

Electronic Supporting Information (ESI) for

One-pot direct synthesis route to self-assembled highly ordered Zn-decorated mesoporous aluminum oxide toward efficient and sustainable metathesis heterogeneous catalyst design

Abdelnasser Abidli*^{ab}

^aDepartment of Soil Sciences and Agri-Food Engineering, Laval University. G1V 0A6, Quebec City, Quebec, Canada

^bCentre in Green Chemistry and Catalysis (CGCC), H3A 0B8, Montreal, Quebec, Canada.

E-mail: abdelnasser.abidli.1@ulaval.ca; Tel: +1-581-777-0860; Fax: +1-418-656-3723

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S1. Details of experiments and instrumentations used in materials characterization

A. Materials and chemicals

Pluronic F127 (EO₁₀₆PO₇₀EO₁₀₆, MW = 12 600), aluminum isopropoxide Al(OPrⁱ)₃ (≥98.0%), aluminum-tri-*sec*-butoxide Al(OBu^s)₃ (97.0%), citric acid (≥99.5%), L-(+)-tartaric acid (≥99.5 %), fumaric acid (≥99.5 %), oxalic acid (>99.0%), maleic acid (≥99.0%), malonic acid (99.0%), acetic acid (≥99.7%), zinc chloride (ZnCl₂, 99.9%) and methyltrioxorhenium (VII) (MTO, CH₃ReO₃ with Re 71.0-76.0 %) were purchased from Sigma-Aldrich Canada (Oakville, ON, Canada). Aluminum tri-*tert*-butoxide Al(OBu^t)₃ (97.0%) was purchased from VWR International (Mississauga, ON, Canada). Aluminum nitrate nonahydrate Al(NO₃)₃•9H₂O (99.9%), hydrochloric acid (HCl, 36.5-38 wt%) and malonic acid (≥99.0%) were purchased from Acros Organics (Morris Plains, NJ, USA). Cyclohexane (99.9%), hexane (99.0%), and ethanol (99.9%) were purchased from Fisher Scientific (Ottawa, Ontario, Canada). All reagents were used as received without further purification. All gases used were provided by Praxair at a purity of at least 99.995%.

B. Brunauer–Emmett–Teller (BET) surface area measurements

The textural properties and surface analysis of calcined samples were performed by nitrogen adsorption/desorption isotherms. The samples were initially out-gassed under vacuum (10⁻⁴ Torr) at 250-300 °C during 12 h. Then, the multipoint BET surface area measurement was carried out using a volumetric adsorption analyzer (Model Autosorb-1, Quantachrome Instruments, Boyton Beach, FL) at liquid nitrogen temperature -196 °C (77 K). The specific surface area was evaluated using the Brunauer–Emmett–Teller (BET) method. Total pore volume was estimated from the amount adsorbed at the relative pressure P/P₀ = 0.990 single point. Pore size distribution curves were calculated using the desorption branch of the N₂-adsorption/desorption isotherms and the Barrett-Joyner-Halenda (BJH) method as reported in the literature for this type of materials.¹⁻³

C. Powder X-ray diffraction (XRD) measurements

The crystal structures of the calcined samples were analyzed by XRD using a Ultima III Rigaku monochromatic diffractometer (Model D/MAX-2200, with CuK α radiation source ($\lambda=1.54059$ Å) operated at a voltage of 40 kV and a current of 44 mA. Small angle XRD measurements were performed over the 2θ angle range of $0.6-6^\circ$ at a scanning rate of $0.5^\circ/\text{min}$.

D. Transmission electron microscopy (TEM) studies

The pore size and morphology were examined by transmission electron microscopy (TEM). The micrographs were taken from a JEM-1230 electron microscope (JEOL, Japan) equipped with a lanthanum hexaboride (LaB $_6$) thermionic emission source, operated at an acceleration voltage up to 80 kV, using Gatan dual-view multiscan camera. For TEM observations, the powdered samples were dispersed in methanol and sonicated for 10 min. A suspension drop of the obtained solution (5 μL) was then placed uniformly onto a Formvar film coated nickel grid (200 meshes) and it was allowed to dry in air at room temperature before analysis.

