Supplementary Material

Layered double alkoxides, a novel group of layered double hydroxides without water content

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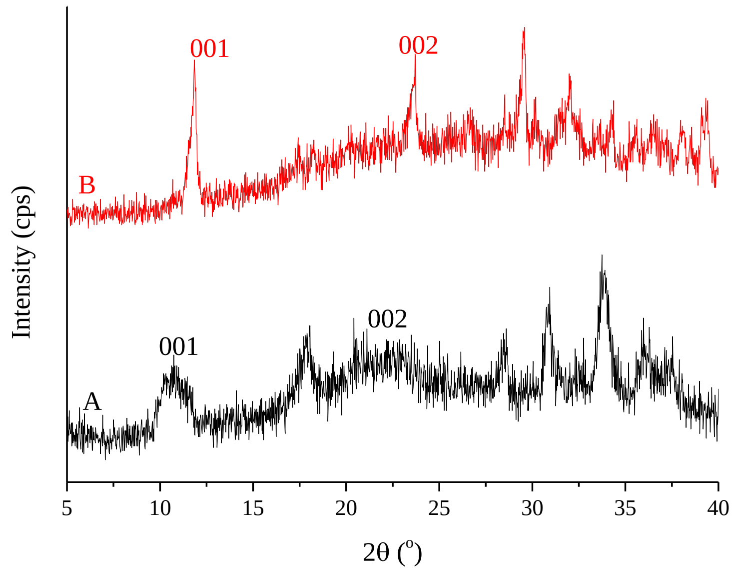
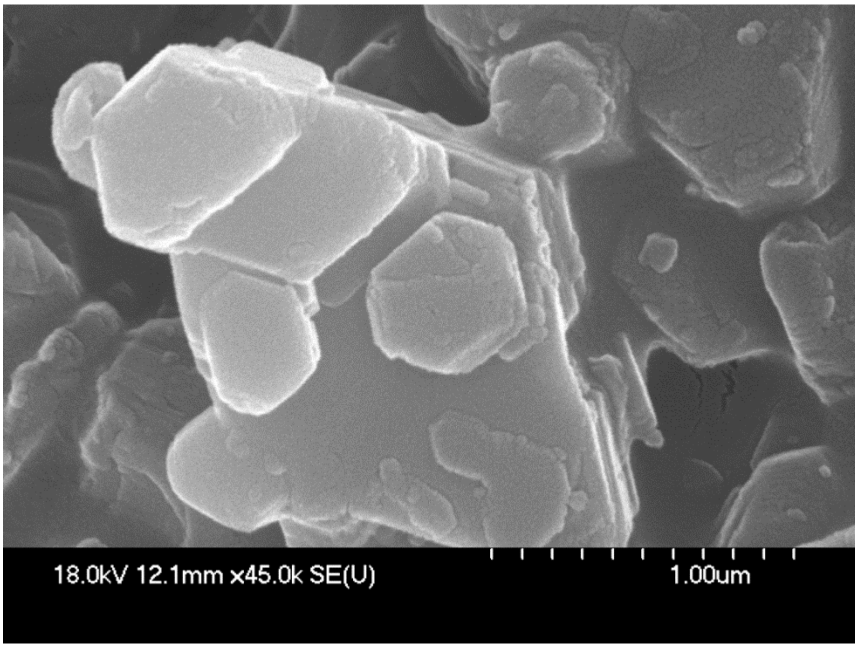
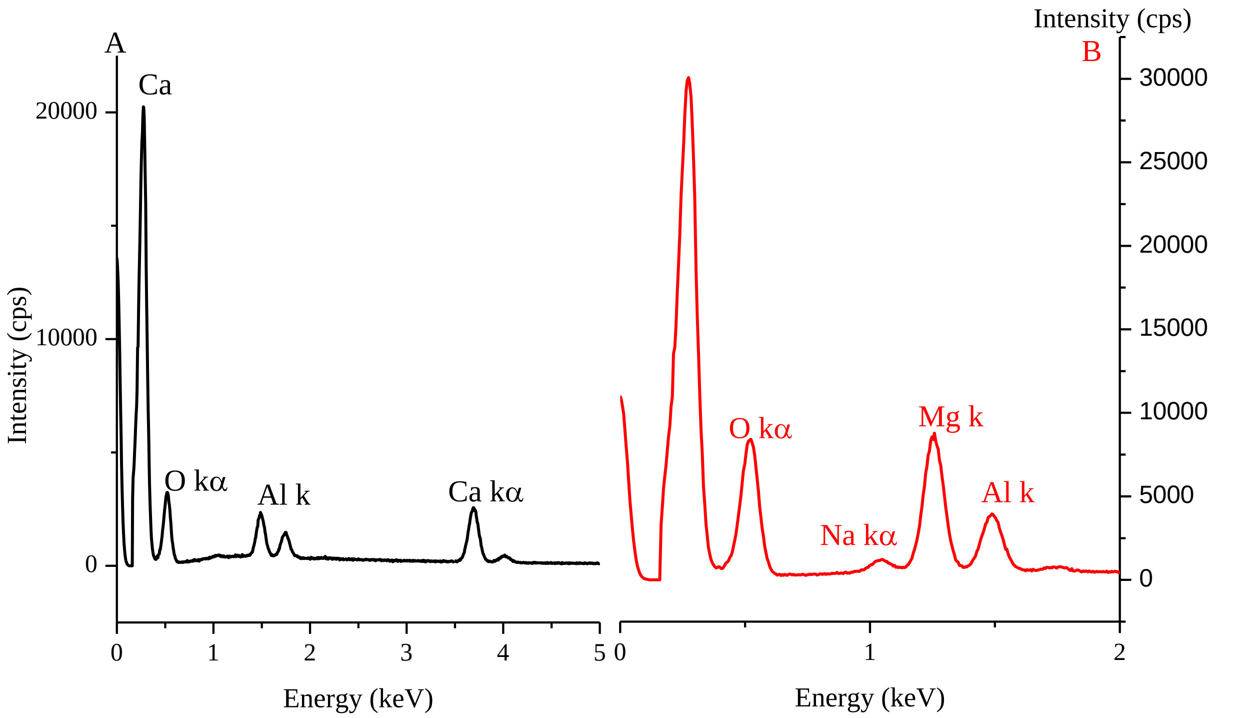


