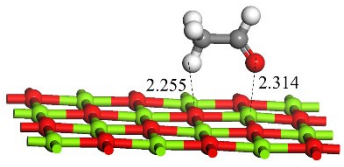
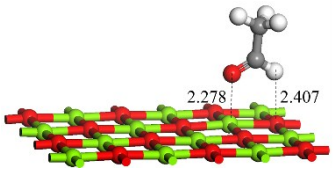
Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

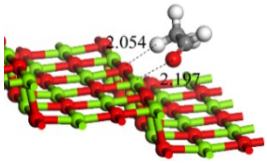
Figure S1. The stable structures of acetaldehyde on different Mg^{2+}-O^{2-} pairs. The unit of selected distances is Å. Green, red, gray, and white balls represent magnesium, oxygen, carbon and hydrogen atoms, respectively.



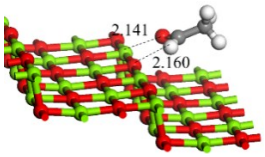
(Mg_{5C}-O_{5C}-T)-A



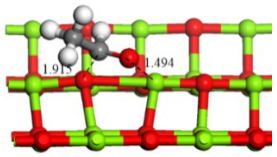
(Mg_{5C}-O_{5C}-T)-B



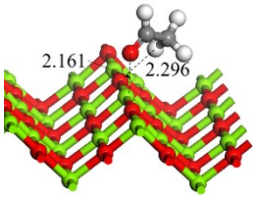
(Mg_{4C}-O_{4C}-S1)-A



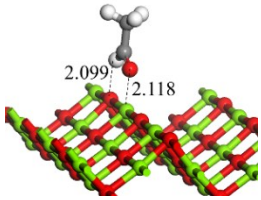
(Mg_{4C}-O_{4C}-S1)-B



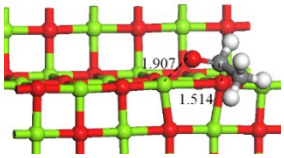
(Mg_{4C}-O_{4C}-S1)-C



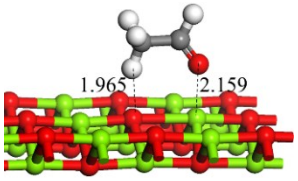
(Mg_{4C}-O_{4C}-S2)-A



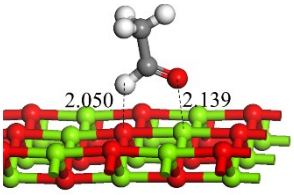
(Mg_{4C}-O_{4C}-S2)-B



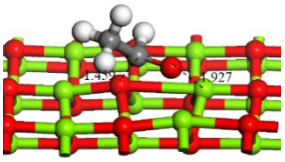
(Mg_{4C}-O_{4C}-S2)-C



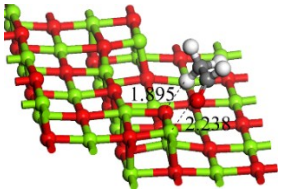
(Mg_{4C}-O_{4C}-110)-A



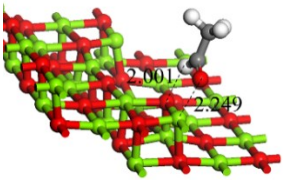