E. Microstructural characterizations SEM/EDX

The microstructure, morphology and elemental composition of the synthesized materials were determined using scanning electron microscopy (SEM) along with energy dispersive X-ray spectrometry (EDX). Before analysis, powdered samples were dispersed on a copper grid (300 mesh) coated with a Lacey amorphous carbon film. The samples were deposited by cathodic sputtering in vacuum chamber (100 mTorr), using an Au/Pd thin film to make the surface electrically conductive for better sensitivity and higher imaging resolution. The characterization was carried out on a JEOL model JSM-840A scanning electron microscope equipped with an energy-dispersive X-ray (EDX) spectrometer operating at an accelerating voltage of 15 kV using secondary electron mode at high vacuum (10^{-6} Torr). EDX spectra of the particles were collected using a single-point quantitative analysis taken from several random areas of the sample. SEM images were acquired using OrionTM software at different magnifications

(X 350-3000). The EDX signals were obtained by focusing a high energy electron beam on the particles and accumulating the spectra within an acquisition time of 60 s using Spirit™ Bruker AXS Microanalysis software. Average atomic ratio of the present elements was calculated from several EDX spectra at different points of the prepared sample.

F. X-ray photoelectron spectroscopy (XPS) measurements

Identification of material surface species and their oxidation/coordination states was achieved by means of XPS analysis. XPS spectra were recorded on an AXIS ULTRA from Kratos Analytical (Manchester, UK) equipped with a double X-ray source for non-monochromatic Al-Mg ($K\alpha$) X-ray irradiation, a monochromatic Al ($K\alpha$) X-ray irradiation source (1486.6 eV), and an electrostatic analyzer of large radius. The base pressure in the UHV XPS chamber was 5×10^{-10} Torr. All spectra were acquired with the Al monochromatic source at room temperature operated at 300 W. The working pressure in the analyzing chamber was less than 10^{-7} Torr. The survey spectrum used to determine the elementary apparent composition was recorded with pass analyzer energy of 160 eV and an energy step of 1 eV, using lenses in the hybrid mode, which maximizes sensitivity.^{4, 5} The detailed spectra were obtained with pass energy of 20 or 40 eV, and an energy step of 50 or 100 meV. The charge neutralizer was used for charge compensation of the non-conducting samples. The binding energies were corrected for charge shifts, with the use of the C1s set at 285 eV peak as internal reference.⁶ The uncertainty in the reported binding energy (BE) values is ± 0.1 eV. The survey spectra were recorded in the binding energy range 0–1150 eV, and detailed spectra were recorded for Al2p, O1s, Zn2p and Cl2p. Curve fitting and deconvolution were performed using mixed Gaussian/Lorentzian line shapes after a Shirley-type background removal by using the CasaXPS 2.3.15 software.⁷

G. ¹H -MAS NMR measurements

Catalyst framework was investigated by solid-state NMR spectroscopy. ¹H-MAS NMR spectra were recorded on a Bruker AVANCE 300 (Bruker BioSpin Ltd.) wide bore NMR spectrometer equipped with superconducting magnet of 7.1

Tesla using a conventional 4mm-broadband resonance magic angle spinning MAS probehead at operating Larmor frequencies of 300.1 MHz. The dehydrated samples were quickly packed into a 4 mm-zirconia (ZrO_2) rotor, and then the spectra were acquired at room temperature at a typical spinning rate of 10 kHz at the magic angle. Single pulse excitation ^1H -NMR experiments were performed for Al_2O_3 -meso and the ZnCl_2 -modified Al_2O_3 -meso using a 90° pulse length of 2.25 μs , an acquisition time of 30 ms, and a recycle delay between scans of 60 s. Eight scans were collected for each ^1H -MAS-NMR spectrum. All the corresponding chemical shift values were referenced to tetramethylsilane (TMS) signal (0.0 ppm in a spinning rotor).

H. ^{27}Al -MAS NMR investigations

The form, coordination state and environment of aluminum, as well as the surface and intrinsic Lewis acidic site concentrations were studied by means of ^{27}Al solid-state magic-angle spinning (MAS) NMR spectroscopy measurements. The experiments were conducted on a Bruker Avance 300 (7.1 T) instrument. ^{27}Al -MAS- NMR spectra were obtained using a high-speed broadband MAS-probe with an outer diameter of 4 mm, and rotated around the Magic Angle at a rate of 10 kHz controlled within ± 2 Hz using a Bruker MAS-controller, with an acquisition time of 15.4 ms. The system was operated at a resonance frequency of 78.1 MHz for ^{27}Al nuclei. All spectra were obtained at room temperature. For the 1D- spectrum measurements, a short single excitation $\pi/10$ pulse of 0.6 μs was applied. The small flip angle of the ^{27}Al pulse was advantageously used to improve signal intensity quantification of the quadrupole nucleus.⁸ The relaxation time was set at 250 ms, and 2000 scans were recorded. The ^{27}Al -NMR ppm scale was referenced to $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ by adjusting the signal to 0 ppm.⁹

