Supplementary Information

Roles of acidic sites in alumina catalysts for efficient D-xylose conversion to lactic acid

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1. Lactic acid production from xylose over the different kinds of catalysts.

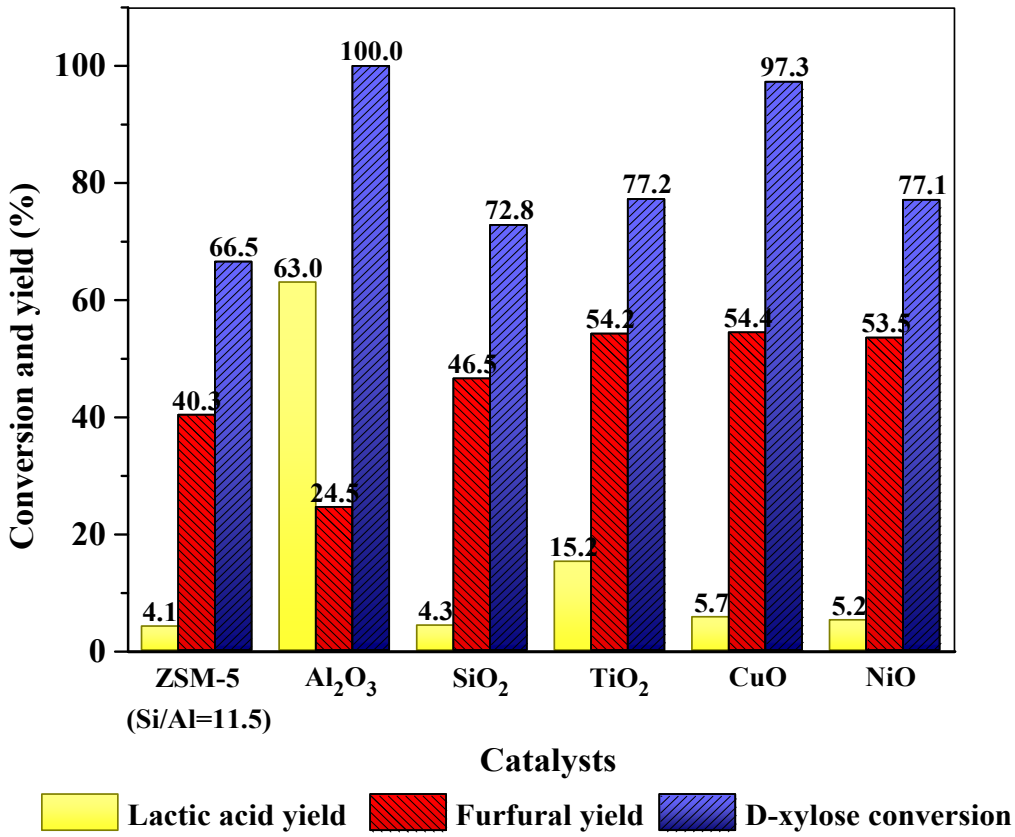


Figure S1 Lactic acid production from xylose over the different kinds of catalysts. Reaction conditions: D-xylose solution, 0.2 M; catalyst weight, 0.5 g; reaction temperature, 170 °C; initial N_2 pressure, 15 bar and reaction time, 4 h.

2. Lactic acid production from sugars over γ-Al_2O_3 catalyst

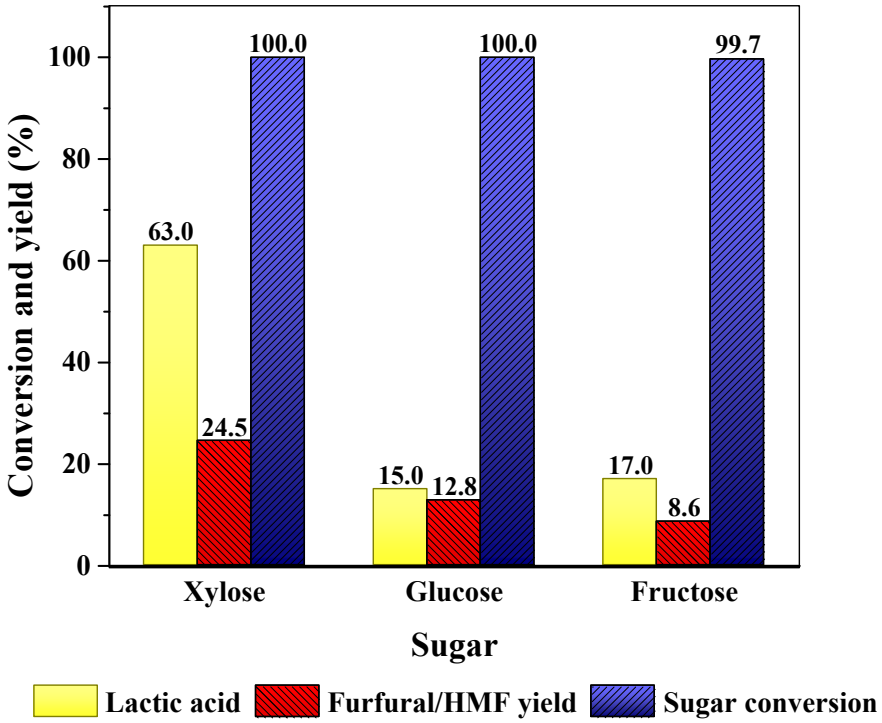
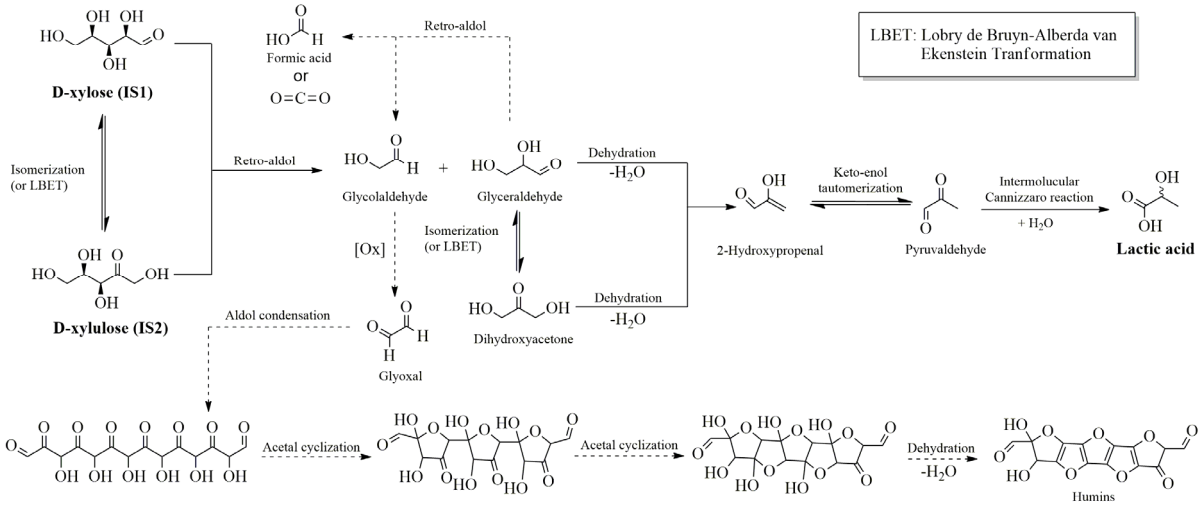


Figure S2 Lactic acid production from sugars including xylose, glucose and fructose over γ-Al_2O_3 catalyst. Reaction conditions: Sugar solution, 0.2 M; catalyst weight, 0.5 g; reaction temperature, 170 °C; initial N_2 pressure, 15 bar and reaction time, 4 h.