(Mg_{4C}-O_{4C}-110)-B



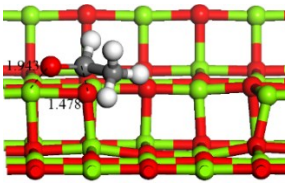
(Mg_{4C}-O_{4C}-110)-C



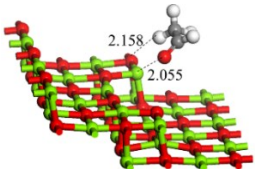
(Mg_{4C}-O_{3C}-D)-A



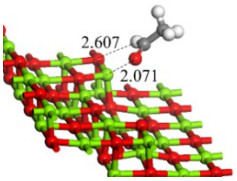
(Mg_{4C}-O_{3C}-D)-B



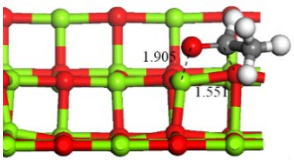
(Mg_{4C}-O_{3C}-D)-C



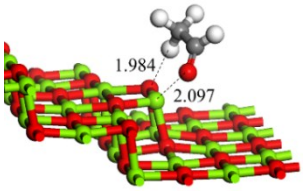
(Mg_{3C}-O_{4C}-D)-A



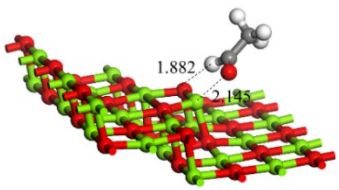
(Mg_{3C}-O_{4C}-D)-B



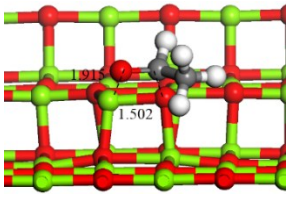
(Mg_{3C}-O_{4C}-D)-C



(Mg_{3C}-O_{3C}-K)-A



(Mg_{3C}-O_{3C}-K)-B



(Mg_{3C}-O_{3C}-K)-C

Figure S2. Relationship between adsorption energy of acetaldehyde molecule and coordination number of Mg^{2+}.

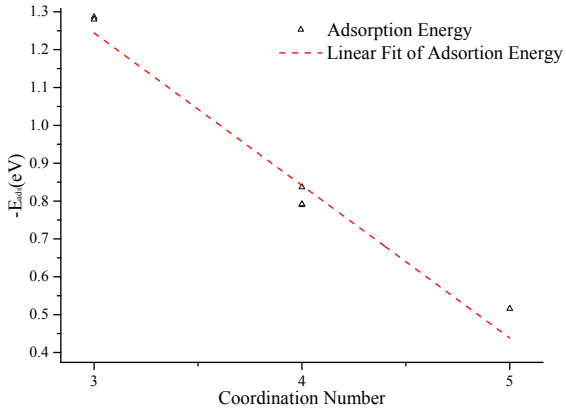
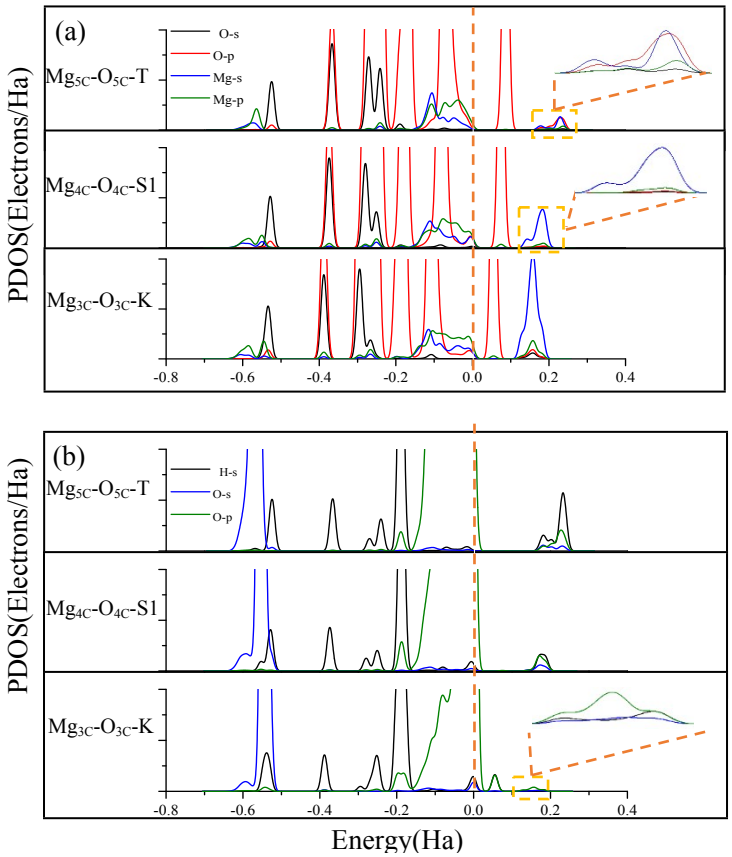


Figure S3. PDOS plots for acetaldehyde molecule adsorbed horizontally on Mg_{5C}-O_{5C}-T, Mg_{4C}-O_{4C}-S1 and Mg_{3C}-O_{3C}-K. (a) PDOS for oxygen and surface Mg^{2+}; (b) PDOS for methyl hydrogen and surface O^{2-}. The PDOS plots were aligned at the Fermi level.