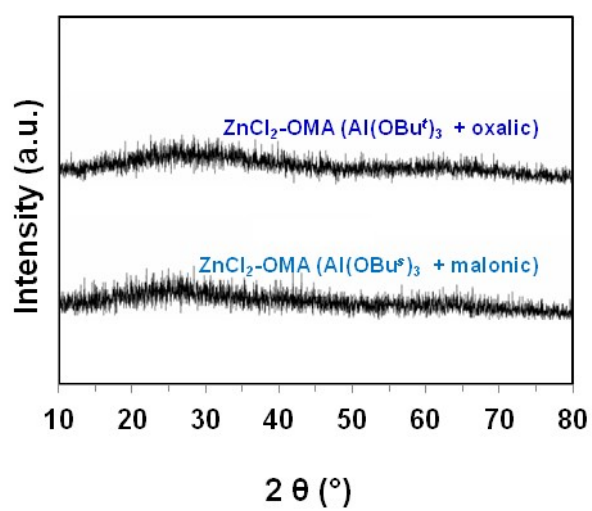


Figure S1. Wide-angle XRD patterns of ZnCl₂-OMA samples calcined at 400 °C, prepared using citric acid with different aluminum precursors.

Table S1 The compositions of the ZnCl₂-OMA materials measured from EDX data.

Sample	Cl (At%)	Zn (At%)	Cl/Zn Ratio*
(e): ZnCl ₂ -OMA (Al(OBu ^s) ₃ + oxalic)	6.58	10.29	0.63
(f): ZnCl ₂ -OMA (Al(OPr ⁱ) ₃ + tartaric)	8.91	14.85	0.60
(g): ZnCl ₂ -OMA (Al(OBu ^t) ₃ + fumaric)	6.37	10.19	0.62
(h): ZnCl ₂ -OMA (Al(NO ₃) ₃ ·9H ₂ O + citric)	8.48	13.16	0.64
ZnCl ₂ -OMA (Al(OBu ^s) ₃ + malonic)	10.83	17.18	0.63
ZnCl ₂ -OMA (Al(OBu ^s) ₃ + maleic)	9.34	15.64	0.59

*Bulk atomic ratio obtained from EDX analysis. e-h samples correspond to the EDX spectra depicted in Fig. 5.