3. Proposed reaction pathway of D-xylose conversion to lactic acid

(a) Lactic acid production (Path A)



(b) Furfural production (Path B and C)

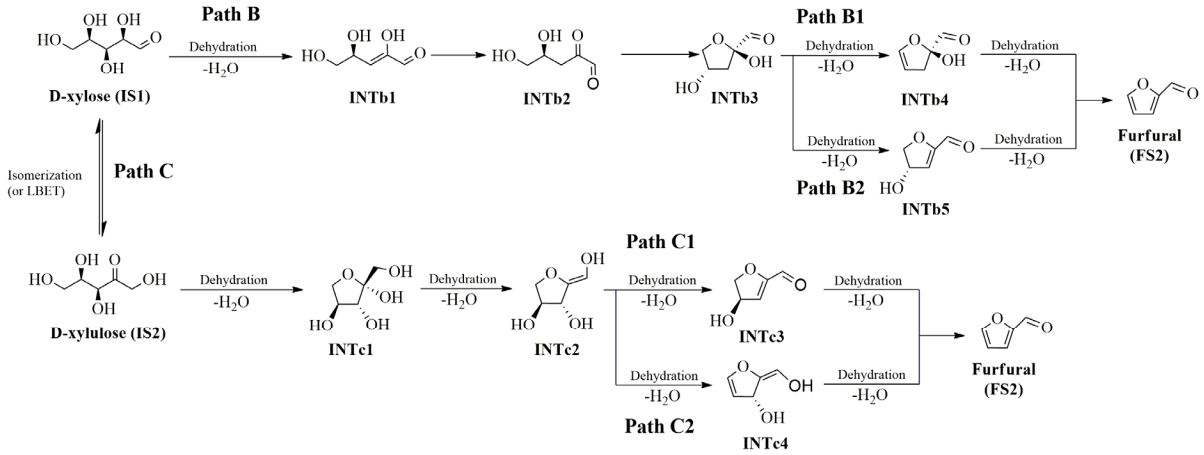


Figure S3 Proposed reaction pathway of D-xylose conversion to lactic acid and furfural modified from literatures [1-3].

4. XRD pattern of the catalysts before and after uses

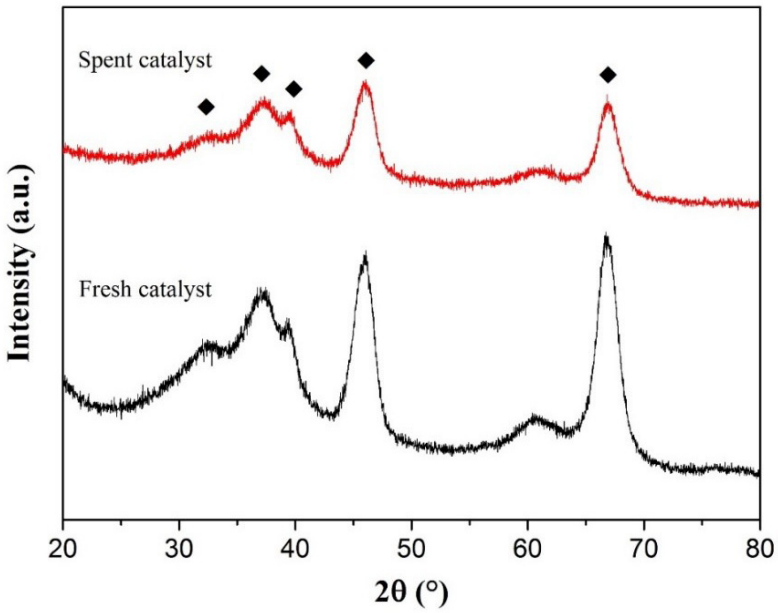


Figure S4 XRD patterns of fresh and spent Al-RT catalyst after the 3rd cycle of the reaction test. Reaction conditions: D-xylose concentration, 0.2 M; catalyst weight, 0.5 g; reaction temperature, 170 °C; and reaction time, 4 h.

5. Computational details

5.1 γ-Al_2O_3 (110) surface

The bulk γ-Al_2O_3 was fully optimized by using 7×5×5 of k-point generated by the Monkhorst-Pack scheme. The (110) surface was cleaved from the optimized bulk, which has a= 5.708 Å, b= 8.186 Å, c= 7.861 Å and β= 90.22°. A size of (1×1) γ-Al_2O_3 (110) surface is 7.861 Å×8.186 Å×22.305 Å. The (110) slab is separated by 15 Å of vacuum. Two bottom atomic layers of six atomic layers were fixed during the calculation.

5.2 Ab initio molecular dynamics simulation of hydroxylated γ-Al_2O_3 (110) surface

Ab-initio Molecular Dynamics (AIMD) simulation was conducted to obtain the hydroxylated Al_2O_3 (110) surface with the OH coverage (Θ) of ~12.4 OH/nm^2. The pre-optimized surface of four water molecules on Al_2O_3 (110) was simulated by Nosé-Hoover thermostat for 5 ps with a time step of 0.5 fs. Γ-point sampling of the Brillouin zone was used for the AIMD calculation. For the pre-optimized configuration, three water molecules dissociate and one molecule is in the molecular form at the Al^{4a**} site. During AIMD simulation around 300K, that molecular water dissociates as shown in **Figure S5**. The change of O-H bond distance of H_2O adsorbed on the Al^{4a**} site is demonstrated in **Figure S5c**. Therefore, all adsorbed water molecules completely dissociate at low temperature. The final configuration at 5000 fs was re-optimized for using in further adsorption calculations.