In Figure 3(a), the significant overlaps between the carbonyl oxygen p orbitals and magnesium s and p orbitals at the position of -0.25 to -0.5 Ha indicate that a Mg_s-O_a bond is clearly formed. As the coordination number of Mg^{2+} decreases, the overlapping area between the two atoms become larger, indicating interaction between the surface Mg^{2+} and carbonyl oxygen is stronger, which is consistent with the fact that acetaldehyde is more stable on Mg_{3C}-O_{3C}-K than that on Mg_{5C}-O_{5C}-T and Mg_{4C}-O_{4C}-S1. Figure 3(b) shows the interaction between methyl hydrogen and surface O^{2-}. In all configurations, hydrogen s orbital partly overlaps with oxygen s orbitals at -0.55 Ha and with oxygen p orbitals at -0.2 Ha, indicating that the methyl hydrogen interacts with surface O^{2-} but does not form a bond.

Figure S4. The Calculated structures of the intermediates and the transition states in step I.

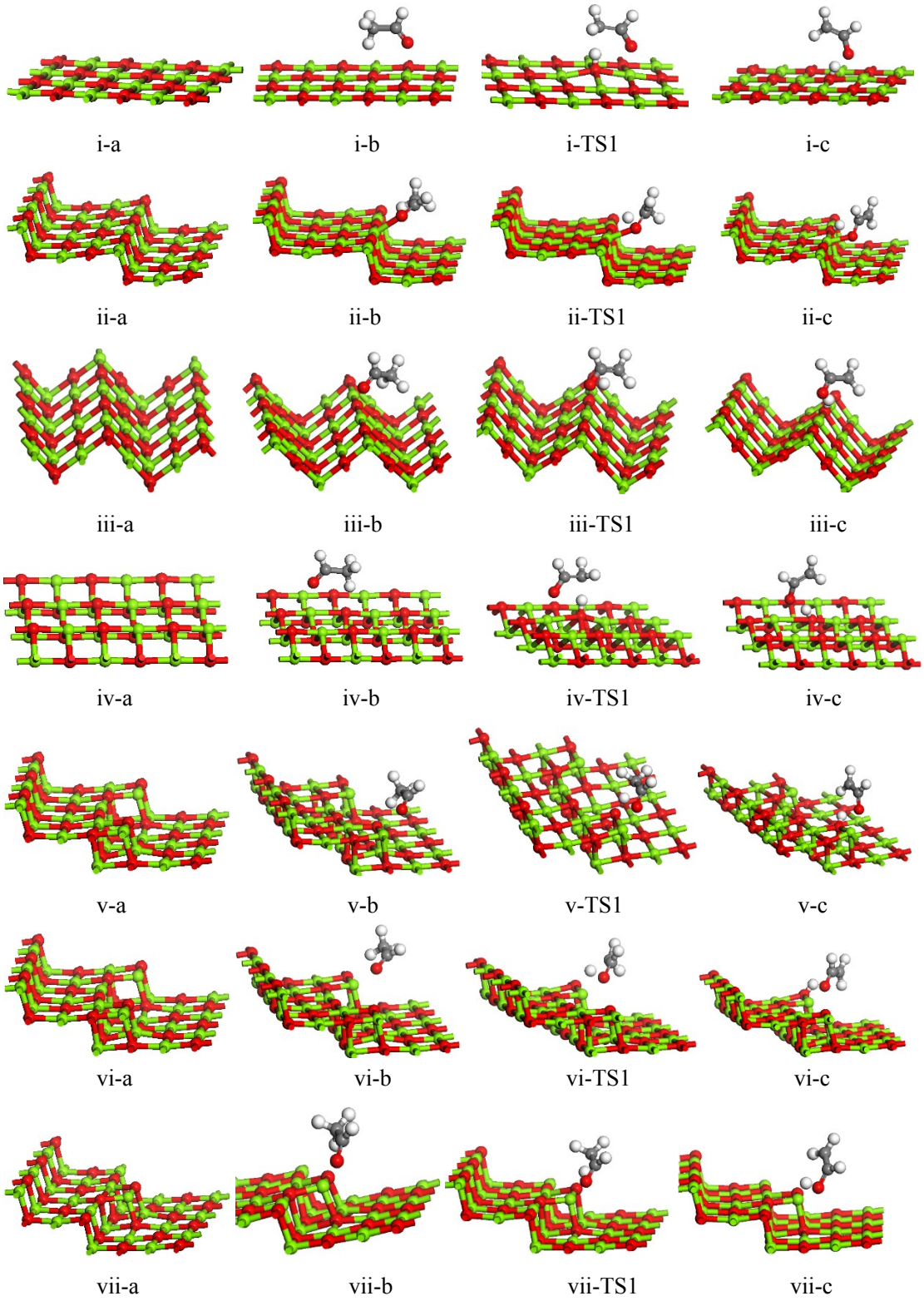
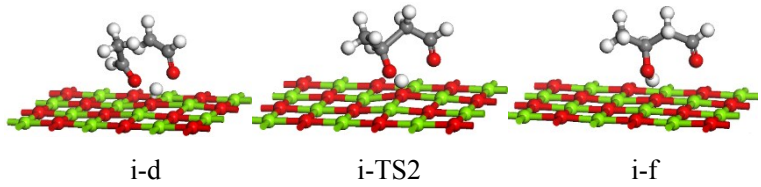
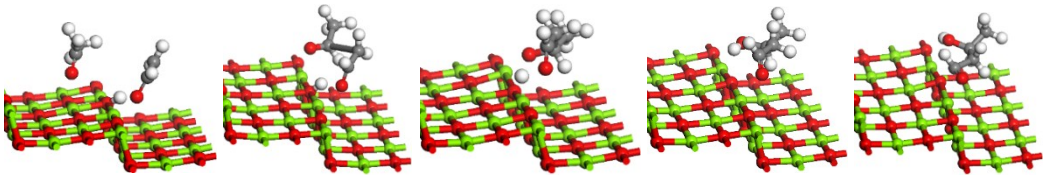


