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Electronic Supplementary Information:

Catalytic Mechanism for the Isomerization of Glucose into Fructose over Aluminum-MCM-41 Framework

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Content

The equations for calculating TOF according to the energetic span model:

The efficiency of catalyst can be determined by the turnover frequency (TOF) of the catalytic cycle. Based on the transition state theory (TST), the TOF can be calculated by Eqs. (i) and (ii) proposed by Kozuch et al., in which δE (the energetic span) is defined as the energy difference between the summit and trough of the catalytic cycle.[1-6]

$$\mathrm{TOF} = \frac{k_{\mathrm{B}}T}{h} e^{-\frac{\delta E}{RT}} \tag{i}$$

$$\delta E = \begin{pmatrix} G_{\mathrm{TDTS}} - G_{\mathrm{TDI}} & \text{if TDTS appears after TDI} \\ G_{\mathrm{TDTS}} - G_{\mathrm{TDI}} + \Delta G_{\mathrm{r}} & \text{if TDTS appears before TDI} \end{pmatrix} \tag{ii}$$

where k_{B} is the Boltzmann constant, T is the absolute temperature, and h is the Planck constant. G_{TDTS} and G_{TDI} are the Gibbs free energies of the TOF determining transition state (TDTS) and the TOF determining intermediate (TDI), and ΔG_{r} is the global free energy of the whole cycle.

References:

1. C. Amatore and A. Jutand, *J. Organomet. Chem.*, 1999, **576**, 254-278.
2. S. Kozuch and S. Shaik, *J. Am. Chem. Soc.*, 2006, **128**, 3355-3365.
3. S. Kozuch and S. Shaik, *J. Phys. Chem. A*, 2008, **112**, 6032-6041.
4. S. Kozuch and S. Shaik, *Acc. Chem. Res.*, 2011, **44**, 101-110.
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6. S. Kozuch, *ACS Catal.*, 2015, **5**, 5242-5255.

Description of the calculation method for the stability of the Al active sites:

To estimate the relative stability between the chemisorbed species, Tielens' group performed calculations using the atomistic thermodynamics approach. [7-10] To take into account deviations in surface composition and the presence of gas phases, the approximation of the Gibbs free-surface energy was also calculated by introducing an appropriate chemical potential, which corrected the deviations in surface composition and the presence of gas phases.

Based on the atomistic thermodynamics approach, we calculated the stability of the Al active sites on Al-MCM-41. According to the reaction given (equation 1), the Gibbs free energy of [Al-1] and [Al-2] as follows:

$$\Delta G_{[\mathrm{Al-1}]} = E_{[(\mathrm{SiO})_8(\mathrm{SiOH})(\mathrm{Si})_2(\mathrm{OH})_2\mathrm{Al}(\mathrm{OH})_1]} + E_{\mathrm{SiO_2}} - E_{[(\mathrm{SiO})_9(\mathrm{Si})_3(\mathrm{OH})_3]} - E_{\mathrm{HAlO_2}} \qquad \text{(a)}$$

$$\Delta G_{[\mathrm{Al-2}]} = E_{[(\mathrm{SiO})_8(\mathrm{SiOH})(\mathrm{Si})_2(\mathrm{OH})1\mathrm{Al}(\mathrm{OH})_2]} + E_{\mathrm{SiO_2}} - E_{[(\mathrm{SiO})_9(\mathrm{Si})_3(\mathrm{OH})_3]} - E_{\mathrm{HAlO_2}} \qquad \text{(b)}$$

The formula for calculating the variation of energy (kJ $\mathrm{mol^{-1}}$) with temperature in equation (a) and (b) is as follows:

$$E_y = \left(E + G_0 / 627.51\right) \times 2625.5 \qquad \text{(c)}$$

where y represents each species in equation 1, E is the total energy (Ha) of each species after the optimized structure, and G_0 is the corrected value of free energy at different temperatures after calculating frequency (kcal $\mathrm{mol^{-1}}$, including zero vibration energy).

