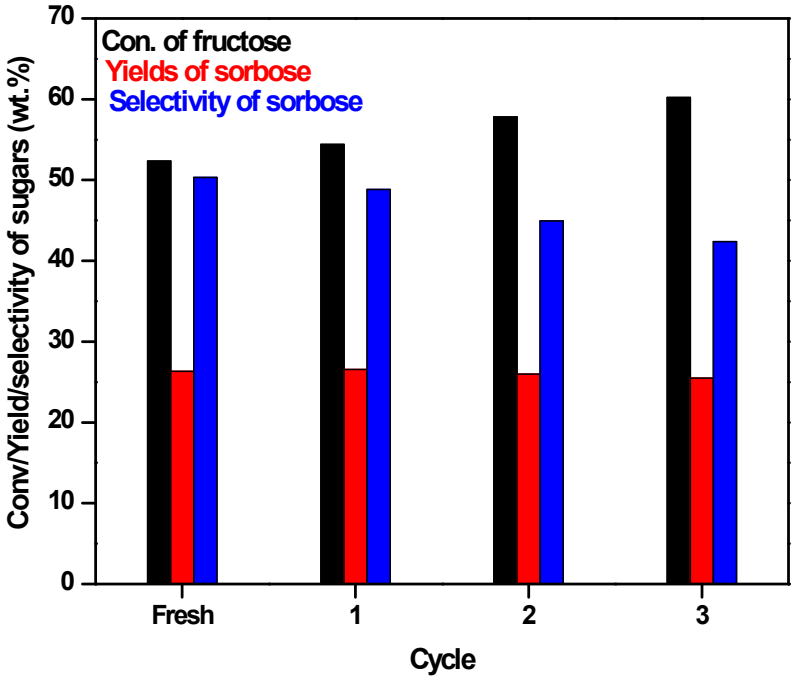

Figure S11: Result of catalytic efficiency of MoS_2 in fructose epimerization to L-sorbose under optimum conditions in water. (Reaction condition: solvent-water, temperature 130 ºC, concentration of fructose 50 mg, time 2 h, catalyst dosage 10 mg).

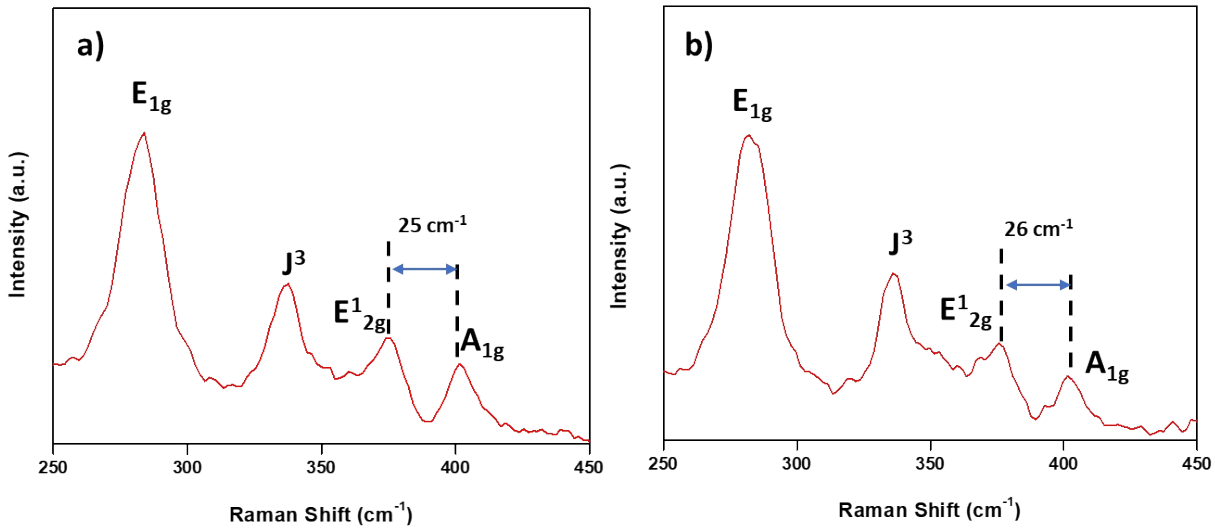

Figure S12: Raman spectra of recovered catalyst from (a) glucose epimerization reaction and (b) fructose epimerization reaction.