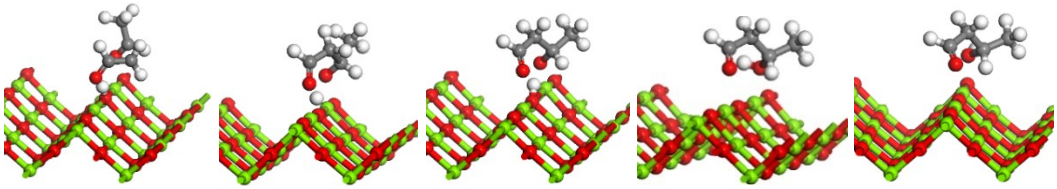
Figure S5. The Calculated structures of the intermediates and the transition states in step II and step III over different Mg^{2+}-O^{2-} pairs.



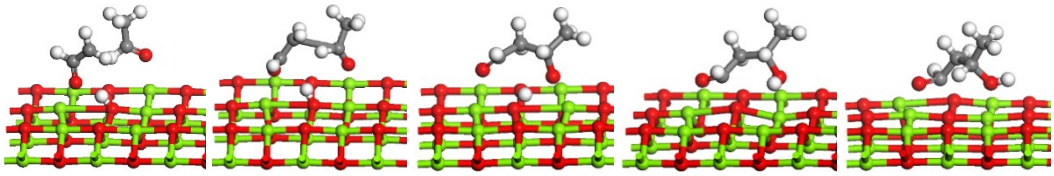
i-d i-TS2 i-f



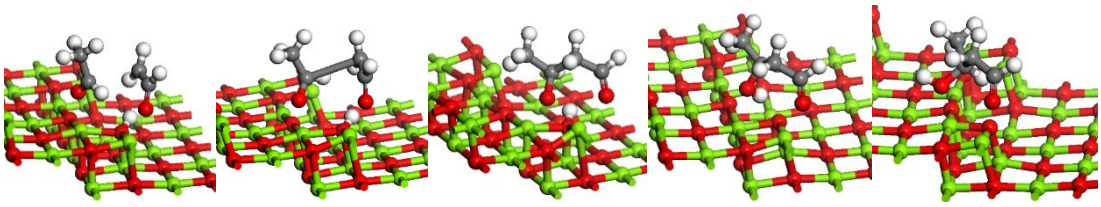
ii-d ii-TS2 ii-e ii-TS3 ii-f



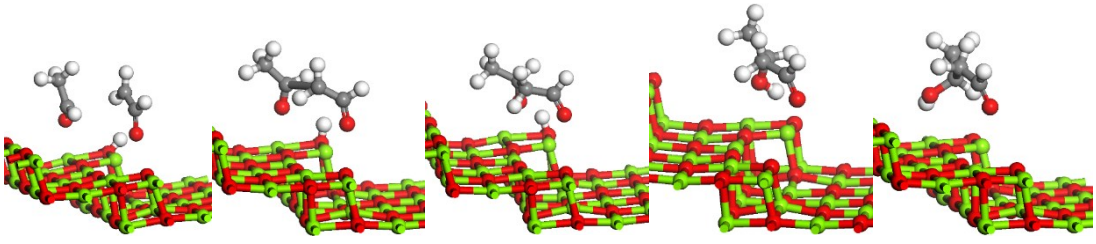
iii-d iii-TS2 iii-e iii-TS3 iii-f



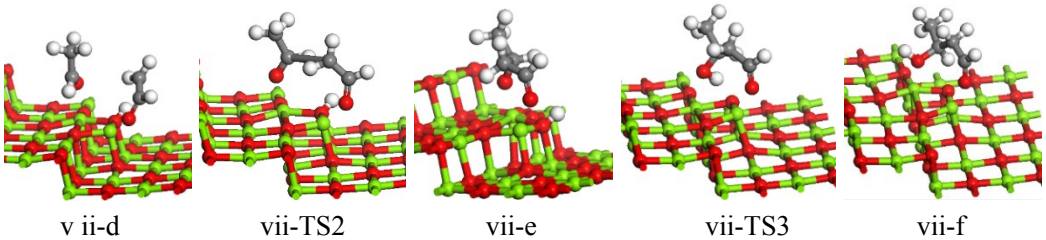
iv-d iv-TS2 iv-e iv-TS3 iv-f



v-d v-TS2 v-e v-TS3 v-f

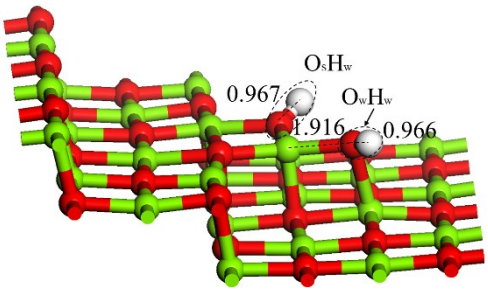


vi-d vi-TS2 vi-e vi-TS3 vi-f



v ii-d vii-TS2 vii-e vii-TS3 vii-f

Figure S6. Optimized structure of a H_2O molecule adsorbed on Mg_{3C}-O_{3C}-K.



Mg_{3C}-O_{3C}-K-OH

Figure S7. PDOS plots for Mg^{2+} in low coordinated Mg^{2+}-O^{2-} pairs and Mg-OH group. (a) five-coordinated Mg^{2+}; (b) four-coordinated Mg^{2+}; (c) three-coordinated Mg^{2+}.