References:

1. M. M. Islam, D. Costa, M. Calatayud and F. Tielens, *J. Phys. Chem. C.*, 2009, **24**, 10740–10746.
2. H. Guesmi and F.Tielens, *J. Phys. Chem. C.*, 2012, **116**, 994–1001.
3. A. Wojtaszek, I. Sobczak, M. Ziolek and F. Tielens, *J. Phys. Chem. C*, 2010, **114**, 9002–9007.
4. H. Guesmi, R. Grybos, J. Handzlikc and F. Tielens, *Phys.Chem.Chem.Phys.*, 2014, **16**, 18253--18260.

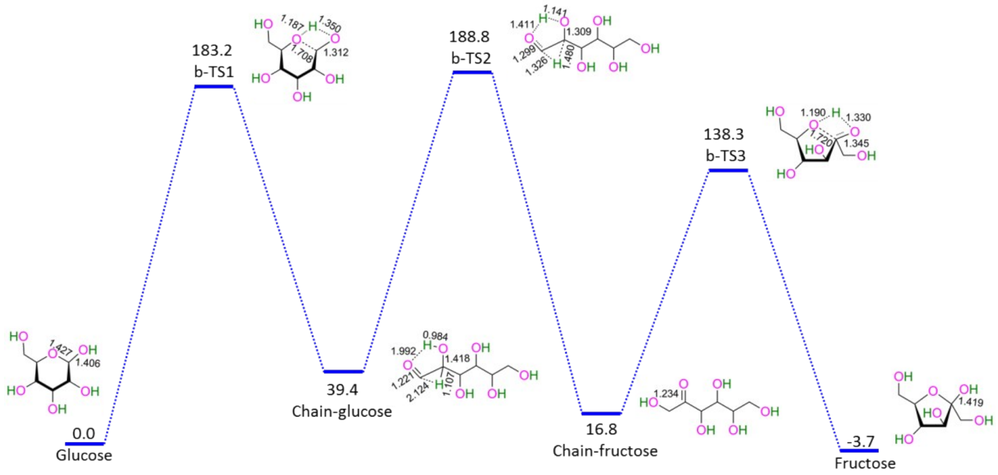


Figure S1: The geometric structures and the schematic energy diagrams (b) with the relative energy (Er, kJ mol−1) relative to the reactants for the isomerization of glucose to fructose without catalyst. For clarity, hydrogen atoms on carbon are not shown. Bond lengths are reported in Å.

Notes: The geometric structures and the schematic energy diagrams for the isomerization of glucose to fructose without catalyst are shown Fig. S1.

As shown in Fig. S1, at the beginning, from glucose to chain-glucose, a [1,3]-H shift takes place via a four-membered cyclic b-TS1, resulting in the ring-opening, with the energy height of the highest point (EHHP) of 183.2 kJ mol^{-1} at b-TS1 and the highest energy barrier (HEB) of 183.2 kJ mol^{-1} at the reaction step of Glucose → b-TS1. Then the aldose−ketose tautomerization takes place through the intramolecular H-shift via a chair six-membered b-TS2, with the EHHP of 188.8 kJ mol^{-1} at b-TS2 and the HEB of 149.4 kJ mol^{-1} at the reaction step of Chain-glucose → b-TS2. Finally, from chain-fructose to fructose, a [1,3]-H shift takes place via a four-membered b-TS3, accomplishing the ring-closure, with the EHHP of 138.3 kJ mol^{-1} at b-TS3 and the HEB of 121.5 kJ mol^{-1} at the reaction step of Chain-fructose → b-TS3.