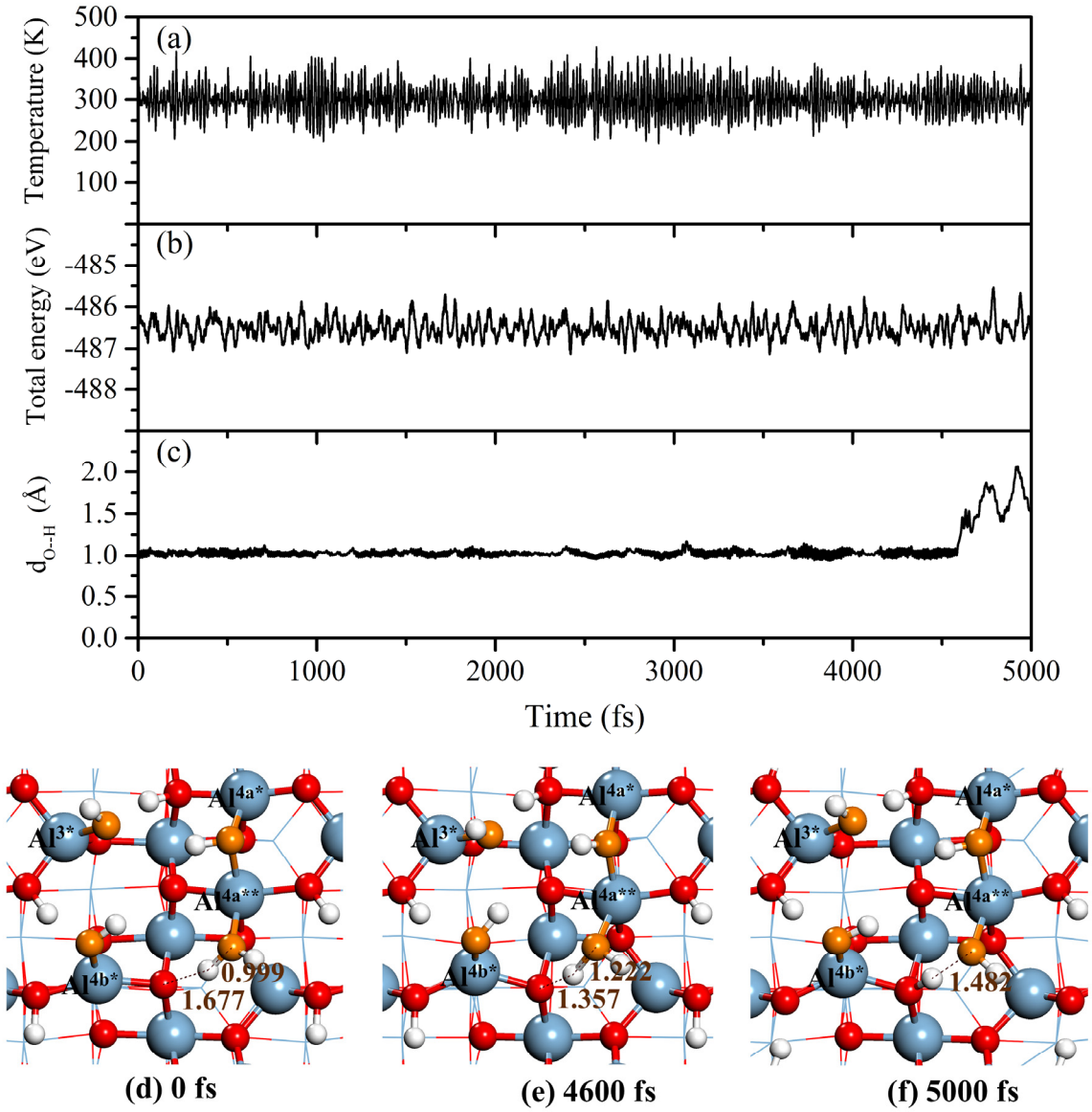
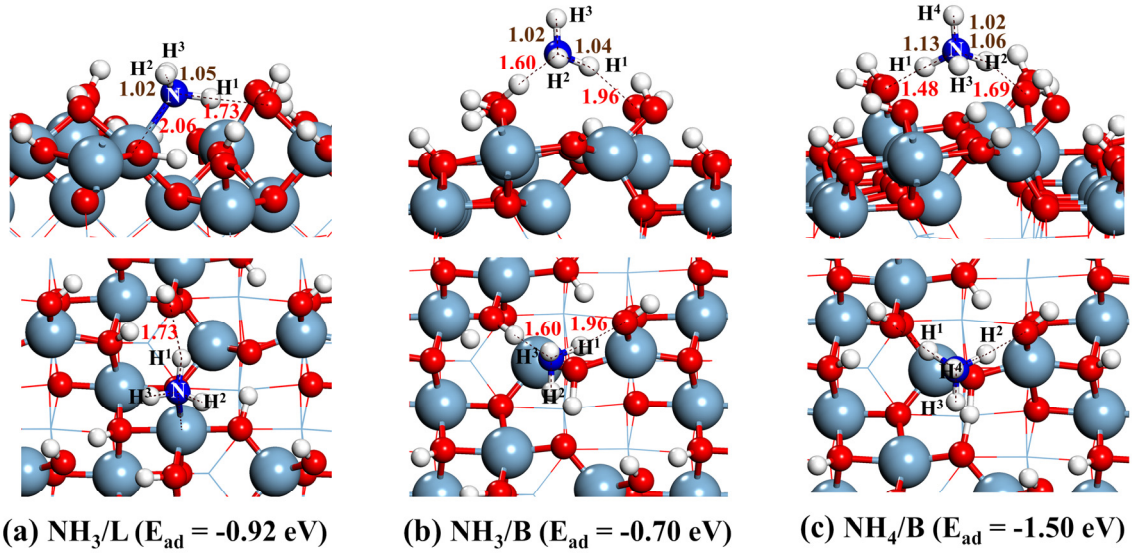


Figure S5 (a) Temperature, (b) Total energy and (c) O-H bond distance of H_2O adsorbed on the Al^{4a**} site during AIMD simulation of four water molecules γ-Al_2O_3 (110) surface. The top view of configurations at (d) 0 fs, (e) 4600 fs and (f) 5000 fs. The red and orange balls represent the oxygen atoms of the catalyst and the water molecules, respectively.

5.3 Adsorption on hydroxylated γ-Al_2O_3 (110) in gas phase

The interaction between gas species and the hydroxylated Al_2O_3 (110) surface was further investigated via the adsorption calculation. The adsorption energy (E_{ads}) can be calculated from $E_{ads} = E_{molecule/surface} - E_{surface} - E_{molecule}$. $E_{molecule/surface}$ is a total energy of a molecule adsorbed surface, while $E_{surface}$ and $E_{molecule}$ are the total energies of a clean surface and an isolated molecule, respectively. The 1x1 slab was used for NH_3 and NH_4 adsorption calculations.



(a) NH_3/L (E_{ad} = -0.92 eV) **(b) NH_3/B (E_{ad} = -0.70 eV)** **(c) NH_4/B (E_{ad} = -1.50 eV)**

Figure S6 Adsorption configurations of (a) NH_3/Al (NH_3L), (b) NH_3/B and (ce) NH_4/B on hydroxylated γ-Al_2O_3 (110) (Θ = 12.4 OH/nm^2) Al and O of the top two layers are represented by light blue and red balls, respectively. The blue and white balls represent N and H, respectively.