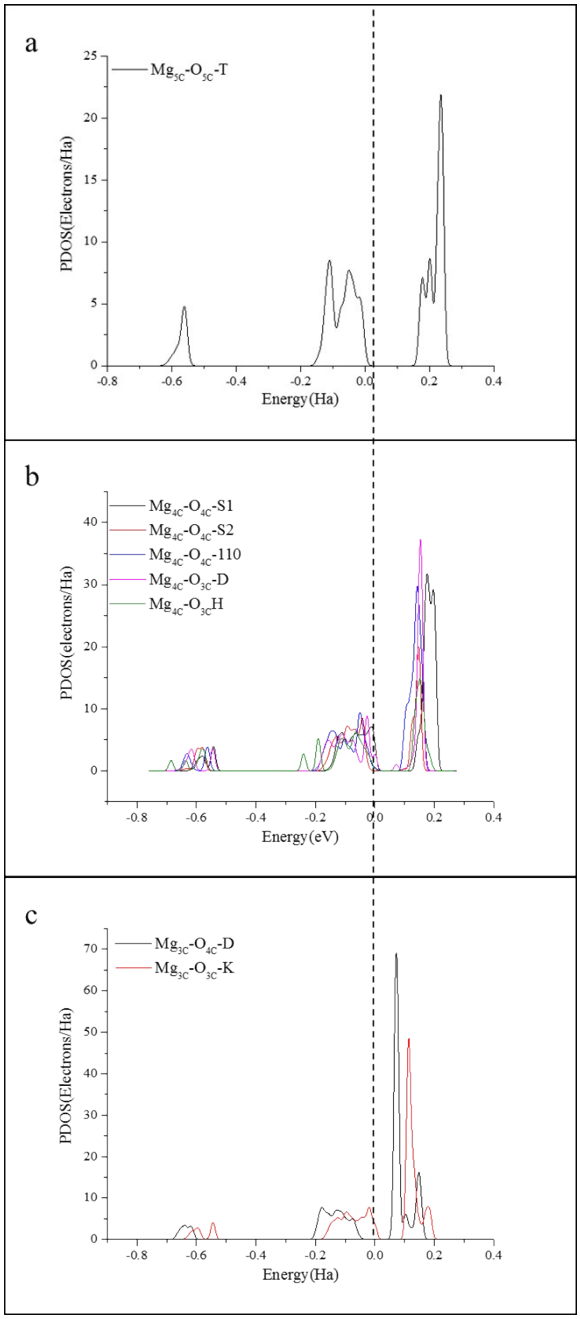
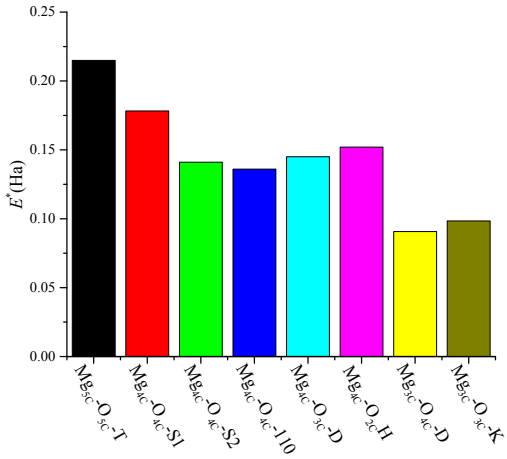
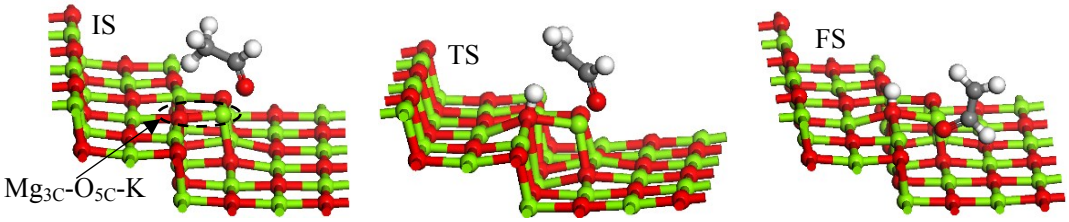


Figure S8. E^* values calculated for the Mg^{2+} in in low coordinated Mg^{2+}-O^{2-} pairs and Mg-OH group.

