Supplementary Material

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

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\textbf{Figure 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°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$_2$Al–NO$_3^-$–LDH | 8.58        | 4.8           | 3.08            | 22.91           |
| CaAl–LDA           | 7.49        | —             | 5.92            | 15.01           |
| Ca$_2$Al–NO$_3^-$–LDH | 8.26        | 2.4           | 5.45            | 17.16           |
| C$_2$H$_5$O$^-$–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$_{(002)}$*
Figure 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–NO₃–LDH.
Figure 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

[Graph showing yield (%) vs. catalyst loading (g) for MgAl–LDA, CaAl–LDA, and MgAl–LDH]

**Figure 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, $v(\text{EtOH}) = 3.0 \text{ cm}^3$.

**Table 2.** Effect of the solvent for the Knoevenagel condensation between benzaldehyde (10.0 mmol) and malononitrile (15.0 mmol); $T = 125^\circ\text{C}$/reflux, $t = 180$ min, $v(\text{solvent}) = 3.0 \text{ cm}^3$, $m_{\text{cat}} = 0.2$ 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–LDH).
**Figure 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.

**Scheme 1** The reaction sequence between benzaldehyde and malononitrile.

**References**

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