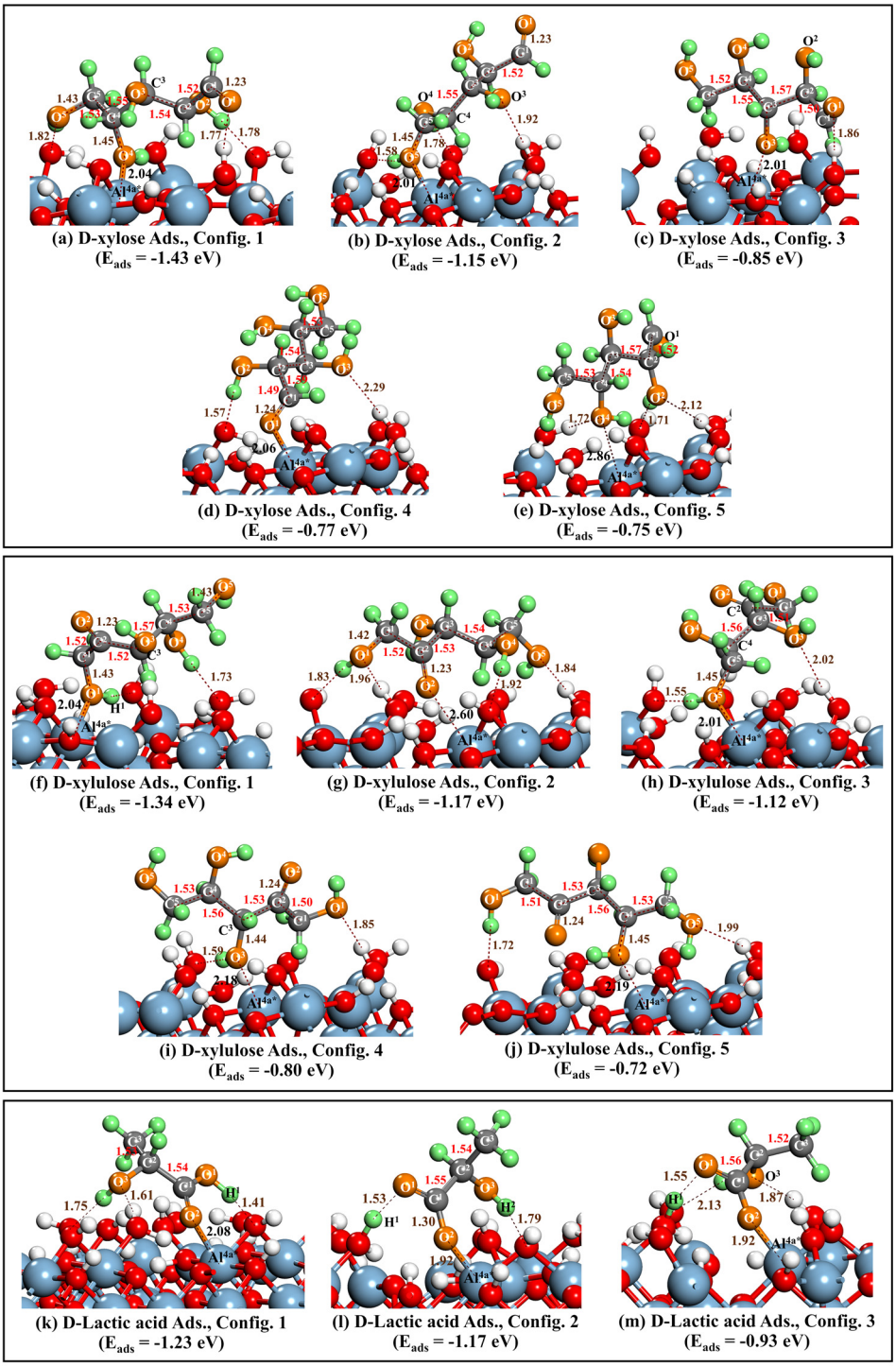


Figure S7 Selected possible configurations and E_{ads} values of (a)-(e) D-Xylose, (f)-(j) D-Xylulose, and (k)-(l) D-Lactic acid on hydroxylated γ-Al_2O_3 (110). The orange and green balls represent O and H of adsorbed molecules, respectively.

5.4 Effect of solvation on the stability of intermediates

Solvation energy

The implicit solvation method implemented in VASPsol, in which the solvent is treated as a continuum dielectric, was used in this work. To simulate the implicit aqueous system, the dielectric constant (ε), or relative permittivity, of water was used. This dielectric constant is typically expressed as a ratio relative to the vacuum permittivity (ε=1) and it is varied as a function of temperature. According Bradley and Pltzer's work [4], the dielectric constant of water at temperature T, ε(T), can be calculated by following equations.

$$\varepsilon(T) = \varepsilon(1000) + C\ln((B+P)/(B+1000)) \quad \text{(Eq. S-1)}$$

$$\varepsilon(1000) = U_1 \exp[U_2T + U_3T^2] \quad \text{(Eq. S-2)}$$

$$C = U_4 + U_5/(U_6+T) \quad \text{(Eq. S-3)}$$

$$B = U_7 + U_8/T + U_9T \quad \text{(Eq. S-4)}$$

In Eq. S-1, ε(1000), C and B are temperature dependent parameters and they can be calculated by Eq. S-2 to S-4. The values of constants in Eq. S-2 to S-4 for the ε of water were given in [4].

The ε of water at 298 K (or room temperature) and 443 K (or 170 °C) are 78.4 and 39.9, respectively. These ε values were applied to simulate the implicit water systems at room temperature and the optimum temperature for the reaction observed in this work. The role of water towards the adsorption of molecules on the catalyst surface and also thermodynamic stability of intermediates are compared to vacuum calculations.

Energy profiles

An isolated molecule in catalyst free condition was calculated in a 20 Å×20 Å×20 Å box. The energy profiles of intermediates along the lactic acid- and furfural production pathways were investigated according the proposed scheme in **Figure S3**. In **Figure S8**, IS1, IS2, FS1 and FS2 states represent D-xylose, D-xylulose, D-lactic acid and furfural, respectively. Path A is the lactic acid production path. Following the Retro-aldol (RA) path, the INTa1 state represents the relative energy of glycolaldehyde and dihydroxyacetone ($E_{glycolaldehyde}$+ $E_{dihydroxyacetone}$) compared to the reference state (IS1). INTa2 represents the relative energy of glycolaldehyde and glyceraldehyde compared to the reference state. For the C3 intermediates, dihydroxyacetone reveals more energetic stable than glyceraldehyde. In the next step, INTa3 represents the relative energy state of glycolaldehyde, 2-Hydroxypropenal and one water. INTa4 represents the relative energy state of glycolaldehyde, pyruvaldehyde and one water. Intermediates of two dehydration pathways are depicted in **Figure S9**. The possible structures of each molecule were optimized in gas phase first. Then the most stable form was further optimized in implicit solvent.

The relative energies of molecules and intermediates in gas phase and solution phase compared to energies of D-xylose in gas and solution, respectively. The solvation energy (ΔE_{sol}) is the total energy difference of solution and vacuum calculations. The calculated ΔE_{sol} values are given in **Table S1**. At ε =78.4, our calculated ΔE_{sol} of H_2O is -0.32 eV, which agrees well with the literature [5].