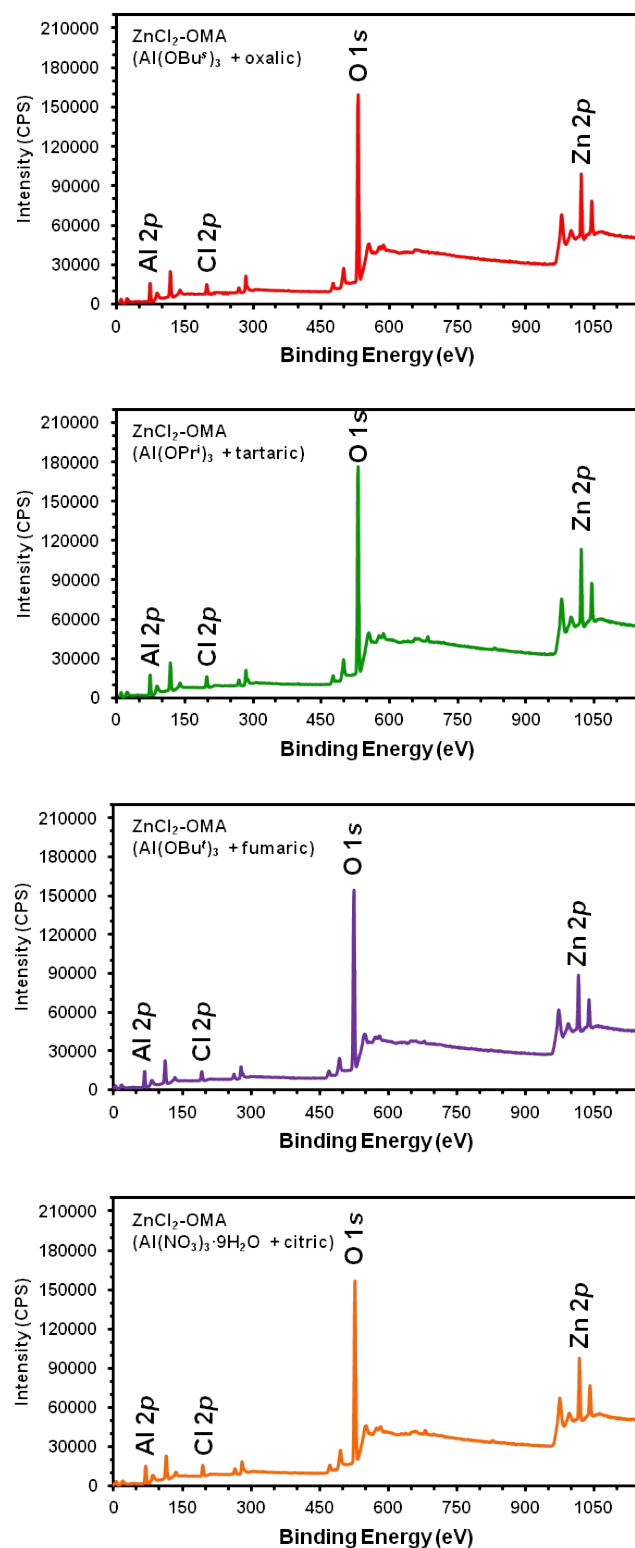


Figure S2. XPS survey spectra of the ZnCl₂-OMA samples synthesized using diverse carboxylic acids and aluminum precursors. All samples were calcined at 400 °C. All shifts for the samples were corrected by normalization of the C 1s binding energy to 285.0 eV.

Table S2 The calculated Al/Zn atomic ratios measured by XPS data for the analyzed ZnCl₂-OMA samples.

Entry	Sample	Al (At%)	Zn (At%)	Al/Zn Ratio*
1	ZnCl ₂ -OMA (Al(OBu ^s) ₃ + oxalic)	19.83	2.67	7.43
2	ZnCl ₂ -OMA (Al(OPr ⁱ) ₃ + tartaric)	20.49	2.47	8.29
3	ZnCl ₂ -OMA (Al(OBu ^t) ₃ + fumaric)	20.48	2.62	7.82
4	ZnCl ₂ -OMA (Al(NO ₃) ₃ ·9H ₂ O + citric)	20.88	2.35	8.88
5	ZnCl ₂ -OMA (Al(OBu ^s) ₃ + malonic)	20.81	2.87	7.25
6	ZnCl ₂ -OMA (Al(OBu ^s) ₃ + maleic)	19.23	2.65	7.26

*Surface atomic ratio calculated from XPS analysis by using peak areas normalized on the basis of sensitivity factors. Entries 1-4 correspond to the XPS survey spectra depicted in Fig. S2.