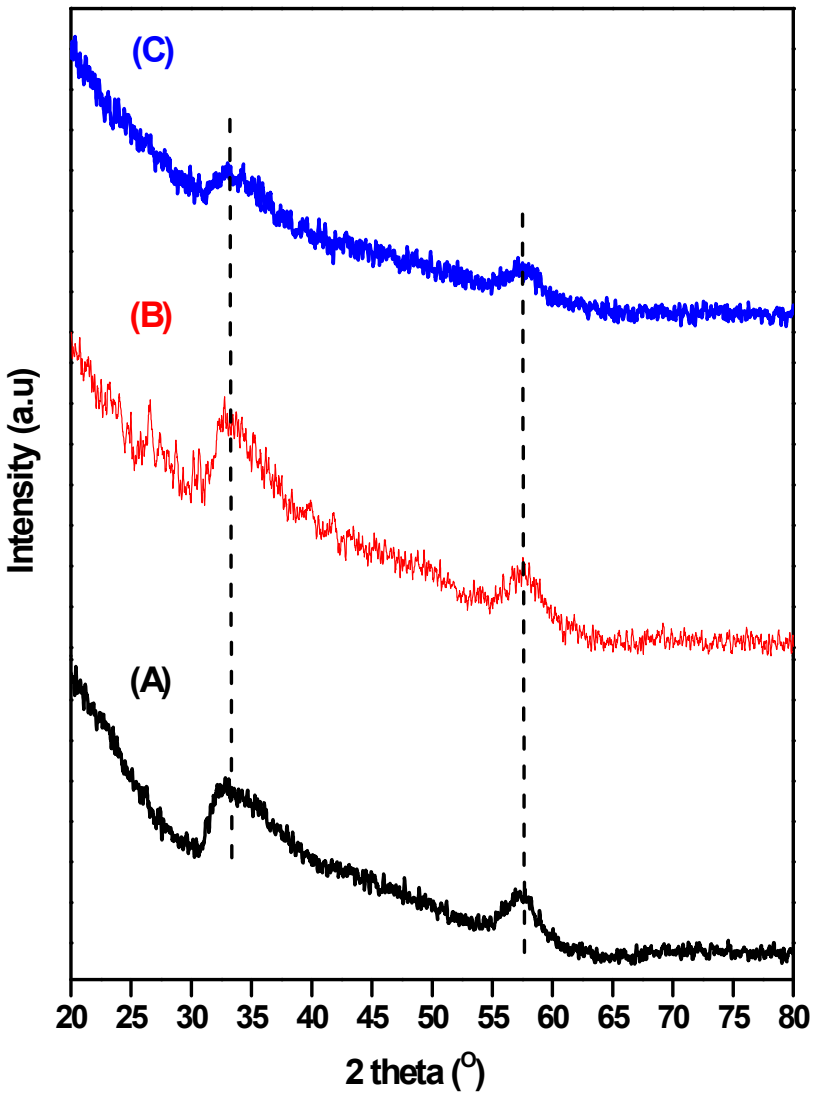

Figure S13: Comparative XRD results: (a) as-synthesized MoS_2 (fresh), (b) recovered MoS_2 after three recycles of glucose epimerization to mannose, and (c) recovered MoS_2 after three recycles of fructose epimerization to sorbose.