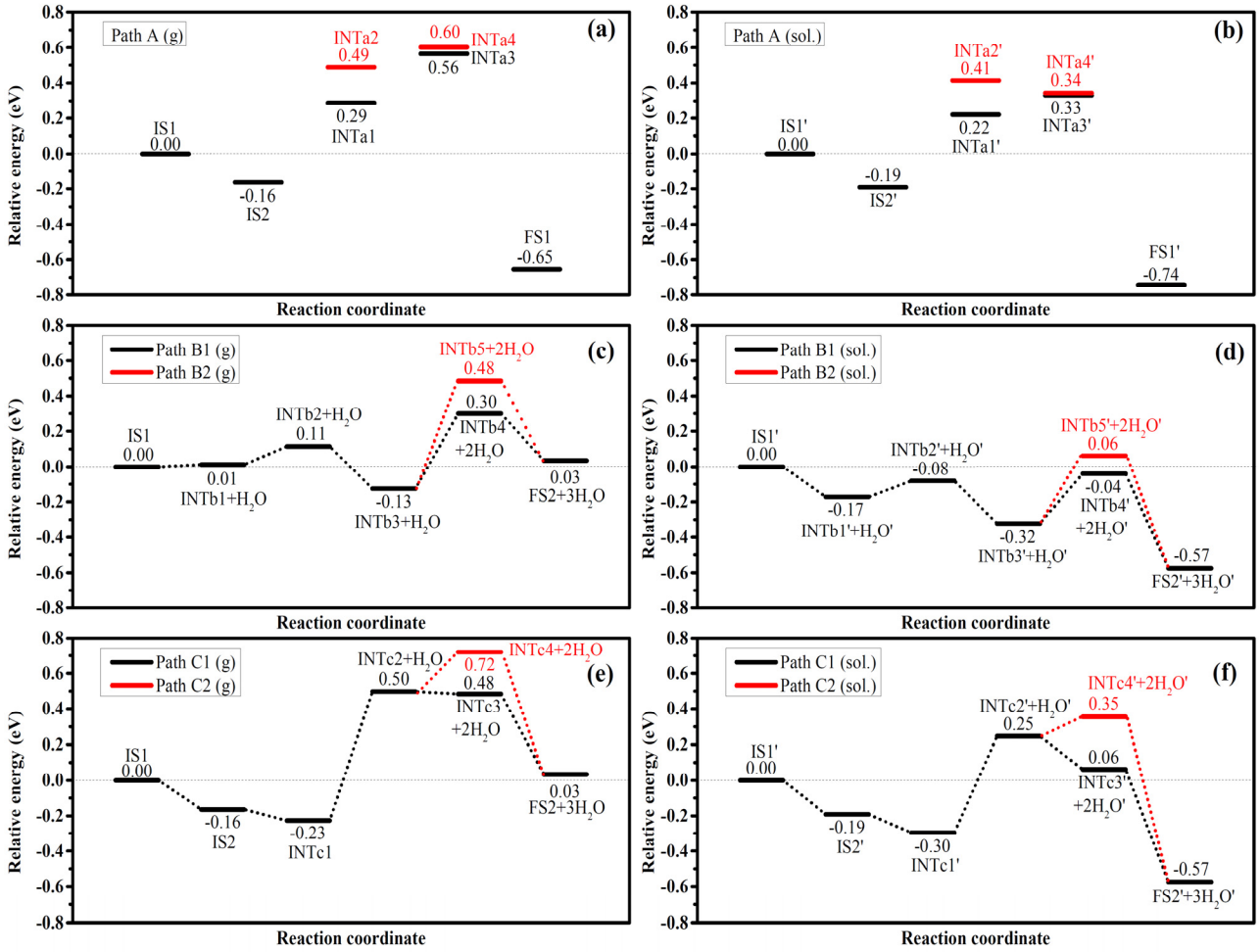


Figure S8 Energy profiles of the lactic acid production via (a) path A in gas phase, (b) path A in aqueous phase, and the furfural production via (c) path B in gas phase, (d) path B in aqueous phase, (e) path C in gas and (f) path C in aqueous phase. The ε of 78.4, representing water at 298 K, was used in the solution calculation.

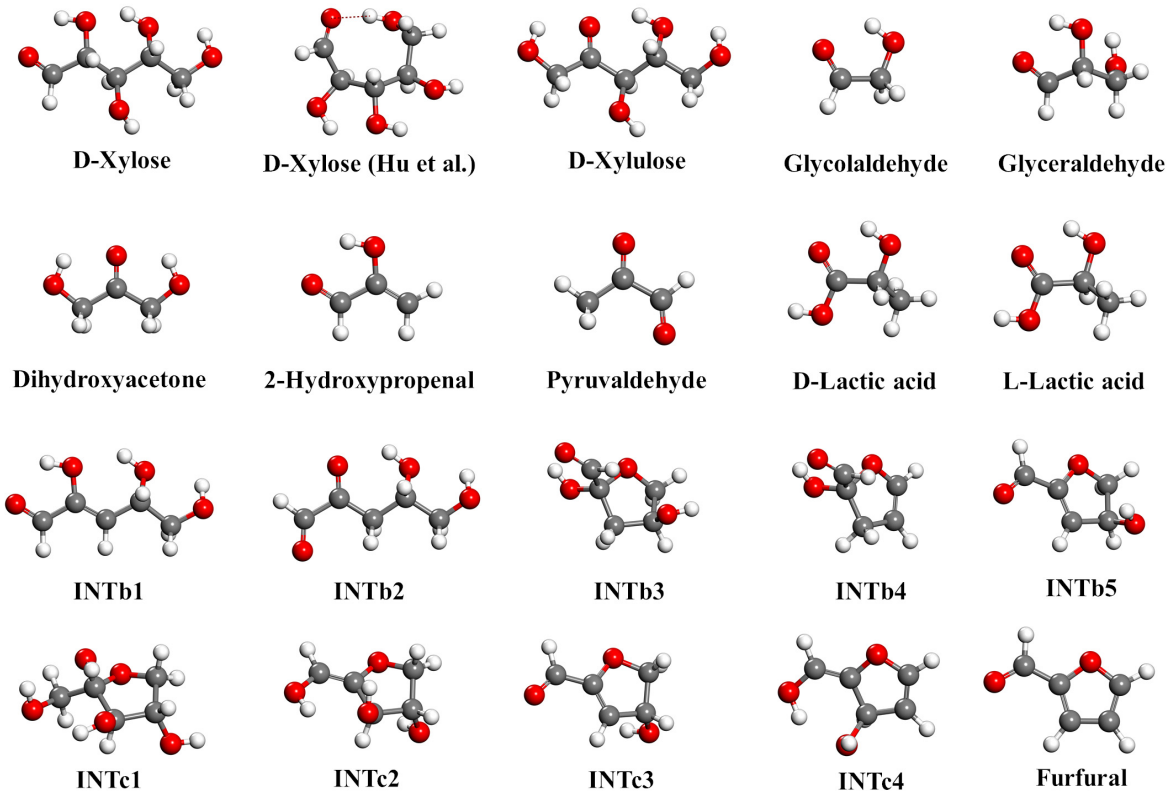


Figure S9 Three dimensional structures of molecules and intermediates of proposed pathways

Table S1 The calculated solvation energy (ΔE_{sol}) of molecules, intermediates, bare hydroxylated Al_2O_3 surface and gas adsorbed surfaces calculated by VASPsol.

System	ΔE_{sol} in water (eV)	
	at 298 K (ε =78.4)	at 443 K (ε =39.9)
H_2O	-0.32	-0.28
D-Xylose	-0.59	-0.50
D-Xylulose	-0.62	-0.52
Glycolaldehyde	-0.28	-0.24
Dihydroxyacetone	-0.38	-0.32
Glyceraldehyde	-0.38	-0.32
2-Hydroxypropenal	-0.23	-0.19
Pyruvaldehyde	-0.25	-0.21
D-Lactic acid	-0.40	-0.34
L-Lactic acid	-0.40	-0.34
Furfural	-0.25	-0.21
INTb1	-0.46	-0.38
INTb2	-0.47	-0.39
INTb3	-0.47	-0.40
INTb4	-0.29	-0.25
INTb5	-0.38	
INTc1	-0.66	
INTc2	-0.52	
INTc3	-0.38	
INTc4	-0.32	
Hydroxylated Al_2O_3 (2×2) slab	-22.50	-15.70
D-xylose/hydroxylated Al_2O_3 (Config. 1)	-22.16	-16.80
D-xylulose/hydroxylated Al_2O_3 (Config. 1)	-22.42	-15.83
D-lactic acid/hydroxylated Al_2O_3 (Config. 1)	-21.71	-15.83

Table S2 The calculated E_{ads} energies in gas and solution calculations.