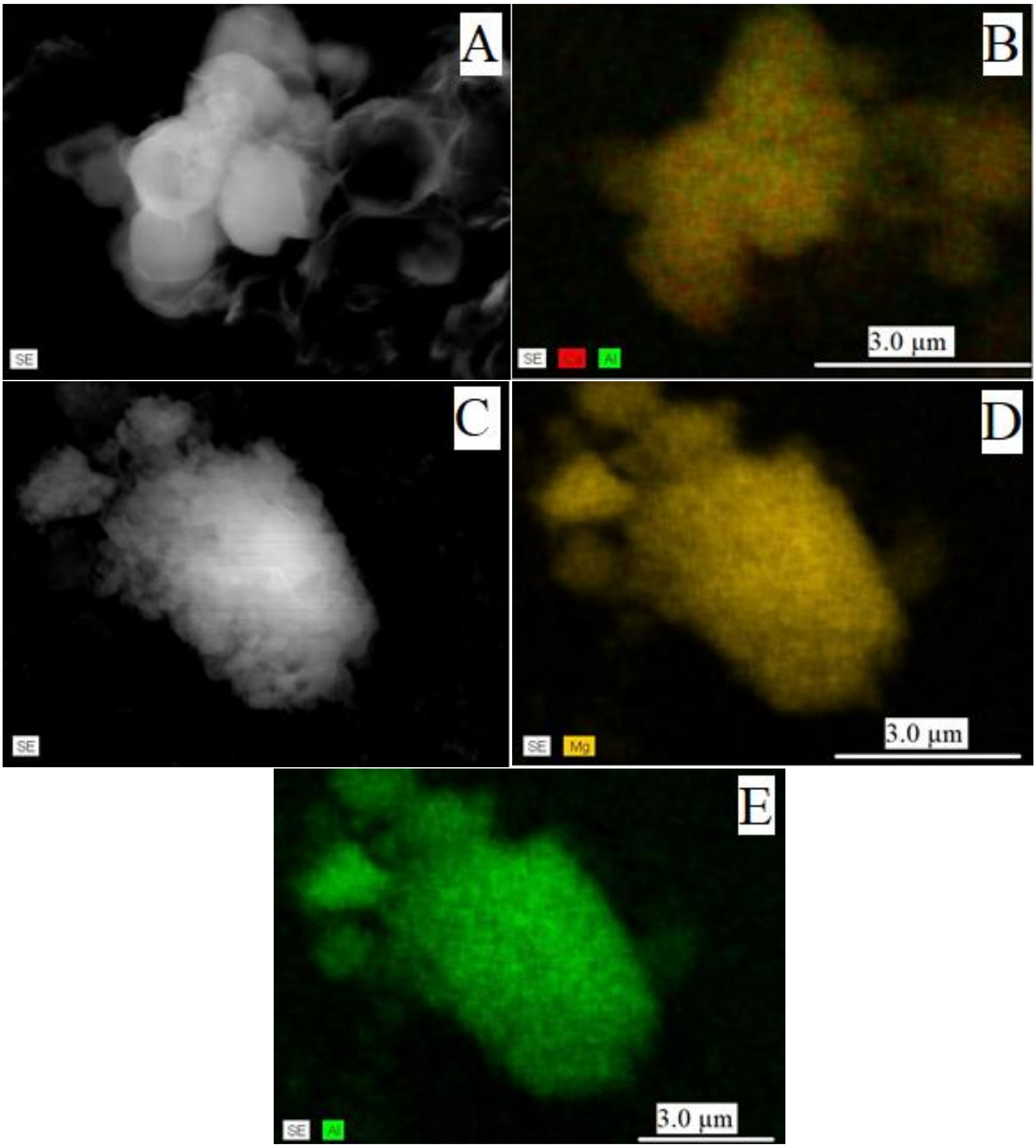
SFigure 1. XRD pattern of the water-free CaAl-LDH after solvolysis-co-precipitation of Ca(II) and Al(III) ethoxides using propanol for solvolysis (A) at 30°C and (B) at 60°C. XRD patterns were indexed on the basis of JCPDS#89-6723.