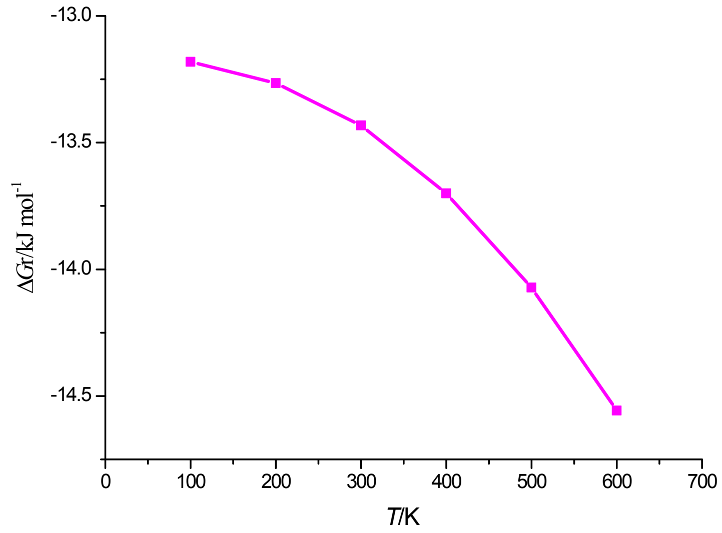


Figure S2: Diagram (relative Gibbs free energies (**[Al-1]-[Al-2]**) *vs*. temperature) showing the stability ranges for the different aluminum doped MCM-41 in the gas phase.

Notes: As shown in **Figure S2**, in the gas phase, [Al-1] active site is more stable than [Al-2] active site, over the temperature range of 100 ~ 600 K.