Adsorption system	**E_{ads} (eV)**		
	Gas phase (ε =1)	**Aqueous at 25 °C (ε =78.4)**	**Aqueous at 170 °C (ε =39.9)**
D-xylose	-1.43	-0.51	-2.03
D-xylulose	-1.34	-0.64	-1.52
D-lactic acid	-1.23	-0.04	-1.01

Table S3 The coordinates of the optimized structures in xyz format calculated by VASPsol.

Molecule/ Intermediate	Optimized structure in solution (ε =78.4)	Optimized structure in solution (ε =39.9)
H_2O	O 9.674894 10.138355 10.106200 H 8.907768 10.738545 10.106200 H 10.447336 10.731499 10.106200	O 9.674886 10.138664 10.106200 H 8.908099 10.738390 10.106200 H 10.447015 10.731346 10.106200
D-Xylose	C 6.789362 10.327091 9.388465 C 8.021343 10.988866 9.942778 C 9.288612 10.219568 9.475016 C 10.568866 11.051962 9.702487 C 11.824959 10.234518 9.436279 O 13.013148 10.994493 9.678909 O 5.962365 10.972189 8.748111 O 8.034811 12.366115 9.594736 O 9.291050 9.018240 10.249519 O 10.613686 12.173966 8.809771 H 7.992694 10.883012 11.044768 H 9.217417 9.992332 8.397030 H 10.586912 11.397901 10.755299 H 6.674440 9.240376 9.567338 H 11.802078 9.866352 8.393147 H 11.860792 9.371511 10.112648 H 12.969117 11.789465 9.113916 H 7.240568 12.514517 9.028152 H 9.613281 8.285535 9.693621 H 9.746096 12.629791 8.912213	C 6.785160 10.334520 9.383520 C 8.023000 10.989100 9.935921 C 9.288280 10.217280 9.467219 C 10.569720 11.043900 9.706000 C 11.828780 10.227119 9.450260 O 13.009681 11.002920 9.676220 O 5.966180 10.985240 8.739020 O 8.041020 12.365320 9.584500 O 9.282240 9.009820 10.232739 O 10.626940 12.164460 8.812980 H 7.994280 10.885039 11.038620 H 9.219920 10.000800 8.386700 H 10.579960 11.390840 10.758300 H 6.657400 9.250180 9.568820 H 11.807899 9.840700 8.413520 H 11.873680 9.376280 10.141820 H 12.928020 11.810560 9.133420 H 7.242180 12.511740 9.023300 H 9.624020 8.284639 9.679500 H 9.763201 12.627380 8.911780
D-Xylulose	C 6.850414 10.306332 9.704378 C 8.098253 10.946416 9.164895 C 9.388214 10.145894 9.145705	C 6.850020 10.305480 9.703340 C 8.099580 10.944700 9.165820 C 9.389480 10.144200 9.145781

	C 10.585400 11.025291 9.593542	C 10.586760 11.023120 9.594339
	C 11.882848 10.230644 9.627895	C 11.884720 10.229540 9.624760
	O 12.973395 11.023891 10.104454	O 12.975860 11.027580 10.089660
	O 5.738726 11.176597 9.617368	O 5.740640 11.176480 9.611460
	O 8.043978 12.110853 8.743832	O 8.046640 12.110420 8.748840
	O 9.230323 8.991994 9.964897	O 9.229800 8.990540 9.966000
	O 10.783894 12.108330 8.678158	O 10.785379 12.107400 8.680960
	H 7.040126 10.002084 10.749741	H 7.038600 10.003720 10.749920
	H 9.557526 9.865082 8.088911	H 9.559060 9.863521 8.088799
	H 10.379481 11.412395 10.610174	H 10.381100 11.408060 10.611859
	H 6.672756 9.371543 9.141725	H 6.672580 9.368700 9.143680
	H 12.093750 9.839848 8.614721	H 12.089260 9.833020 8.612000
	H 11.784355 9.383867 10.319096	H 11.792660 9.386700 10.321160
	H 13.066215 11.787243 9.503180	H 13.037320 11.805700 9.503580
	H 6.081246 12.015924 9.233541	H 6.088660 12.014740 9.230400
	H 9.656795 8.233553 9.526620	H 9.657440 8.232020 9.530160
	H 9.906107 12.538224 8.560567	H 9.908220 12.540300 8.570880
Glycolaldehyde	C 9.549100 10.979641 11.038560	C 9.548840 10.980379 11.037880
	C 9.098540 10.912060 9.616140	C 9.097960 10.911360 9.614520
	O 8.654440 12.162640 9.127660	O 8.653980 12.162661 9.130140
	O 9.517840 12.031899 11.674260	O 9.515000 12.034640 11.668921
	H 9.913120 10.034680 11.491800	H 9.914440 10.037580 11.495319
	H 9.943200 10.522440 9.015400	H 9.942101 10.522460 9.012900
	H 8.299900 10.147480 9.553020	H 8.299660 10.146760 9.550799
	H 8.749260 12.793200 9.876780	H 8.753400 12.788160 9.883100
Dihydroxyacetone	C 9.842100 10.235120 10.121680	C 9.842120 10.232960 10.122319
	C 8.545800 9.480420 10.001160	C 8.543941 9.480620 10.000660
	C 11.139560 9.483479 10.248739	C 11.141300 9.483140 10.248500
	O 7.438560 10.357881 9.893340	O 7.441160 10.362480 9.892839
	O 12.245720 10.362540 10.356220	O 12.243320 10.366381 10.356460

	O 9.840720 11.470940 10.115360 H 8.440360 8.824320 10.883841 H 8.608120 8.820120 9.117559 H 11.247740 8.825480 9.367741 H 11.076380 8.824560 11.133300 H 7.811080 11.267780 9.922980 H 11.873060 11.271980 10.319080	O 9.840840 11.468740 10.117680 H 8.435019 8.823640 10.882501 H 8.604780 8.818280 9.118100 H 11.251640 8.824420 9.368000 H 11.080800 8.822100 11.131880 H 7.821460 11.269160 9.923780 H 11.862840 11.272679 10.318280
Glyceraldehyde	C 9.779120 10.613260 10.649700 C 11.070139 9.785720 10.546080 C 8.565020 9.727440 10.607380 O 9.730120 11.593241 9.624900 O 11.156799 9.069220 9.316620 O 7.683920 9.880000 9.765759 H 9.782001 11.091841 11.651440 H 11.097120 9.044940 11.357620 H 11.925120 10.470680 10.673321 H 8.505160 8.928460 11.375999 H 8.883380 11.445360 9.145480 H 11.192660 9.723619 8.593100	C 9.780860 10.610960 10.646700 C 11.072081 9.784560 10.550520 C 8.562820 9.729580 10.603880 O 9.737720 11.583900 9.615720 O 11.165260 9.069201 9.321020 O 7.680220 9.892660 9.766760 H 9.777519 11.095039 11.646040 H 11.096940 9.043180 11.361620 H 11.926021 10.469980 10.681520 H 8.500020 8.926680 11.368660 H 8.884340 11.442539 9.146060 H 11.186780 9.725500 8.598920
2-Hydroxypropenal	C 9.880980 10.409540 10.303220 C 11.041221 9.973660 10.834520 C 8.635220 9.660660 10.520639 O 9.772540 11.534580 9.551080 O 7.565840 10.046061 10.036900 H 11.035380 9.059660 11.426220 H 11.982300 10.503420 10.692680 H 8.707980 8.741480 11.135100 H 8.825940 11.621540 9.289240	C 9.882640 10.407640 10.303840 C 11.043839 9.973780 10.833960 C 8.634380 9.662060 10.520240 O 9.770480 11.532240 9.551040 O 7.568740 10.056660 10.036360 H 11.042959 9.060480 11.426740 H 11.982519 10.507040 10.690380 H 8.700580 8.740160 11.132200 H 8.821259 11.610519 9.294880
Pyruvaldehyde	C 8.774560 10.399780 9.737020 C 10.012701 11.226681 9.739000	C 8.774580 10.399700 9.737020 C 10.013080 11.227280 9.739000