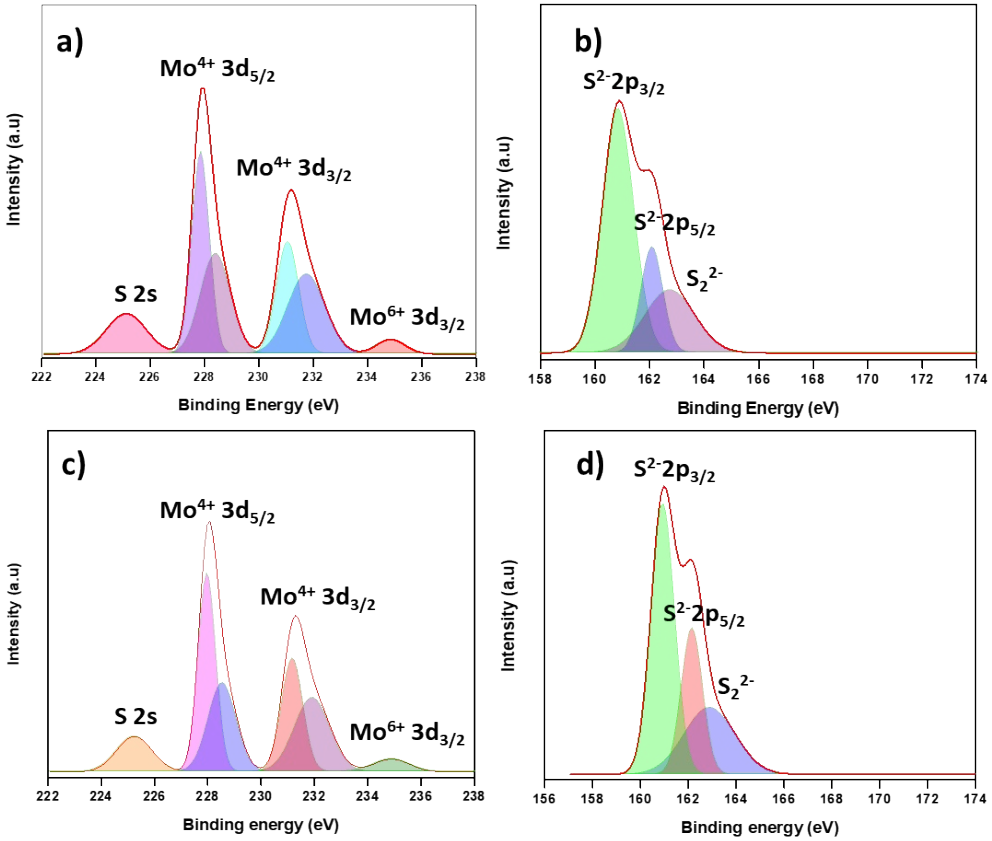

Figure S14: XPS spectra of recovered catalyst from glucose epimerisation reaction (a &b) and fructose epimerisation reaction (c&d).

Table S10: Green metrics of glucose and fructose epimerization reactions over MoS_2 nanosheets.

Green metric parameters	Ideal value	Process: Glucose epimerisation	Process: Fructose epimerization
E-Factor	0.0	3.4	3.8
Process Mass Intensity (PMI)	1.0	3.3	3.1
Mass Productivity (MP, %)	100.0	29.8	31.8
Carbon Efficiency (CE, %)	100.0	29.3	26.3
Atom Economy (AE, %)	100.0	100.0	100.0
Reaction Mass Efficiency (RME, %)	100.0	29.8	31.8

Table S11: Penalty points of epimerization of glucose and fructose reactions to calculate E-scale values.

Parameters	Penalty points		
	Ideal	**Glucose epimerization**	**Fructose epimerization**
Yield	(100 – % yield)/2	35	37
Price of reaction components (to obtain 10 mmol of end product)			
Inexpensive (< $10)	0	0	0
Expensive (> $10 and < $50)	3	-	-
Very expensive (> $50)	5	5	5
Safety[a]			
N (dangerous for environment)	5	-	-
T (toxic)	5	-	-
F (highly flammable)	5	-	-
E (explosive)	10	-	-
F+ (extremely flammable)	10	-	-
T+ (extremely toxic)	10	-	-
Technical setup			
Common setup	0	0	0
Instruments for controlled addition of chemicals[b]	1	-	-
Unconventional activation technique[c]	2	-	-
Pressure equipment, > 1 atm[d]	3	-	-
Any additional special glassware	1	-	-
(Inert) gas atmosphere	1	-	-
Glove box	3	-	-
Temperature/time			
Room temperature, < 1 h	0	0	0
Room temperature, < 24 h	1	-	-
Heating, < 1 h	2	-	-
Heating, > 1 h	3	3	3
Cooling to 0°C	4	-	-
Cooling, < 0°C	5	-	-
Workup and purification			
None	0	0	0
Cooling to room temperature	0	0	0
Adding solvent	0	0	0
Simple filtration	0	0	0
Removal of solvent with bp < 150°C	0	0	0
Crystallization and filtration	1	-	-
Removal of solvent with bp > 150°C	2	-	-
Solid phase extraction	2	-	-
Distillation	3	-	-
Sublimation	3	-	-
Liquid-liquid extraction[e]	3	-	-
Classical chromatography	10	10	10
Total		**53**	**55**

[a]Water:Methanol; [b]Special items, like dropping funnel, syringe pump, high-pressure gas regulator, etc.; [c]Microwave irradiation, ultrasound or photochemical activation, etc.; [d]high-pressure hydrogenation equipment, etc.; [e]Solvent drying process (filtration and desiccation).