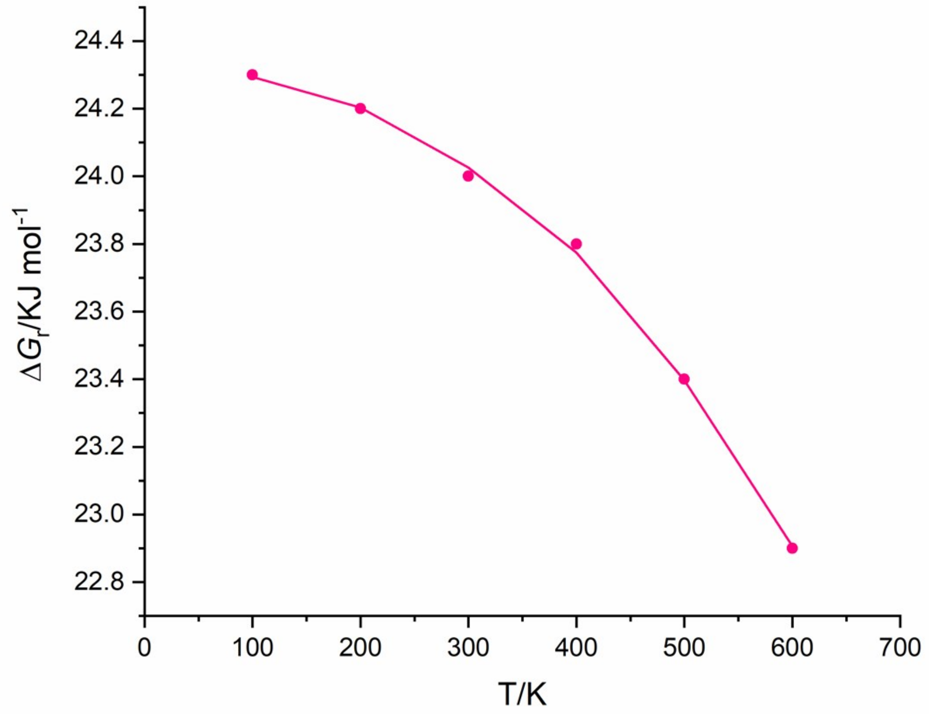


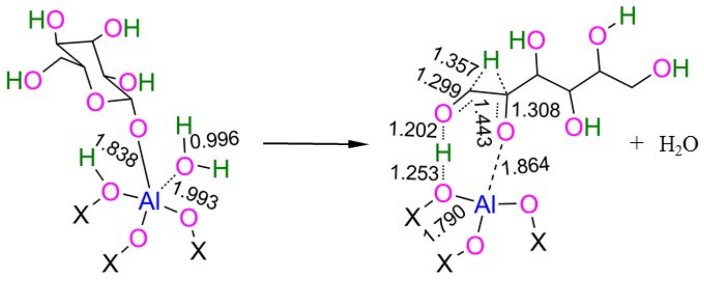
Figure S3: Diagram (relative Gibbs free energies (**[Al-1]-[Al-2]**) *vs*. temperature) showing the stability ranges for the different aluminum doped MCM-41 in aqueous solution.

Notes: For the the stabilities of Al-containing active sites on Al-MCM-41 in aqueous solution, the single-point energy calculation was employed, based on the optimized geometric structures in the gas phase. The single-point energy calculation was implemented in DMol^3 program.[1] Conductor-like screening model (COSMO) with a dielectric constant of 78.54 was adopted to consider the water solvent effect.[2] All electron relativistic method with a double numerical basis set together with polarization functions (DNP) was adopted to form the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional within the generalized gradient approximation (GGA).[3,4] A Fermi smearing of 0.005 hartree for orbital occupancy was used to improve the computational performance.

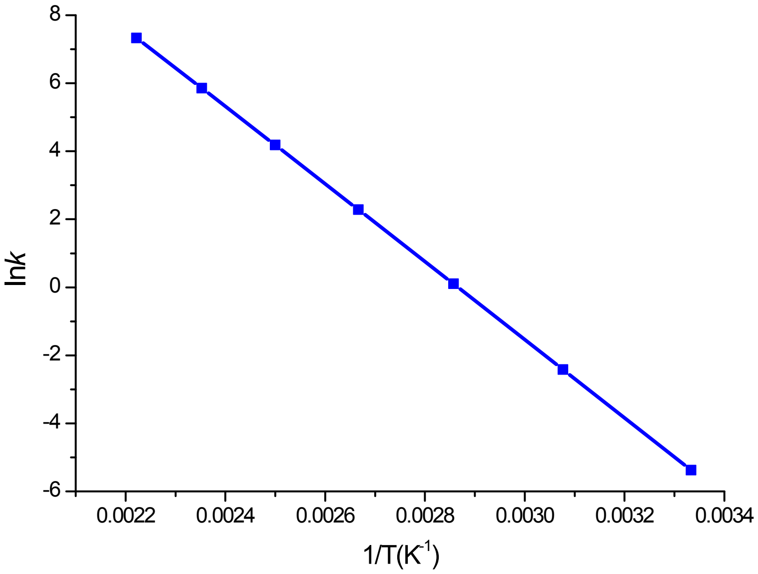
Refences:

1. B. Delley, J. Chem. Phys., 2000, 113, 7756-7764.
2. B. Delley, Mol. Simul., 2006, 32, 117-123.
3. B. Delley, J. Chem. Phys., 1990, 92, 508-517.
4. J. P. Perdew, K. Burke and M. Ernzerhof, Phys. Rev. Lett., 1996, 77, 3865–3868.

As shown in **Figure S2**, in aqueous solution, [Al-2] active site is more stable than [Al-1] active site, over the temperature range of 100 ~ 600 K.