	C 11.367960 10.501160 9.745300	C 11.367940 10.500860 9.745300
	O 10.044360 12.456660 9.736700	O 10.044760 12.456779 9.736680
	O 11.475640 9.285920 9.750220	O 11.475460 9.285980 9.750240
	H 8.778360 9.733700 8.860380	H 8.778040 9.733300 8.860701
	H 8.770160 9.742360 10.620260	H 8.769840 9.741980 10.619960
	H 7.884840 11.036960 9.729820	H 7.884960 11.036880 9.729820
	H 12.244821 11.186840 9.745480	H 12.244760 11.187220 9.745480
D-Lactic acid	C 9.334460 10.162899 9.062119	C 9.333700 10.162640 9.061840
	C 8.605360 10.403759 10.383821	C 8.605300 10.403600 10.383739
	C 10.814080 10.494040 9.156580	C 10.813340 10.493919 9.156080
	O 8.751861 10.934581 8.014040	O 8.752640 10.934720 8.013920
	O 11.464220 9.757980 10.064520	O 11.464439 9.757640 10.065340
	O 11.342879 11.353320 8.452780	O 11.342421 11.352620 8.453160
	H 9.266560 9.090020 8.804480	H 9.265800 9.089660 8.804140
	H 8.710040 11.451620 10.698500	H 8.710060 11.451360 10.697941
	H 9.000840 9.750139 11.172300	H 9.001120 9.750300 11.172180
	H 7.539260 10.180240 10.247400	H 7.539220 10.180540 10.247740
	H 9.478340 11.485681 7.646720	H 9.481220 11.484940 7.649520
	H 12.415280 10.012079 10.083341	H 12.413960 10.014460 10.080980
L-Lactic acid	C 10.159860 9.941280 11.129780	C 10.159921 9.939620 11.130600
	C 9.454781 9.073561 10.088039	C 9.454000 9.073020 10.088100
	C 11.621680 10.172120 10.786400	C 11.621040 10.172979 10.787060
	O 9.507880 11.202360 11.264139	O 9.510080 11.200700 11.265181
	O 12.331240 9.040580 10.711360	O 12.333740 9.042000 10.711599
	O 12.088300 11.296140 10.607380	O 12.084940 11.297379 10.607759
	H 10.143419 9.418100 12.103620	H 10.144360 9.415300 12.104140
	H 9.507380 9.541960 9.095780	H 9.506660 9.541920 9.095820
	H 8.400140 8.960740 10.371480	H 8.399180 8.964100 10.371460
	H 9.911520 8.076700 10.038700	H 9.907300 8.074580 10.038260
	H 10.193581 11.884520 11.089140	H 10.198621 11.878780 11.085481

	H 13.269020 9.246160 10.491800	H 13.268940 9.253839 10.492140
Furfural	C 8.938620 11.099239 10.071620	C 8.935980 11.093360 10.069560
	C 9.411140 9.800360 10.066580	C 9.416780 9.797700 10.066280
	C 10.825159 9.880740 10.053340	C 10.830420 9.887040 10.060300
	C 11.137400 11.220480 10.051001	C 11.133900 11.228480 10.060240
	C 7.626580 11.692440 10.086761	C 7.621960 11.683640 10.076480
	O 10.011840 11.977640 10.061379	O 10.003800 11.978001 10.065680
	O 6.571400 11.041340 10.102700	O 6.567600 11.033020 10.081240
	H 8.798440 8.904060 10.071699	H 8.810360 8.897260 10.068140
	H 11.533260 9.058420 10.046721	H 11.544060 9.069860 10.056620
	H 12.075339 11.765800 10.043499	H 12.067861 11.780439 10.057079
	H 7.616600 12.804880 10.083880	H 7.613060 12.796579 10.077560
INTb1	C 6.914760 10.215020 9.153920	C 6.914340 10.221439 9.154980
	C 8.121260 11.013980 9.371680	C 8.127380 11.009920 9.371720
	C 9.334300 10.423079 9.477779	C 9.337400 10.415120 9.483960
	C 10.627720 11.160721 9.674920	C 10.630060 11.153140 9.679840
	C 11.822300 10.260361 9.381200	C 11.827420 10.260080 9.377400
	O 13.068260 10.888260 9.680861	O 13.069340 10.900540 9.664520
	O 5.805840 10.751240 9.038420	O 5.812680 10.770659 9.035960
	O 7.945300 12.360260 9.453780	O 7.957460 12.357960 9.445840
	O 10.755180 12.305380 8.809540	O 10.753241 12.301840 8.819901
	H 9.352301 9.332260 9.417600	H 9.352640 9.323940 9.431520
	H 10.695961 11.490680 10.732059	H 10.701580 11.478280 10.738440
	H 7.047800 9.116260 9.099700	H 7.036120 9.121080 9.104060
	H 11.781040 9.946119 8.321500	H 11.778919 9.944099 8.318460
	H 11.758260 9.362440 10.011240	H 11.777400 9.362660 10.009260
	H 13.143179 11.681200 9.117060	H 13.109560 11.713600 9.126480
	H 6.985640 12.543820 9.321060	H 6.997800 12.539840 9.308200
	H 10.043301 12.937540 9.027699	H 10.019040 12.914439 9.019480

