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Supporting Information

CaMnAl-hydrotalcite solid basic catalyst toward aldol condensation reaction with a comparable level to liquid alkali catalysts

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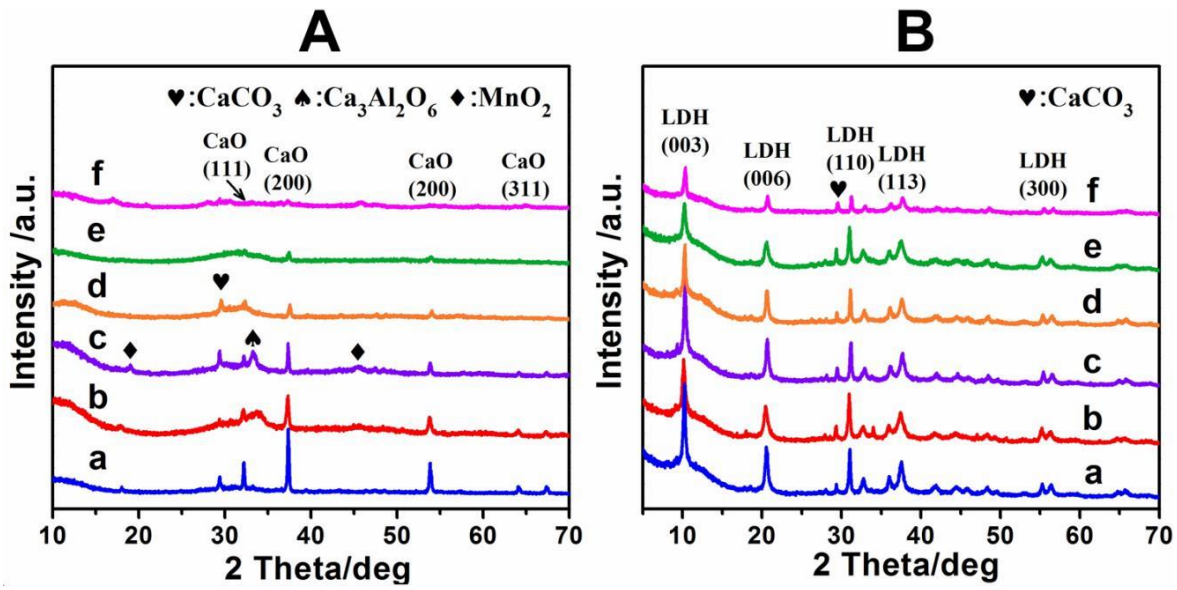

Figure S1. XRD patterns of (A) Ca_4Mn_xAl-LDH precursors and (B) calcination samples with Mn/Al ratio of: (a) 0, (b) 0.3, (c) 0.5, (d) 0.8, (e) 1.0 and (f) 1.5.