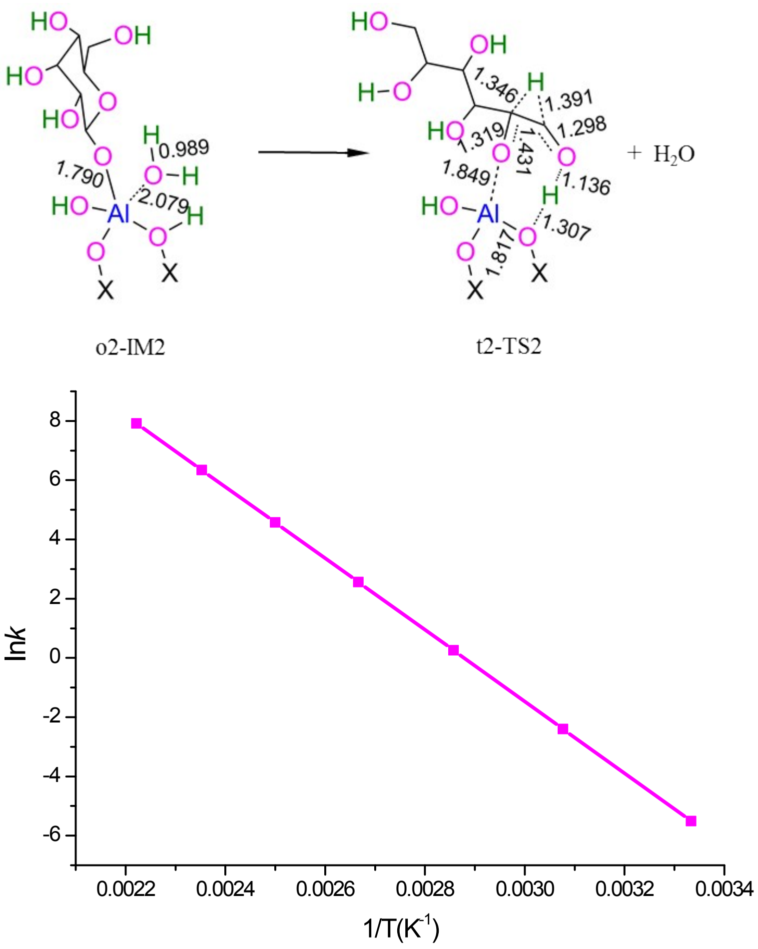


o1-IM2 t1-TS2



$$k_{\text{W-1}} = 1.70\times10^{14}\exp(-95,096/RT)$$

Figure S4: Arrhenius plots of rate constants for the crucial reaction step of o1-IM2 → t1-TS2 + H_2O in the isomerization of glucose to fructose catalyzed by **[Al-1]**.



$$k_{\text{W-2}} = 1.27 \times 10^{15} \exp(-100,458 / RT)$$

Figure S5: Arrhenius plots of rate constants for the crucial reaction step of o2-IM2 → t2-TS2 + H_2O in the isomerization of glucose to fructose catalyzed by **[Al-2]**.

Table S1: Sum of electronic energies (E, hartree) and the relative energies (E_{r}, kJ mol^{-1}) of various species with respect to the reactants for the reaction of Glucose → Fructose catalyzed by **[Al-1]** at the hybrid quantum mechanics (QM, GGA-PBE/DNP) and molecular mechanics (MM, Universal) calculations.

Species	E	E_{r}
Glucose	-686.69845	
Chain-glucose	-686.68343	
Chain-fructose	-686.69206	
Fructose	-686.69987	
H_2O	-76.37872	
[Al-1]	-2535.06733	
[Al-1] + Glucose	-3221.76578	0.0
o1-IM1	-3221.77655	-28.3
o1-TS1	-3221.76923	-9.1
o1-IM2	-3221.79468	-75.9
o1-IM3	-3145.40030	
o1-IM3 + H_2O	-3221.77902	-34.8
o1-TS2	-3145.38886	
o1-TS2 + H_2O	-3221.76758	-4.7
o1-IM4	-3145.39376	
o1-IM4 + H_2O	-3221.77247	-17.6
1-IM5	-2535.08739	
1-IM5 + Chain-glucose	-3221.77082	-13.2
1-TS3	-2535.05916	
1-TS3 + Chain-glucose	-3221.74259	60.9
[Al-1] + Chain-glucose	-3221.75076	39.4
t1-IM1	-3221.76522	1.5
t1-TS1	-3221.75528	27.6
t1-IM2	-3221.77697	-29.4
t1-IM3	-3145.39444	
t1-IM3 + H_2O	-3221.77316	-19.4
t1-TS2	-3145.35942	
t1-TS2 + H_2O	-3221.73813	72.6
t1-IM4	-3145.39034	
t1-IM4 + H_2O	-3221.76906	-8.6
1-IM5 + Chain-fructose	-3221.77945	-35.9
1-TS3 + Chain-fructose	-3221.75122	38.2
[Al-1] + Chain-fructose	-3221.75939	16.8
c1-IM1	-3221.77475	-23.6
c1-TS1	-3221.77108	-13.9
c1-IM2	-3221.78326	-45.9
c1-IM3	-3145.38946	
c1-IM3 + H_2O	-3221.76817	-6.3
c1-TS2	-3145.38658	
c1-TS2 + H_2O	-3221.76530	1.3