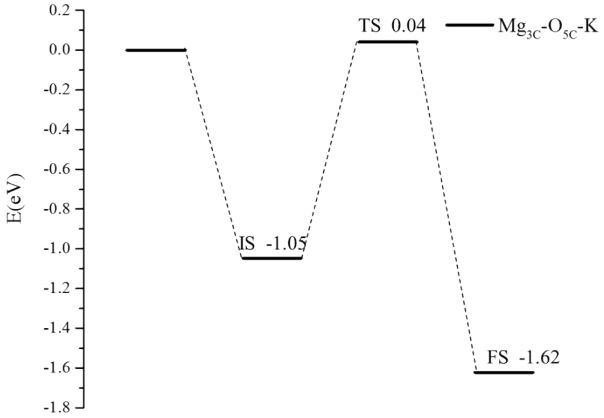


The values of E^* of Mg^{2+} with same coordination numbers are close indicating a similar Lewis acidity and the lower the Mg^{2+} coordination, the stronger, generally, the Lewis acidity. In spite of that, there are still some small differences in E^* of the same coordinated Mg^{2+}, such as the case for four coordinated Mg^{2+}.

Figure S9. The enolization step on Mg_{3C}-O_{5C}-K.



(a) The Calculated structures of the intermediates and the transition states in enolization step on Mg_{3C}-O_{5C}-K. The black lines are drawn around Mg_{3C}-O_{5C}-K site to guide the eye. IS, TS and FS represent the initial structure, transition state and finial structure, respectively.



(b) The calculated energy profiles in step I with or without water on Mg_{3C}-O_{5C}-K.

The energy barrier of step I on Mg_{3C}-O_{5C}-K is 1.09 eV, which is much lower than that on Mg_{5C}-O_{5C}-T, 1.46 eV. This result indicates that the basic site with weak basic property will catalyze the enolization step with the help of low coordinated Mg^{2+}.

Table S1. Bond parameters of acetaldehyde molecule before and after adsorption on Mg^{2+}-O^{2-} pairs with different coordination numbers. The unit of distances is Å.

Bond parameters[a]	Free molecule	Mg_{5C}-O_{5C}-T		Mg_{4C}-O_{4C}-S1			Mg_{4C}-O_{4C}-S2			Mg_{4C}-O_{4C}-110			Mg_{4C}-O_{3C}-D			Mg_{3C}-O_{4C}-D			Mg_{3C}-O_{3C}-K		
		Mode A	Mode B	Mode A	Mode B	Mode C	Mode A	Mode B	Mode C	Mode A	Mode B	Mode C	Mode A	Mode B	Mode C	Mode A	Mode B	Mode C	Mode A	Mode B	Mode C
$d(C_a$-$O_a)$	1.216	1.224	1.227	1.230	1.314	1.350	1.230	1.259	1.336	1.233	1.240	1.399	1.233	1.238	1.368	1.249	1.244	1.356	1.243	1.244	1.378
$d(C_a$-$C_b)$	1.499	1.491	1.491	1.482	1.487	1.533	1.487	1.487	1.533	1.478	1.485	1.528	1.481	1.450	1.528	1.482	1.480	1.523	1.474	1.488	1.521
$d(C_a$-$H_a)$	1.118	1.113	1.055	1.110	1.108	1.120	1.109	1.114	1.120	1.111	1.111	1.110	1.115	1.121	1.117	1.105	1.106	1.111	1.108	1.118	1.112
$d(C_b$-$H_b)$	1.094	1.099	1.094	1.105	1.094	1.097	1.107	1.095	1.100	1.108	1.095	1.098	1.120	1.095	1.099	1.101	1.094	1.097	1.127	1.094	1.097
$d(C_b$-$H_c)$	1.100	1.100	1.100	1.102	1.099	1.105	1.095	1.101	1.103	1.101	1.101	1.097	1.104	1.100	1.110	1.102	1.100	1.104	1.104	1.100	1.098
$d(C_b$-$H_d)$	1.100	1.002	1.101	1.102	1.101	1.099	1.101	1.101	1.097	1.108	1.099	1.103	1.102	1.100	1.099	1.102	1.101	1.097	1.097	1.100	1.097

[a] The name of atoms in acetaldehyde molecule refers to Scheme 1.

Table S2. Mulliken charge of the acetaldehyde before and after adsorption on different Mg^{2+}-O^{2-} pairs.