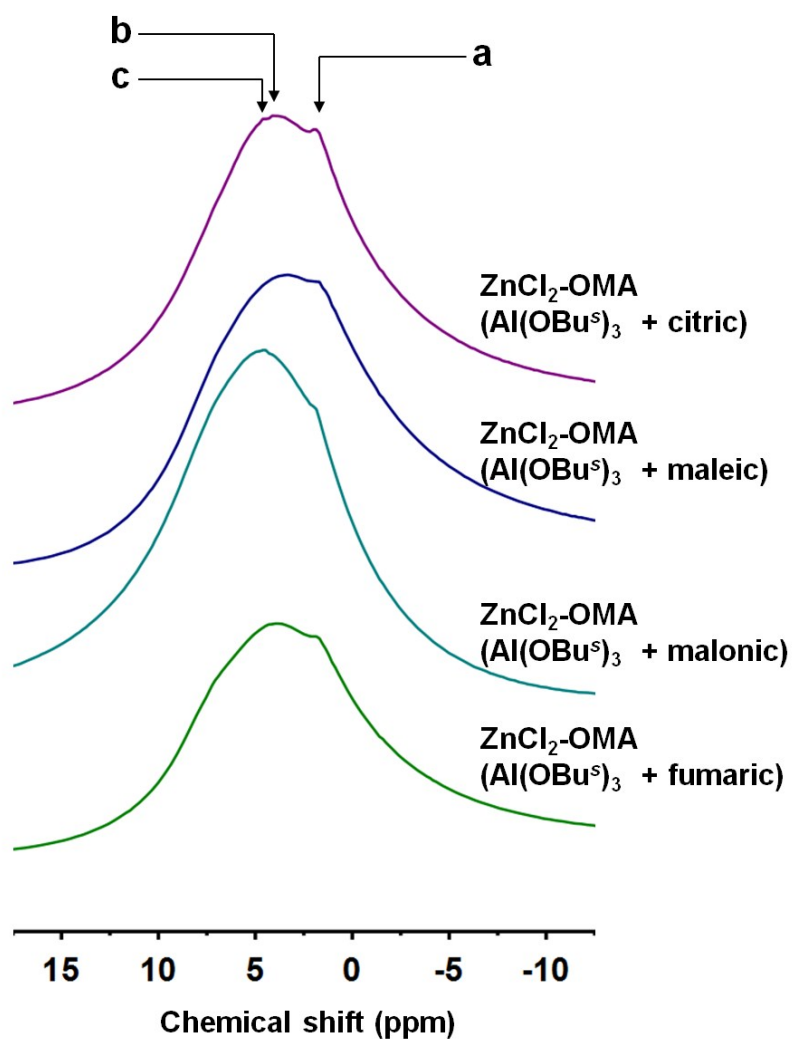


Figure S3. ^1H MAS NMR spectra of ZnCl₂-OMA samples prepared using Al(OBu^s)₃ aluminum precursor with different carboxylic acids. Indicating (a) basic terminal hydroxyl groups (b) acidic bridging hydroxyl groups, and (c) hydrogen bonded water physisorbed on alumina surface. All samples were calcined at 400 °C.

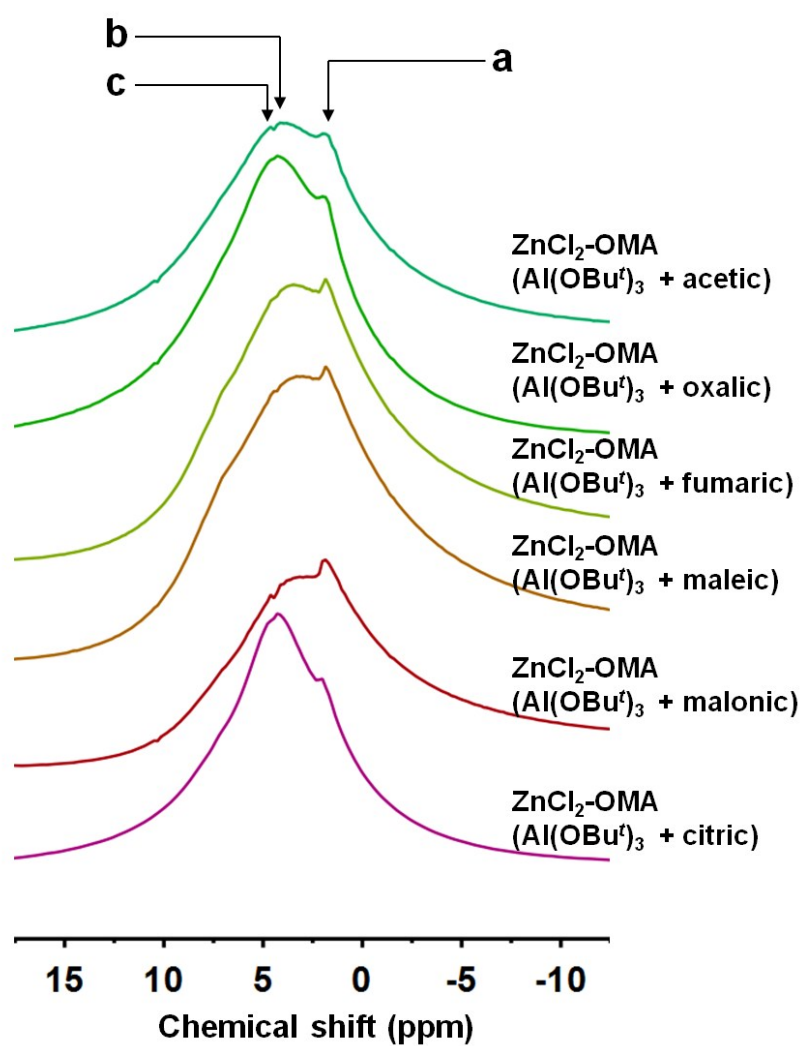


Figure S4. ^1H MAS NMR spectra of ZnCl₂-OMA samples prepared using Al(OBu^t)₃ aluminum precursor with different carboxylic acids. Indicating (a) basic terminal hydroxyl groups (b) acidic bridging hydroxyl groups, and (c) hydrogen bonded water physisorbed on alumina surface. All samples were calcined at 400 °C.

