Supporting Information

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Supporting Information

$^{27}$Al MAS NMR was measured on a Gemini Varian at 400 MHz spectrometer using Al(OH)$_6^{3+}$ as reference. Infrared spectra were recorded on a Nicolet 740 FT-IR spectrometer either as neat liquids or KBr pellets. X-ray photoelectron spectra were recorded on a KRATOS AXIS 165 with a dual anode (Mg and Al) apparatus using the Mg K$\alpha$ anode. The pressure in the spectrometer was about $10^{-9}$ Torr. For energy calibration, we have used the carbon 1s photoelectron line. The carbon 1s binding energy was taken to be 285.0 eV. The spectra were deconvoluted using Sun Solaris based Vision 2 curve resolver. The location and the full width at half maximum (FWHM) for a species was first determined using the spectrum of a pure sample. The location and FWHM of products, which were not obtained as pure species, were adjusted until the best fit was obtained. Symmetric Gaussian shapes were used in all cases. Binding energies for identical samples were, in general, reproducible to within ± 0.1 eV. Thermogravimetric (TG) and differential thermal analysis (DTA) of the catalyst were studied by means of a
TGA/SDTA 851° Mettler Toledo System, using open aluminium crucibles, containing samples weighing about 8-10 mg with a linear heating rate of 10 K min⁻¹. Nitrogen was used as a purge gas for all these measurements. X-ray diffraction patterns were determined on a powder X-ray diffractometer, Siemens/D-5000 instrument (diffraction geometry; θ-2θ, in range of 5-65°), using Cu-Kα radiation. The SEM (scanning electron microscopy) of the catalysts was done on a Hitachi SEM S-520, instrument.

**Characterization**

**LDH-DA**

Mg to Al ratio and carbon contents of the samples were determined by inductively coupled plasma (ICP) analysis and CHN analyzer respectively. The elemental analysis of the catalysts gave Mg:Al ratio (2.80 for cat. A, 2.91 for cat. B), which are very close to the originally charged nitrate layered double hydroxides and calcined layered double hydroxides, respectively. Since this ratio does not vary upon reaction with diisopropylamide anion, no selective dissolution of metal (Mg or Al) takes place during the preparation of the catalyst.¹

**Powder X-ray Diffraction.**

The X-ray diffraction of the powder samples of fresh and used cat. A show a characteristic pattern of LDHs (Figure S1).² The X-ray powder diffraction patterns of the precursor layered double hydroxide material and the diisopropylamide supported LDHs (uncalcined-nitrate form) (cat. A) hardly differ in the range of 2θ = 30°- 65° (Figure S1a). In the case of nitrate LDHs, cat. A, no change in the interlamellar distance is observed. cat. B show characteristic pattern of mixed oxide form of LDHs (Figure S1b),
indicating the formation of homogeneous solid solution binding to the defective Al center. Both catalysts are compared with their precursors (Figure S1c and S1d).

**Figure S1.** X-ray powder-diffraction patterns of various LDHs catalysts (a) cat. A, (b) cat. B, (c) calcined LDHs, (d) LDH-NO$_3$.

**Thermal Analysis**

The TGA and DTA profiles for cat. A and cat. B, LDH-NO$_3$, calcined LDHs and LDA (lithium diisopropylamide) are shown in Fig. 2. The DTA curves of all the layered double hydroxide samples are similar to those reported in the literature.$^{[3]}$ As can be see in (Fig. 2a, 2b, 2c, and 2d), the first endothermic peak observed below 100 °C is attributed to the
release of surface (physically absorbed) water and the decomposition of diisopropylamide. The observed weight loss in the temperature range 25 - 100 °C is 2.73 and 1.40 % in the uncalcined (cat. A) and calcined catalyst (cat. B), respectively. This clearly indicates that the observed weight loss (1.40 %) in the calcined catalyst (cat. B) is only due to the partial decomposition of diisopropylamide. The shallow endotherms observed between 100-250 °C are due to the loss of water present in the brucite interlayers. The endothermic peaks observed between 250-450 °C are attributed due to the structural dehydroxylation, decomposition of brucite layers, decomposition of NO$_3^-$ (in case of cat. A) and/or diisopropylamide. The DTA of a pure lithium diisopropylamide shows peaks at 75 °C, 200 °C, 270 °C and a predominant peak at 340 °C (Figure S2f), owing to its decomposition. The thermal decomposition experiments demonstrated that the decomposition of diisopropylamide anion is shifted to 330 °C in cat. A and cat. B, which indicates that the electrostatic interaction between diisopropylamide and positively charged brucite layer is stronger.
Figure S2. TGA and DTA of various LDHs catalysts and its precursor. (a) TGA of cat. A, (b) DTA of cat. A, (c) TGA of cat. B, (d) DTA of cat. B, (e) TGA of LDA, (f) DTA of LDA, (g) TGA of LDH-NO$_3$, (h) DTA of LDH-NO$_3$. 