SFigure 2. SEM image of water-free CaAl–LDH (CaAl–LDA) using propanol for solvolysis-co-precipitation at 60^{o}C.



SFigure 3. EDX spectra of (A) CaAl-LDA and (B) MgAl-LDA.

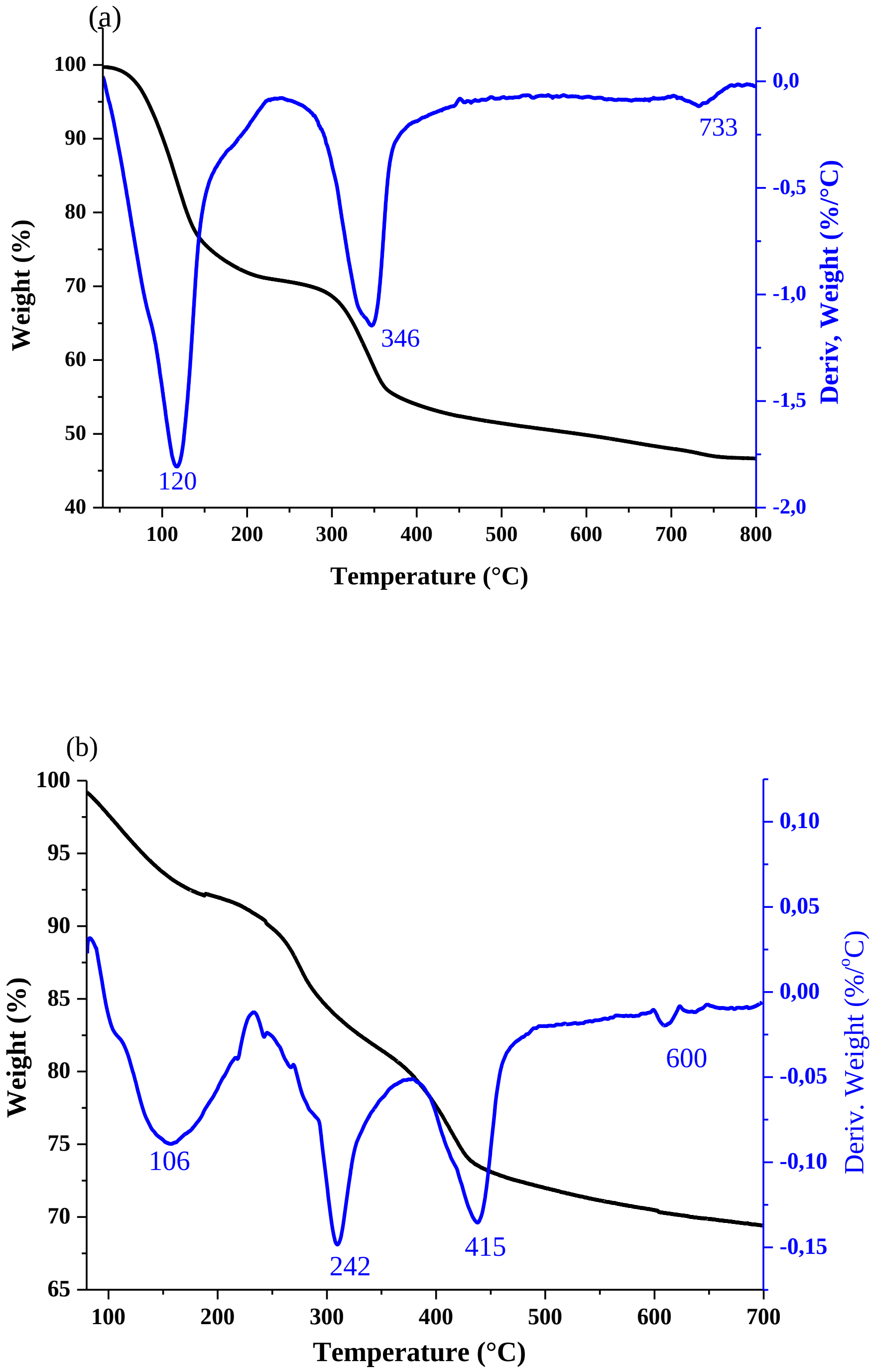