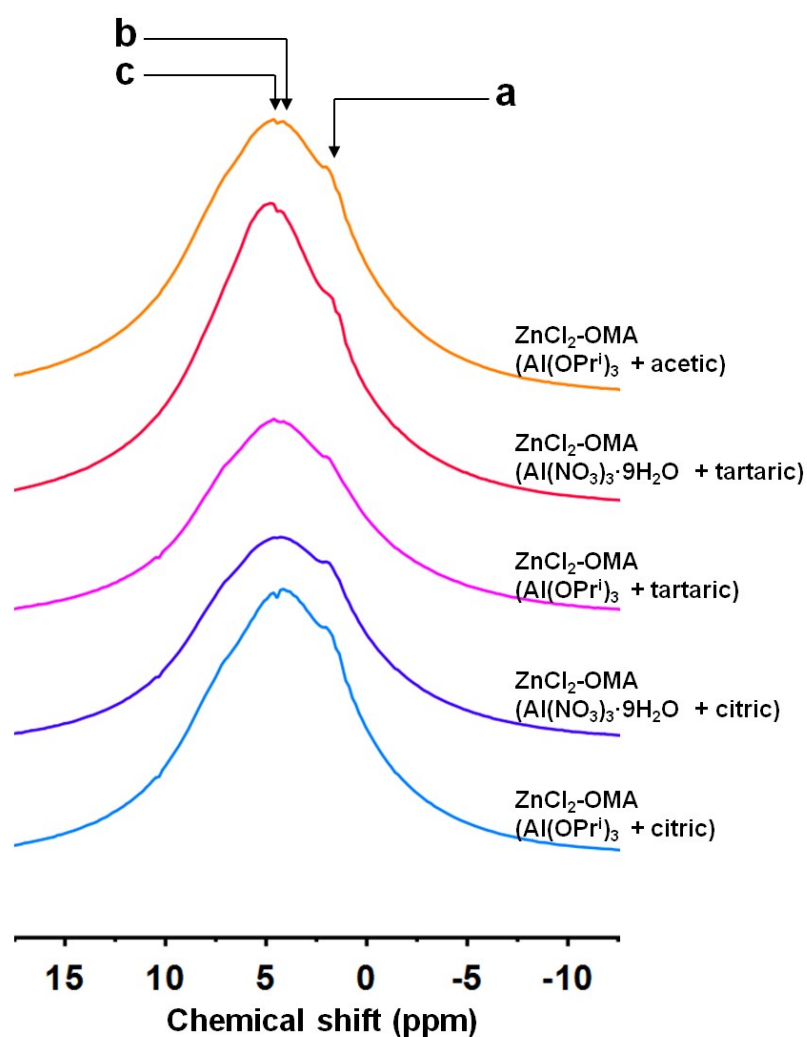


Figure S5. ^1H MAS NMR spectra of ZnCl₂-OMA samples prepared using different aluminum precursors with different carboxylic acids. Indicating (a) basic terminal hydroxyl groups (b) acidic bridging hydroxyl groups, and (c) hydrogen bonded water physisorbed on alumina surface. All samples were calcined at 400 °C.