Atoms[a]	Mulliken charge ($\|e\|$)							
	Free molecule	Mg_{5C}-O_{5C} -T	Mg_{4C}-O_{4C} -S1	Mg_{4C}-O_{4C} -S2	Mg_{4C}-O_{4C} -110	Mg_{4C}-O_{3C} -D	Mg_{3C}-O_{4C} -D	Mg_{3C}-O_{3C} -K
O_a	-0.355	-0.364	-0.397	-0.384	-0.407	-0.404	-0.452	-0.453
H_a	0.005	0.059	0.069	0.074	0.071	0.054	0.093	0.082
H_b	0.075	0.175	0.193	0.172	0.213	0.230	0.180	0.219
H_c	0.068	0.122	0.119	0.112	0.118	0.109	0.139	0.138
H_d	0.067	0.124	0.121	0.139	0.115	0.100	0.131	0.114
C_a	0.298	0.262	0.284	0.282	0.284	0.273	0.277	0.292
C_b	-0.158	-0.349	-0.353	-0.358	-0.352	-0.355	-0.343	-0.367
CH_3CHO	0.000	0.029	0.036	0.037	0.042	0.007	0.025	0.025

[a] The name of atoms in acetaldehyde molecule refers to Scheme 1.

Table S3. Adsorption energies of the intermediates in step II and step III on different coordinated Mg^{2+}-O^{2-} pairs.

Model	Mg_{5C}-O_{5C}-T	Mg_{4C}-O_{4C}-S1	Mg_{4C}-O_{4C}-S2	Mg_{4C}-O_{4C}-110	Mg_{4C}-O_{3C}-D	Mg_{3C}-O_{4C}-D	Mg_{3C}-O_{3C}-K
Acetaldehyde[a]	-0.761	-0.571	-1.114	-1.136	-0.875	-0.647	-0.751
3-hydroxybutanal	-0.740	-2.344	-1.270	-3.595	-0.965	-1.470	-1.436

[a]the adsorption energy of the second acetaldehyde adsorbed on Mg^{2+}-O^{2-} pairs

For the adsorption energy of the desired product, the adsorption energies of 3-hydroxybutanal on the Mg_{4C}-O_{4C} are very high with the value of -2.34, -1.20 and -3.60 eV on Mg_{4C}-O_{4C}-S1, Mg_{4C}-O_{4C}-S2 and Mg_{4C}-O_{4C}-110 respectively, indicating the desorption processes on the three surfaces are difficult to occur, especially on Mg_{4C}-O_{4C}-S1 and Mg_{4C}-O_{4C}-110. Therefore, structures with the row of Mg^{2+} and O^{2-} may be unfavorable to the aldol condensation reaction for it is difficult for 3-hydroxybutanal to transfer to the acid sites to form the crotonaldehyde.

Table S4. Bond parameters of acetaldehyde molecule after adsorption at different adsorption sites over Mg_{3C}-O_{3C}-K-OH surface. (a) Mg_S-O_WH_W, (b) O_WH_W, (c) O_SH_W. The unit of distances is Å.

Bond parameters[a]	Configurations		
	a	b	c
$d(C_a\text{-}O_a)$	1.232	1.244	1.224
$d(C_a\text{-}H_a)$	1.108	1.116	1.114
$d(C_a\text{-}C_b)$	1.486	1.497	1.495
$d(C_b\text{-}H_b)$	1.102	1.095	1.095
$d(C_b\text{-}H_c)$	1.102	1.100	1.100
$d(C_b\text{-}H_d)$	1.102	1.101	1.101

[a] The name of atoms in acetaldehyde molecule refers to Scheme 1.

Table S5. The calculated E^* values for all the Mg^{2+} states in low coordinated Mg^{2+}-O^{2-} pairs and Mg-OH group.

MgO surfaces	E^*
Mg_{5C}-O_{5C}-T	0.215
Mg_{4C}-O_{4C}-S1	0.178
Mg_{4C}-O_{4C}-S2	0.141
Mg_{4C}-O_{4C}-110	0.136
Mg_{4C}-O_{3C}-D	0.145
Mg_{3C}-O_{4C}-D	0.091
Mg_{3C}-O_{3C}-K	0.098
Mg_{4C}-O_{2C}H	0.152