Exo

Endo

Temperature °C
FT-IR Spectroscopy

Cat. A and cat. B were subjected to FT-Infrared spectroscopy to probe the structural modifications before and after modification of the catalyst and the spectra are represented in Fig. 3. Cat. A and cat. B give similar absorption bands at 1502, 1440 cm\(^{-1}\) and 1505, 1438 cm\(^{-1}\) which are very close to that of homogeneous analogue, LDA (Figure S3d). The molecular vibration of NO\(_3^\text{-}\) anion in cat. A (Figure S3b), which is observed around 1384 cm\(^{-1}\), is very close to that of literature value (1385 cm\(^{-1}\)). It can also be seen that the cat. A, obtained from uncalcined LDH-NO\(_3\) (Figure S3c) shows the peak at 1385 cm\(^{-1}\) in elongated form to indicate the presence of unexchanged nitrates too. There is no such projection for the cat. B (Figure S3a), since it is devoid of NO\(_3^\text{-}\). In all the IR spectra, strong absorption bands in the range 3400-3600 cm\(^{-1}\) due to the hydroxyl (OH) stretching vibration, and the corresponding deformation mode appeared around 1630 cm\(^{-1}\) in all the samples of LDHs.\(^{[4]}\)
Figure S3. FT-IR spectra of various LDHs catalysts and its precursor. (a) cat. B, (b) cat. A, (c) LDH-NO$_3$, (d) LDA, (e) used cat. B.

$^{27}$Al MAS NMR Studies

To understand in-depth the change in coordination of Al during the exchange process, a solid state, $^{27}$Al MAS NMR study of the LDH-NO$_3$, calcined LDHs, cat. A and cat. B was undertaken. The $^{27}$Al MAS NMR spectra of the cat. A and cat. B and their precursors reveal actual coordination environment of the aluminium sites present in the brucite layer. The $^{27}$Al MAS NMR of cat. A (Figure S4b) and its precursor, uncalcined LDH-NO$_3$ (Figure S4d) show a single peak centered at $\delta$ 9.7 and 9.4 ppm, to indicate the presence of octahedral aluminium only, while the cat. B (Figure S4a) and its calcined...
precursor (Figure S4c), exhibit two peaks centered at δ 11.9 and 70 ppm, 8 and 68 ppm, respectively corresponding to both tetrahedral and octahedral Al. During the calcination, the Al$^{3+}$ cations adopt a tetrahedral coordination due to dehydration.$^{[5]}$

Figure S4. $^{27}$Al MAS NMR spectra of various LDHs catalysts and their precursors. (a) cat. B, (b) cat. A, (c) Calcined LDHs, (d) LDH-NO$_3$. 
Scanning Electron Microscopy

The cat. A and cat. B were subjected to scanning electron microscopy. The cat. A and cat. B samples are seen as particles of agglomerated flat crystallites (Figure S5a and S5b).

Figure S5. Scanning electron micrographs of LDHs catalysts. (a) cat. A, (b) cat. B.

X-ray Photoelectron Spectroscopy (XPS)

XPS a semi-quantitative surface–oriented technique has been widely used to study the coordination state of aluminum in oxide environments. From these studies it is revealed that the Al 2p binding energy peaks reflect on the tetrahedral/octahedral coordination of Al atom and also the binding energy of Al 2p electron of tetrahedral Al\textsuperscript{3+} (73.2 eV) is always lower than the binding energy of the octahedral Al\textsuperscript{3+} (74.1 eV). The XPS high resolution narrow scan peaks observed for Al 2p in the present study for various LDHs are described in (Table 1). Pure LDH-NO\textsubscript{3} shows a single binding energy peak at 74.322 eV comparable with the octahedral Al of pure gibbsite, Al(OH)\textsubscript{3}\textsuperscript{[6]} indicating the presence of octahedral Al only in the LDHs framework. On the other hand, in calcined LDH-NO\textsubscript{3} catalyst the observed XPS binding energy peak for Al 2p could be deconvoluted into two peaks at 74.322 eV and 72.77 eV which can be attributed due the presence of Al in both...
octahedral and tetrahedral coordination respectively. The binding energy peak at 72.77 eV assigned to the presence of tetrahedral Al (Table 1), is in consonance to the earlier report of Al (2p) for pure $\text{Na}_2\text{Al}_2\text{O}_4$ [6]. Further, the XPS spectra of the Al (2p) for cat. A shows a single line at 74.37, whereas cat. B exhibits two distinct lines at 74.88 and 72.86 eV. This observation clearly demonstrates that the cat. A prepared from uncalcined sample has octahedral Al sites only and cat. B prepared from calcined sample contains both octahedral and tetrahedral Al sites in the brucite layers (Figure S6).

Figure S6. Al 2p XPS of cat. B.
Table 1. Al 2p XPS (ESCA) binding energies (± 0.1 eV) for various LDHs catalysts containing either octahedral or tetrahedral aluminium.

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<tr>
<td>1</td>
<td>LDH-NO₃</td>
<td>74.322</td>
<td>-</td>
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<td>2</td>
<td>Calcined LDH-NO₃ (3:1)</td>
<td>74.510</td>
<td>72.77</td>
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<td>3</td>
<td>LDH-DA (3:1) (cat. A)</td>
<td>74.37</td>
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<td>4</td>
<td>LDH-DA (3:1) (cat. B)</td>
<td>74.88</td>
<td>72.86</td>
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References