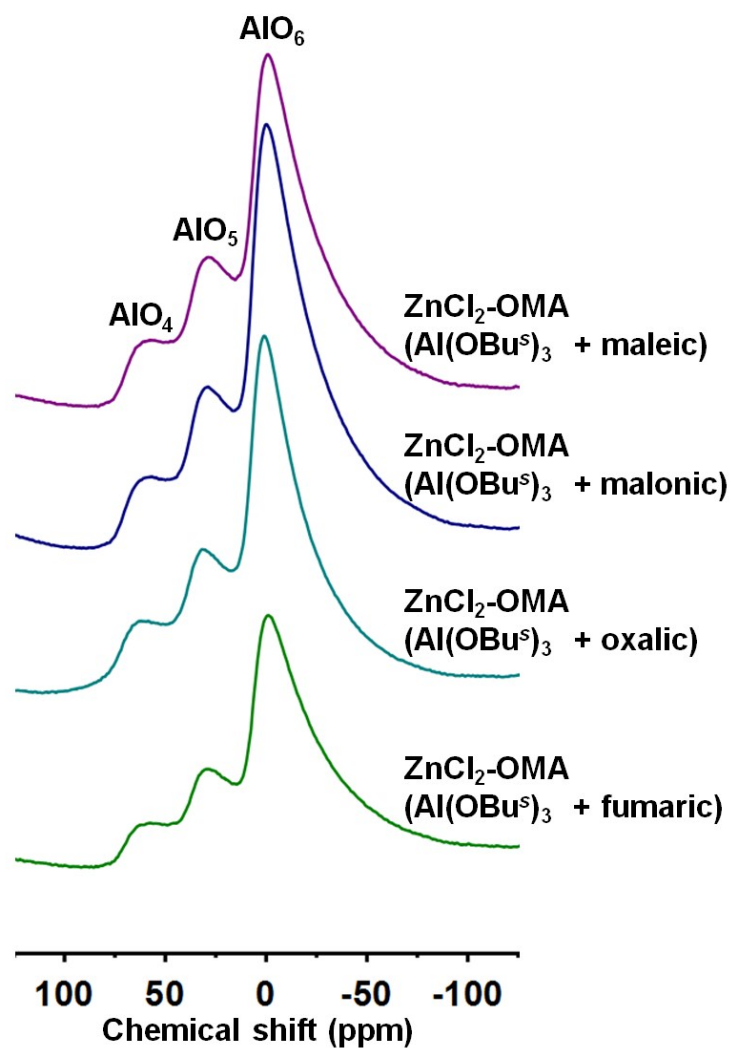


Figure S6. ^{27}Al MAS NMR spectra of $\text{ZnCl}_2\text{-OMA}$ samples prepared using $\text{Al(OBu}^s)_3$ aluminum precursor with different carboxylic acids. All samples were calcined at 400 °C.