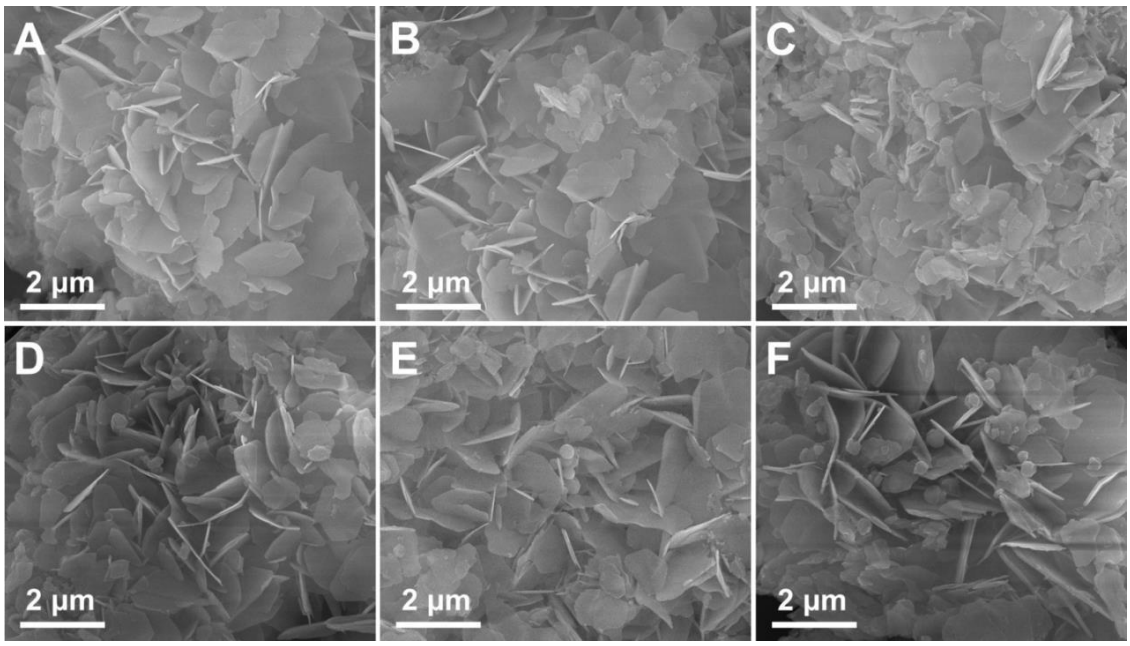

Figure S2. SEM images of (A) re-Ca_4Al-LDH, (B) re-$Ca_4Mn_{0.3}Al$-LDH, (C) re-$Ca_4Mn_{0.5}Al$-LDH, (D) re-$Ca_4Mn_{0.8}Al$-LDH, (E) re-$Ca_4Mn_{1.0}Al$-LDH and (F) re-$Ca_4Mn_{1.5}Al$-LDH.

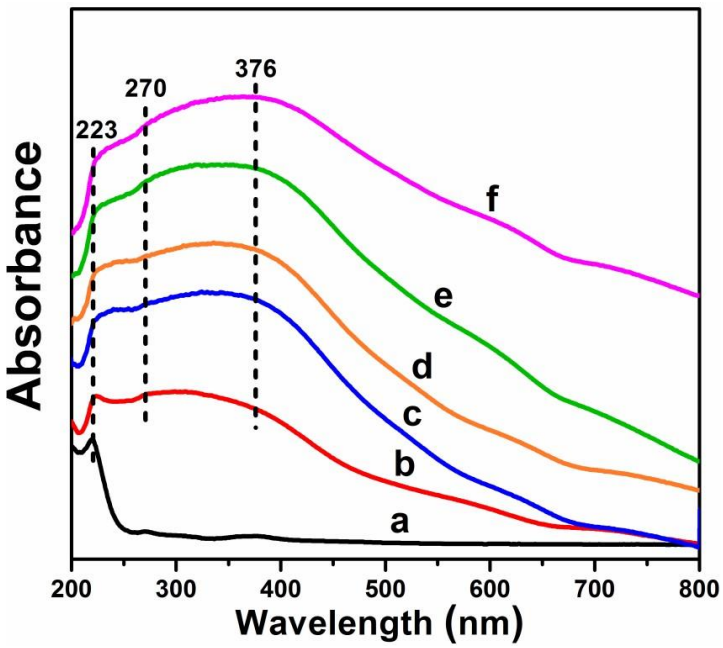

Figure S3. UV–vis spectra of (a) re-Ca_4Al-LDH, (b) re-$Ca_4Mn_{0.3}$Al-LDH, (c) re-$Ca_4Mn_{0.5}$Al-LDH, (d) re-$Ca_4Mn_{0.8}$Al-LDH, (e) re-$Ca_4Mn_{1.0}$Al-LDH and (f) re-$Ca_4Mn_{1.5}$Al-LDH.