SFigure 4. Elemental maps for CaAl-LDA [(A) and (B)] and MgAl-LDA (C), (D) and (E).

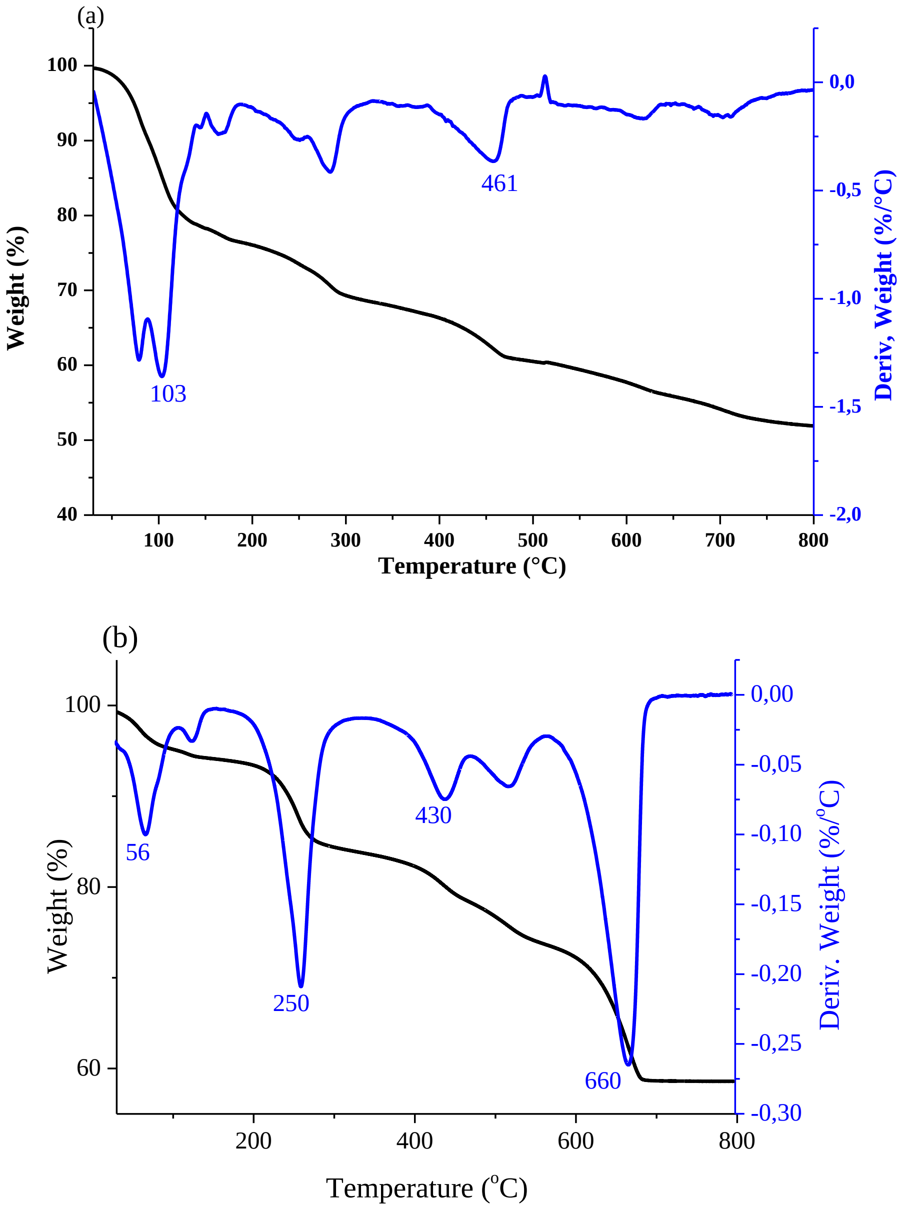
STable 1. Layer thickness, d-spacings and cell parameters for LDAs, nitrate-containing LDHs and alkoxide intercalated LDH