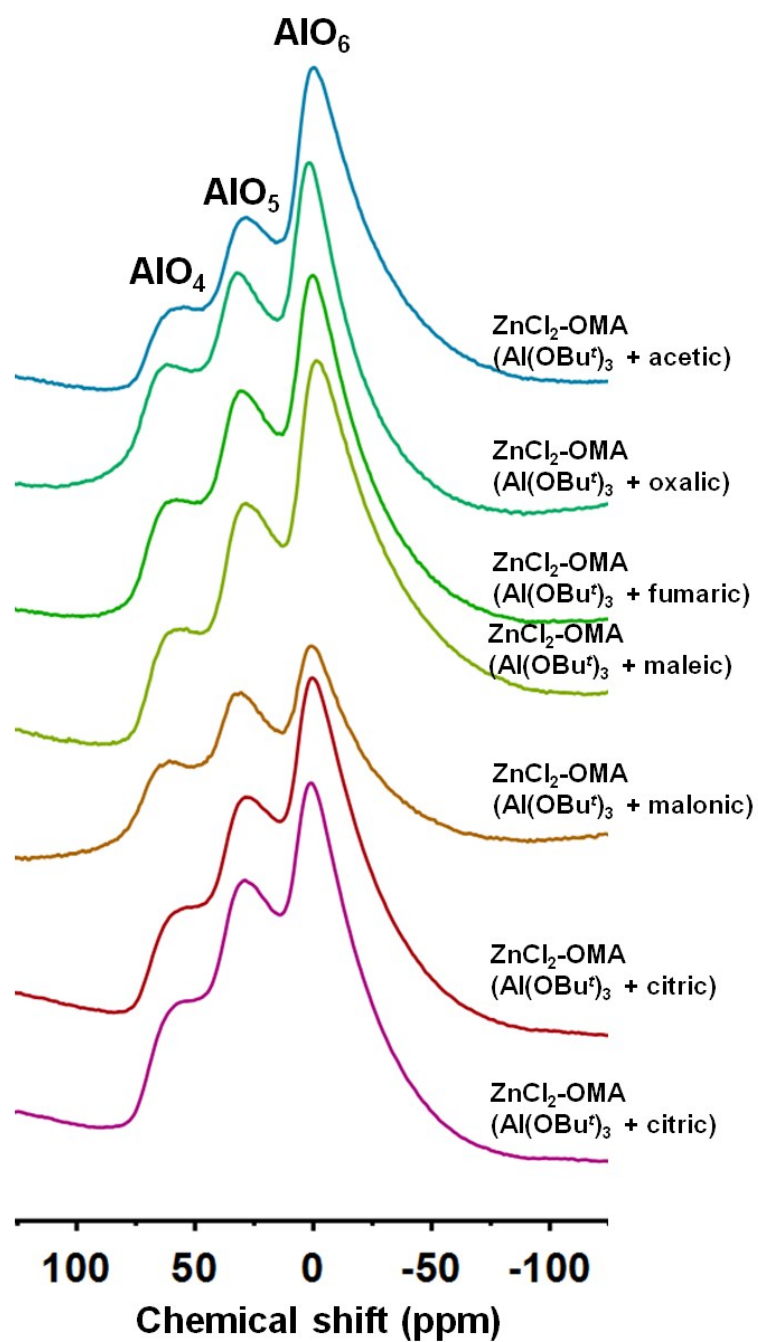


Figure S7. ^{27}Al MAS NMR spectra of $\text{ZnCl}_2\text{-OMA}$ samples prepared using $\text{Al}(\text{OBu}')_3$ aluminum precursor with different carboxylic acids. All samples were calcined at 400 °C.

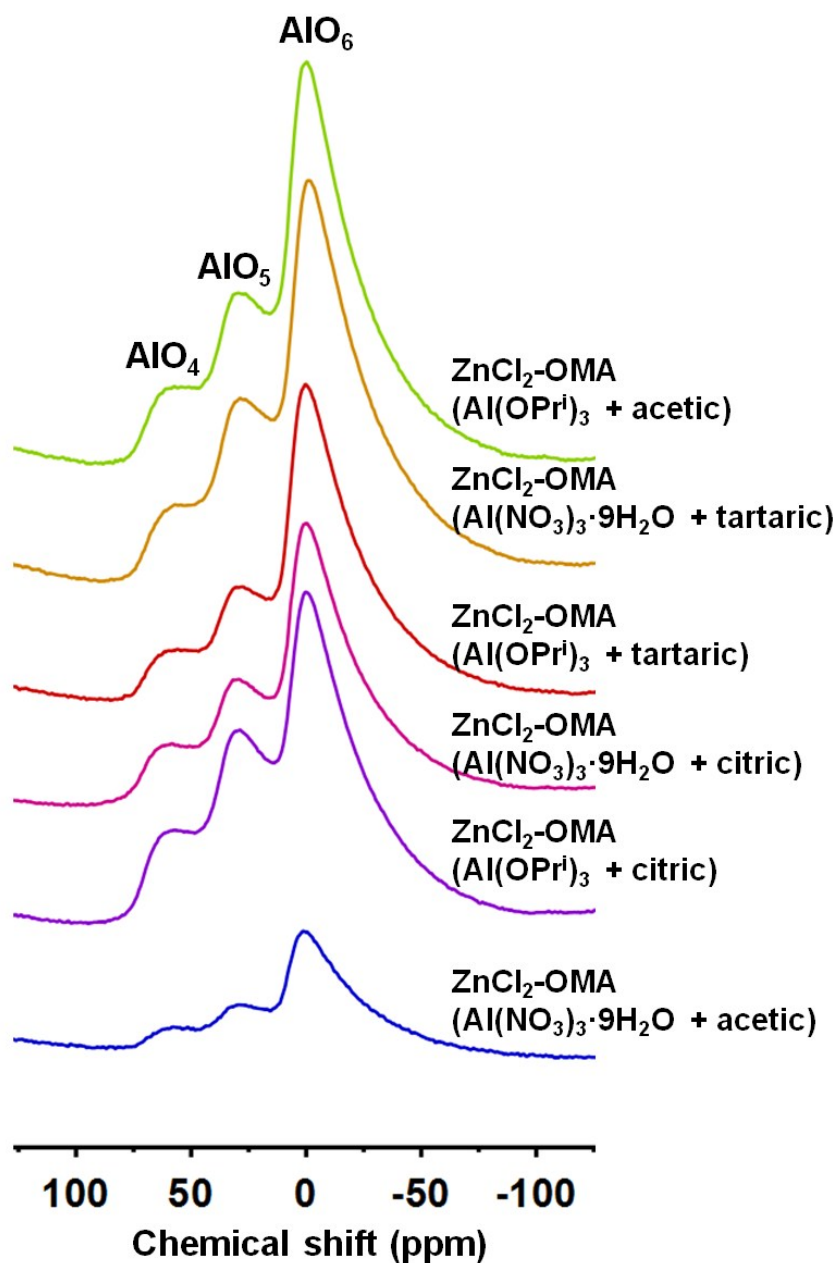


Figure S8. ^{27}Al MAS NMR spectra of $\text{ZnCl}_2\text{-OMA}$ samples prepared using different aluminum precursors with different carboxylic acids. All samples were calcined at 400°C .

Notes and references

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