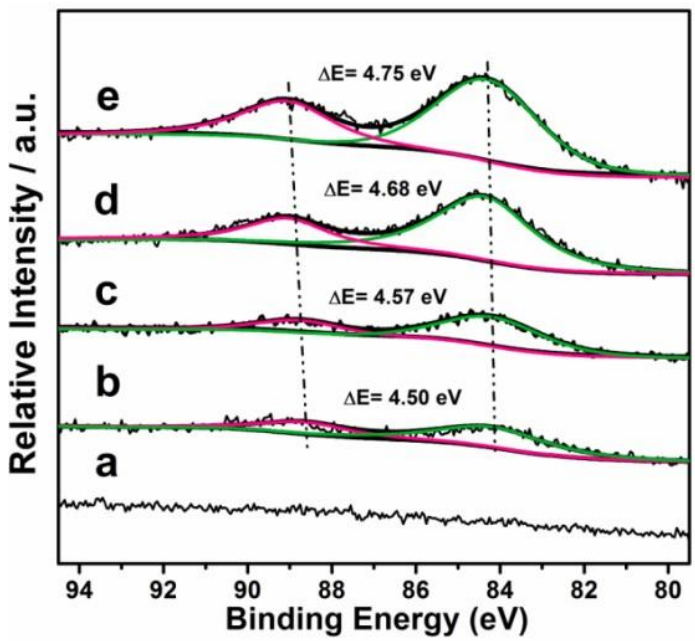

Figure S4. XPS Mn3*s* of (a) re-$Ca_4Mn_{0.3}$Al-LDH, (b) re-$Ca_4Mn_{0.5}$Al-LDH, (c) re-$Ca_4Mn_{0.8}$Al-LDH, (d) re-$Ca_4Mn_{1.0}$Al-LDH and (e) re-$Ca_4Mn_{1.5}$Al-LDH.

Table S1. Chemical compositions of Ca_4Mn_xAl-LDH and re-Ca_4Mn_xAl-LDH samples determined by ICP−AES

Sample	Ca/Mn/Al molar ratio (first time)	Ca/Mn/Al molar ratio (second time)	Ca/Mn/Al molar ratio (average)
Ca_4Al-LDH	3.87 : 0.00 : 1	3.91 : 0.00 : 1	3.89 : 0.00 : 1
$Ca_4Mn_{0.3}Al$-LDH	3.99 : 0.26 : 1	3.90 : 0.28 : 1	3.95 : 0.27 : 1
$Ca_4Mn_{0.5}Al$-LDH	3.98 : 0.56 : 1	4.02 : 0.47 : 1	4.00 : 0.52 : 1
$Ca_4Mn_{0.8}Al$-LDH	3.90 : 0.72 : 1	4.00 : 0.81 : 1	3.95 : 0.77 : 1
$Ca_4Mn_{1.0}Al$-LDH	4.07 : 0.92 : 1	4.10 : 1.03 : 1	4.09 : 0.98 : 1
$Ca_4Mn_{1.5}Al$-LDH	3.96 : 1.55 : 1	3.91 : 1.46: 1	3.94 : 1.51: 1
re-Ca_4Al-LDH	3.91 : 0.00 : 1	3.96 : 0.00 : 1	3.94 : 0.00 : 1
re-$Ca_4Mn_{0.3}Al$-LDH	3.85 : 0.25 : 1	3.99 : 0.27 : 1	3.92 : 0.26 : 1
re-$Ca_4Mn_{0.5}Al$-LDH	3.92 : 0.54 : 1	4.03 : 0.48 : 1	3.98 : 0.51 : 1
re-$Ca_4Mn_{0.8}Al$-LDH	3.94 : 0.83 : 1	3.88 : 0.91 : 1	3.91 : 0.87 : 1
re-$Ca_4Mn_{1.0}Al$-LDH	3.88 : 1.08 : 1	3.93 : 1.14 : 1	3.91 : 1.11 : 1
re-$Ca_4Mn_{1.5}Al$-LDH	4.08 : 1.67 : 1	3.90 : 1.61 : 1	3.99 : 1.64 : 1

Table S2. Spectral characteristics (ν_{C-D}) of O–H group (Brønsted basic site) for re-Ca_4Mn_xAl-LDH catalysts and other LDHs solid base according to adsorption of $CDCl_3$

Samples	ν_{C-D} (cm^{-1})	$\Delta\nu_{C-D}$ (cm^{-1})	Proton Affinity (kJ/mol)
$CDCl_3$	2275	-	-
Physically adsorbed $CDCl_3$	2264	11	818
Mg_4Al-LDH	2252	23	867
	2214	61	931
re-Mg_4Al-LDH	2252	23	867
	2214	61	931
Ca_4Al-LDH	2255	20	858
	2214	61	931
re-Ca_4Al-LDH	2255	20	858
	2214	61	931
re-$Ca_4Mn_{0.3}Al$-LDH	2256	19	854
	2213	62	932
re-$Ca_4Mn_{0.5}Al$-LDH	2257	18	851
	2214	61	931
re-$Ca_4Mn_{0.8}Al$-LDH	2254	21	861
	2216	59	929
re-$Ca_4Mn_{1.0}Al$-LDH	2253	22	864
	2220	55	924
re-$Ca_4Mn_{1.5}Al$-LDH	2252	23	867
	2224	51	919

Table S3. Comparison of catalytic performances toward aldol condensation of isobutyraldehyde with formaldehyde over various catalysts [a]