Composite	d-space (Å)	thickness (Å)	*a* parameter (Å)	*c* parameter (Å)
MgAl-LDA	7.88	4.5	3.02	24.16
$Mg_2Al–NO_3^-$-LDH	8.58	4.8[2]	3.08	22.91
CaAl–LDA	7.49	—	5.92	15.01
$Ca_2Al–NO_3^-$-LDH	8.26	2.4[3]	5.45	17.16
$C_2H_5O^-$–MgAl-LDH	8.18[1]	4.8[2]	3.07[1]	23.98[1]

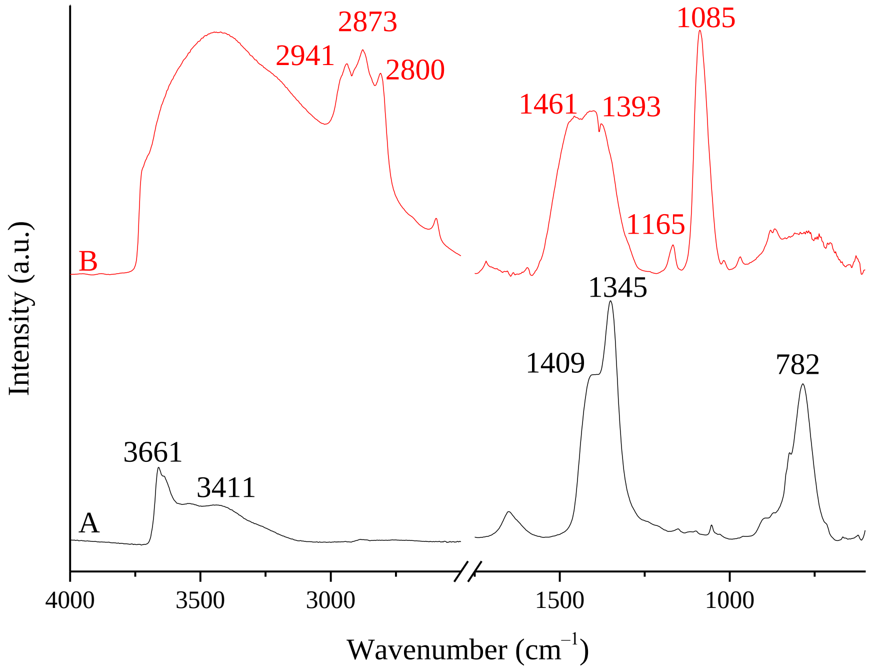
Calculation: MgAl-LDH/LDA: $a = 2d_{(110)}$, $c = (3d_{(003)} + 6d_{(006)} + 9d_{(009)})/3$; *CaAl-LDH/LDA:* $a = 2d_{(110)}$, $c = 2d_{(002)}$