Continued Table S1

Species	E	E_r
c1-IM4	-3145.40320	
c1-IM4 + H_2O	-3221.78192	-42.4
c1-IM5 + Fructose	-3221.78726	-56.4
c1-TS3 + Fructose	-3221.75903	17.7
[Al-1] + Fructose	-3221.76720	-3.7

Table S2: Sum of electronic energies (*E*, hartree) and the relative energies (E_r , kJ mol^{-1}) of various species with respect to the reactants for the reaction of Glucose → Fructose catalyzed by **[Al-2]** at the hybrid quantum mechanics (QM, GGA-PBE/DNP) and molecular mechanics (MM, Universal) calculations.

Species	*E*	E_r
Glucose	-686.69845	
Chain-glucose	-686.68343	
Chain-fructose	-686.69206	
Fructose	-686.69987	
H_2O	-76.37872	
[Al-2]	-3322.40542	
[Al-2] + Glucose	-4009.10387	0.0
o2-IM1	-4009.11472	-28.5
o2-TS1	-4009.10906	-13.6
o2-IM2	-4009.13355	-77.9
o2-IM3	-3932.74321	
o2-IM3 + H_2O	-4009.12193	-47.4
o2-TS2	-3932.73999	
o2-TS2 + H_2O	-4009.11871	-38.9
o2-IM4	-3932.74271	
o2-IM4 + H_2O	-4009.12143	-46.1
2-IM5	-3322.41978	
2-IM5 + Chain-glucose	-4009.10321	1.7
2-TS3	-3322.40070	
2-TS3+ Chain-glucose	-4009.08413	51.8
[Al-2] + Chain-glucose	-4009.08886	39.4
t2-IM1	-4009.11793	-36.9
t2-TS1	-4009.10258	3.4
t2-IM2	-4009.10606	-5.7
t2-IM3	-3932.73241	
t2-IM3 + H_2O	-4009.11113	-19.0
t2-TS2	-3932.70149	
t2-TS2 + H_2O	-4009.08020	62.2
t2-IM4	-3932.73484	
t2-IM4 + H_2O	-4009.11355	-25.4
2-IM5 + Chain-fructose	-4009.11183	-20.9
2-TS3 + Chain-fructose	-4009.09276	29.2
[Al-2] + Chain-fructose	-4009.09748	16.8
c2-IM1	-4009.12255	-49.0
c2-TS1	-4009.10307	2.1
c2-IM2	-4009.11537	-30.2
c2-IM3	-3932.73477	
c2-IM3 + H_2O	-4009.11349	-25.2
c2-TS2	-3932.73139	
c2-TS2 + H_2O	-4009.11010	-16.3

Continued Table S2

pecies	E	E_r
c2-IM4	-3932.74151	
c2-IM4 + H_2O	-4009.12022	-42.9
2-IM5 + Fructose	-4009.11965	-41.4
2-TS3 + Fructose	-4009.10057	8.7
[Al-2] + Fructose	-4009.10530	-3.7