INTb2	C 6.740541 10.240379 9.459900 C 8.060320 11.024360 9.526140 C 9.338340 10.266121 9.360860 C 10.590100 11.100660 9.620980 C 11.846140 10.251160 9.502260 O 13.027580 10.972380 9.861401 O 6.689780 9.024099 9.385620 O 7.979520 12.236920 9.722000 O 10.729620 12.173480 8.672960 H 9.296220 9.387361 10.027121 H 9.345320 9.849660 8.336460 H 10.540640 11.517720 10.643020 H 5.834060 10.883020 9.506820 H 11.922680 9.863940 8.468520 H 11.778400 9.394239 10.186720 H 13.076659 11.756680 9.282220 H 10.033081 12.829380 8.868580	C 6.738560 10.256359 9.470480 C 8.063700 11.033200 9.519840 C 9.337620 10.263580 9.370520 C 10.593740 11.093740 9.624080 C 11.847100 10.240860 9.499599 O 13.031599 10.968500 9.831340 O 6.680480 9.041800 9.380340 O 7.991320 12.250800 9.684700 O 10.734560 12.163600 8.673200 H 9.288799 9.392000 10.045520 H 9.347300 9.834920 8.351320 H 10.551480 11.514740 10.645061 H 5.836540 10.904380 9.539380 H 11.908799 9.840220 8.469900 H 11.789960 9.392940 10.196000 H 13.049940 11.760660 9.261180 H 10.037499 12.819300 8.869101
INTb3	C 7.212540 10.702459 10.372320 C 8.040340 11.241540 9.203940 C 9.274880 10.400240 8.856140 C 10.439661 11.083380 9.565280 C 9.981880 12.538219 9.575640 O 8.543800 12.490240 9.747960 O 5.988820 10.681160 10.346280 O 7.234340 11.445980 8.080999 O 10.546200 10.530760 10.885780 H 9.170200 9.351300 9.161380 H 9.409240 10.431860 7.766960 H 11.387320 10.961480 9.015960 H 7.793740 10.387259 11.263781	C 7.213380 10.704880 10.373159 C 8.041800 11.245260 9.205359 C 9.274600 10.402599 8.853820 C 10.440921 11.083241 9.562019 C 9.985200 12.538641 9.574841 O 8.547780 12.493259 9.747120 O 5.990120 10.680740 10.341681 O 7.230860 11.449900 8.086200 O 10.544559 10.527821 10.881200 H 9.169880 9.353760 9.159500 H 9.405640 10.434000 7.764240 H 11.387900 10.958960 9.012000 H 7.791760 10.390379 11.266760

	H 10.228041 13.031760 8.619761 H 10.401740 13.118540 10.407061 H 6.310081 11.558260 8.397161 H 11.276979 10.985160 11.345779	H 10.233040 13.033700 8.619940 H 10.406321 13.117960 10.406740 H 6.306760 11.539760 8.410541 H 11.269300 10.984720 11.347080
INTb4	C 6.981840 10.892361 10.045860 C 8.140920 11.177920 9.089581 C 9.351060 10.231700 9.229099 C 10.484281 11.173679 9.538940 C 9.990940 12.400219 9.722179 O 8.616060 12.498980 9.565860 O 5.818480 10.924720 9.673900 O 7.706620 11.267839 7.775980 H 9.191740 9.496940 10.033999 H 9.485340 9.669420 8.293880 H 11.531800 10.892780 9.596300 H 7.262020 10.691700 11.100901 H 10.481260 13.338700 9.970981 H 6.757600 11.525440 7.783520	C 6.980980 10.896799 10.042300 C 8.143400 11.179960 9.089640 C 9.352680 10.232759 9.227460 C 10.486421 11.173300 9.539060 C 9.993500 12.399460 9.724880 O 8.619081 12.499599 9.568640 O 5.820140 10.939179 9.663960 O 7.705100 11.273780 7.777880 H 9.193160 9.496180 10.030700 H 9.485940 9.672441 8.291160 H 11.534040 10.892500 9.594680 H 7.254160 10.691080 11.098221 H 10.484039 13.337160 9.975600 H 6.747360 11.498220 7.796820
INTb5	C 6.851120 10.811100 9.105180 C 8.256300 11.153299 9.368800 C 9.375020 10.419001 9.179040 C 10.540640 11.172620 9.758460 C 9.919960 12.566400 9.967520 O 8.467060 12.396160 9.916220 O 6.494640 9.744380 8.605520 O 11.035580 10.542541 10.958139 H 9.415760 9.411220 8.776180 H 11.411520 11.224660 9.092600 H 6.113360 11.591459 9.392220 H 10.193620 13.247180 9.149260	

	H 10.179041 13.014359 10.934100 H 10.275579 10.363040 11.545780	
INTc1	C 7.220080 11.258101 8.416640 C 8.203360 11.277941 9.584960 C 9.367180 10.222380 9.500700 C 10.654520 11.054720 9.655360 C 10.142879 12.399159 10.164221 O 7.473860 11.092680 10.786780 O 6.475340 10.040819 8.379760 O 8.840340 12.554560 9.560280 O 9.275180 9.253060 10.548960 O 11.266541 11.146719 8.361100 H 11.332819 10.571719 10.376659 H 7.769360 11.328760 7.468400 H 9.364180 9.730640 8.518820 H 6.555540 12.136420 8.506120 H 10.763081 13.249081 9.853680 H 10.057420 12.393380 11.265079 H 7.916160 10.343060 11.255280 H 6.022500 9.957000 9.241820 H 8.780900 8.480160 10.215501 H 12.079559 11.678420 8.452860	
INTc2	C 7.088420 10.535940 9.208060 C 8.373140 10.889840 9.384500 C 9.600640 10.013160 9.400540 C 10.748820 11.058260 9.472140 C 10.060019 12.230579 10.156919 O 6.637440 9.267660 8.932179 O 8.713660 12.228720 9.610700 O 9.610661 9.068340 10.488041	

	O 11.256080 11.389740 8.175640 H 11.594600 10.662201 10.047501 H 6.276620 11.260960 9.263741 H 9.714120 9.409679 8.488260 H 10.513161 13.202580 9.931720 H 10.016621 12.081079 11.249360 H 7.371920 8.622520 8.945540 H 9.244440 9.502419 11.282579 H 10.562400 11.854939 7.669559	
INTc3	C 7.009460 10.456380 9.212460 C 8.404160 10.853120 9.454960 C 9.543480 10.145880 9.287000 C 10.710899 11.064159 9.522699 C 10.013861 12.268400 10.182839 O 6.679200 9.331500 8.837300 O 8.584701 12.144960 9.889480 O 11.404280 11.364300 8.294260 H 11.481659 10.644259 10.181641 H 6.254020 11.252280 9.390821 H 9.611160 9.120760 8.934999 H 10.361561 13.234139 9.797441 H 10.121580 12.236080 11.276300 H 10.744801 11.644401 7.629620	
INTc4	C 7.036860 10.374140 9.402380 C 8.320360 10.749060 9.523320 C 9.591360 10.038839 9.115140 C 10.612720 11.091539 9.450080 C 9.992880 12.126141 10.037380 O 6.604000 9.205260 8.844700 O 8.621700 11.987580 10.131460	

	O 9.797620 8.767100 9.795640 H 11.678560 11.000880 9.263460 H 6.216440 10.998501 9.756800 H 9.589380 9.754280 8.050820 H 10.375360 13.054800 10.453020 H 7.356340 8.633660 8.590200 H 9.832020 8.952220 10.754980	

6. References

[1] T. M. Aida, N. Shiraishi, M. Kubo, M. Watanabe and R. L. Smith, J. Supercrit. Fluid., 2010, 55, 208-216.

[2] S. J. You, E. D. Park, and M. Park, Korean J. Chem. Eng., 2016, 33, 806-818.

[3] B. Hu, Q. Lu, Z. Zhang, Y. Wu, K. Li, C. Dong, Y. Yang, Combust. Flame., 2019, 206, 177-188.

[4] D. J. Bradley and K. S. Pitzer., J. Phys. Chem., 1979, 12, 1599–1603.

[5] K. Mathew, R. Sundararaman, K. Letchworth-Weaver, T.A. Arias, and R.G. Hennig, J. Chem. Phys., 2014, 140, 084106.