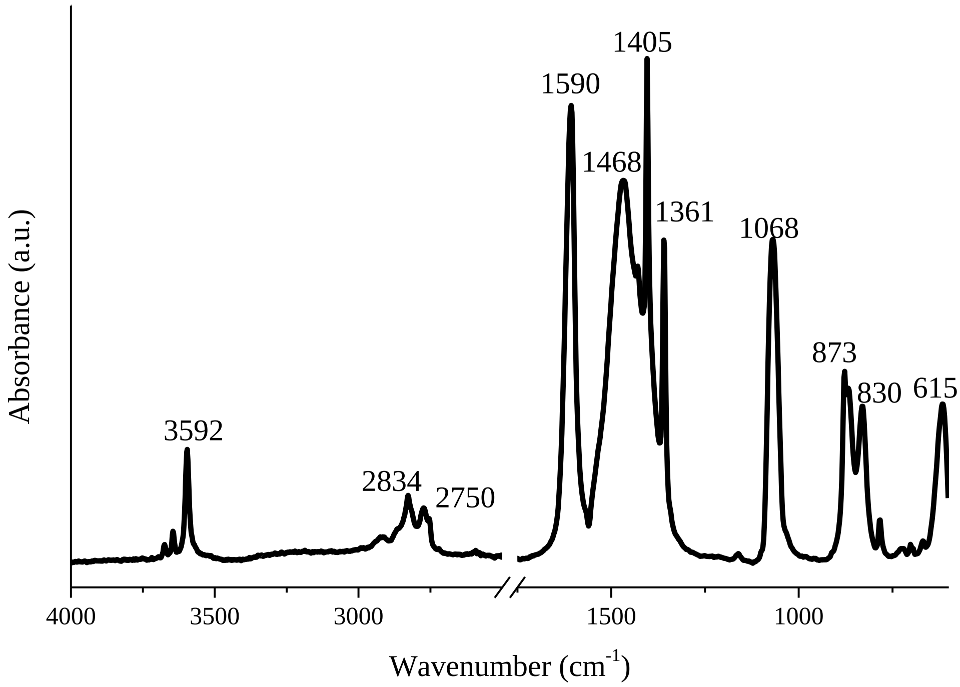
SFigure 5. TG/DTG curves for the (a) MgAl-LDH sample prepared by solvolysis-precipitation from Mg(II)Al(III) ethoxide at 60°C and (b) MgAl–NO_3^-–LDH.



SFigure 6. TG/DTG curves of (a) water-free CaAl–LDA and (b) CaAl–NO_3^-–LDH.

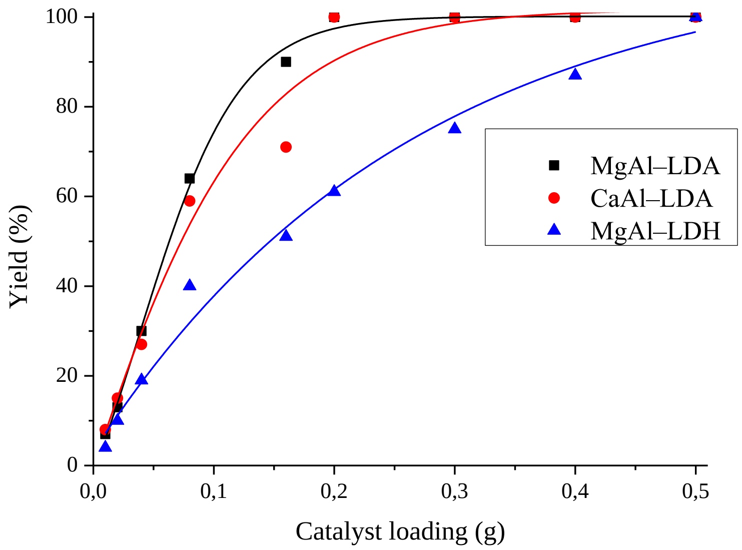


SFigure 7. IR spectra of (A) CaAl–NO_3^-–LDH and (B) water-free CaAl–LDH (CaAl–LDA).



SFigure 8. IR spectra of MgAl–LDA (prepared by solvolysis-co-precipitation of Mg(II) and Al(III)ethoxides at 60°C) after 9-month-long storage in air.