Sample	IBD Conversion (%)	HPA Selectivity (%)	HPA Yield (%)
$Mg(OH)_2$	63.2	19.4	12.3
CaO	66.7	32.9	21.9
MgO	50.1	8.7	4.4
$Ca(OH)_2$	79.7	47.2	37.6
triethylamine	97.6	75.0	73.2
NaOH	98.7	62.3	61.5
Ca_4Al-LDH	65.7	48.3	31.7
$Ca_4Mn_{0.3}$Al-LDH	64.3	46.5	29.9
$Ca_4Mn_{0.5}$Al-LDH	63.8	43.6	27.8
$Ca_4Mn_{0.8}$Al-LDH	65.4	43.9	28.7
$Ca_4Mn_{1.0}$Al-LDH	67.9	44.3	30.1
$Ca_4Mn_{1.5}$Al-LDH	68.4	47.4	32.4
Ca_4Al-MMO	67.1	44.6	29.9
$Ca_4Mn_{0.3}$Al-MMO	68.6	54.3	37.2
$Ca_4Mn_{0.5}$Al-MMO	64.2	52.7	33.8
$Ca_4Mn_{0.8}$Al-MMO	61.7	44.2	27.3
$Ca_4Mn_{1.0}$Al-MMO	59.4	39.8	23.6
$Ca_4Mn_{1.5}$Al-MMO	57.2	34.3	19.6

[a] Reaction conditions: isobutyraldehyde (0.55 mol), formaldehyde (0.80 mol), cetyl trimethyl ammonium bromide (0.1 g), dioxane (0.2 g), catalyst (0.2 g), 70 °C, 8 h, Ar atomosphere.

Table S4. Comparison of catalytic performances toward aldol condensation of isobutyraldehyde with formaldehyde over various catalysts [a]

Number	Catalyst	IBD Conversion (%)	HPA Selectivity (%)	HPA Yield (%)	Ref.
1	re-$Ca_4Mn_{0.5}$Al-LDH	85.9	81.9	70.3	This work
2	$CaTiO_3$	~81	~62	~50.2	1
3	$SrTiO_3$	~65	~49	~31.9	1
4	$BaTiO_3$	~37	~34	~12.6	1
5	$CaZrO_3$	~48	~43	~20.6	1
6	$SrZrO_3$	~91	~58	~52.8	1
7	$BaZrO_3$	~91	~59	~53.7	1
8	$CaCeO_3$	~58	~54	~31.3	1
9	$SrCeO_3$	~68	~57	~38.8	1
10	$BaCeO_3$	~80	~61	~48.8	1
11	AlN	~88	~60	~52.8	1
12	Si_3N_4	~31	~71	~22.0	1

13	Si_3N_4	~48	~68	~32.6	1
14	TiN	~44	~49	~21.6	1
15	Ti	~62	~58	~36.0	1
16	TaN	~16	~64	~10.2	1

[a] Aldol condensation of isobutyraldehyde with formaldehyde in Ref. 1 was carried out in a Berghof DAB-2 pressure autoclave.

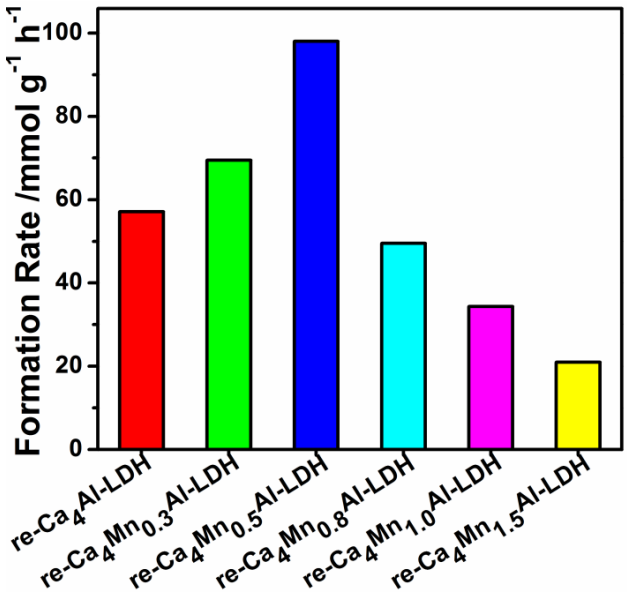

Figure S5. Product formation rate at 2% yield of HPA over re-Ca_4Mn_xAl-LDH catalysts.