Optimisation procedure of the catalytic test reaction

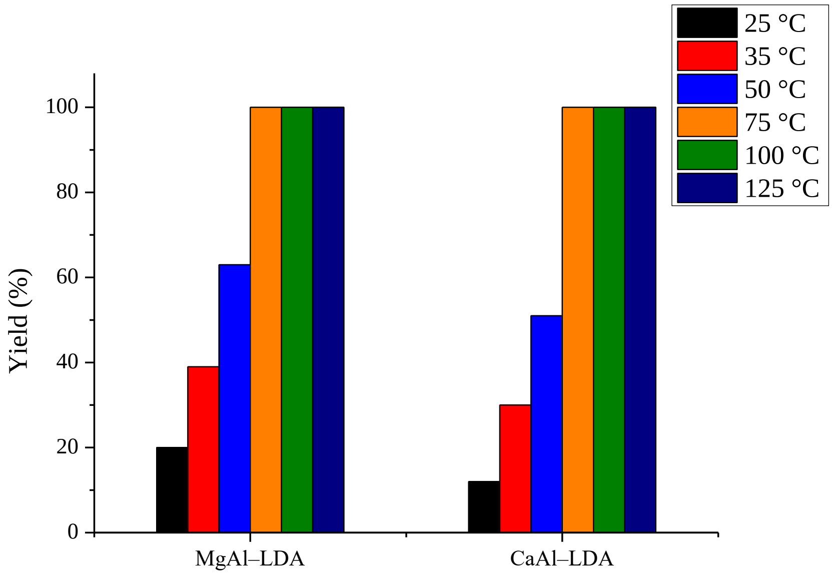


SFigure 9. Effect of the catalyst loading for the Knoevenagel condensation between benzaldehyde (10.0 mmol) and malononitrile (15.0 mmol); under reflux (~75°C), t = 180 min, v(EtOH) = 3.0 cm^3.

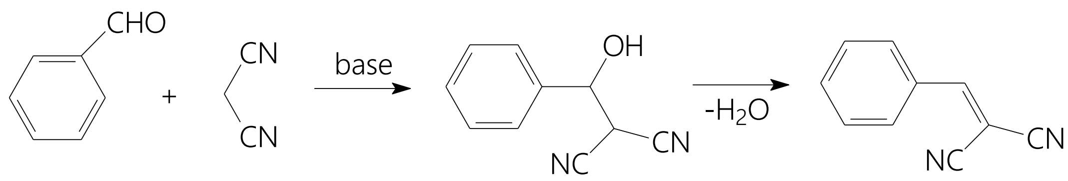
STable 2. Effect of the solvent for the Knoevenagel condensation between benzaldehyde (10.0 mmol) and malononitrile (15.0 mmol); T = 125°C/reflux, t = 180 min, v(solvent) = 3.0 cm^3, mcat = 0.2 g.

Solvent	Yield (%)[a]	Yield (%)[b]
chloroform	1	10
acetonitrile	–	–
ethanol	100	100
solvent-free	**100**	**100**

a: yield for water-free CaAl–LDH (CaAl–LDA), b: yield for water-free MgAl–LDH (MgAl–LDA).



SFigure 10. Effect of the reaction temperature for the Knoevenagel condensation between benzaldehyde (10.0 mmol) and malononitrile (15.0 mmol); t = 180 min, solvent-free, mcat = 0.2 g.



SScheme 1 The reaction sequence between benzaldehyde and malononitrile.

References

[1] Siri-nguan N, Ngamcharussrivichai C. Alkoxide-intercalated Mg–Al layered double hydroxides as selective catalysts for the synthesis of monoglycerides. Reac Kinet Mech Cat. 2016:119:273–289.
[2] Kang H, Kima HJ, Yang JH, Kim TH, Choi G, Paek SM, Choi AJ, Choy JH, Oh JM. Intracrystalline structure and release pattern of ferulic acid intercalated into layered double hydroxide through various synthesis routes. Appl Calay Sci. 2015:112–113:32–39.
[3] Sacerdoti M, Passaglia E, Hydrocalumite from Latium, Italy: its crystal structure and relationship with related synthetic phases. in Neues Jahrbuch für Mineralogie, Monatshefte 1988:462–475.