

## Electronic Supplementary Information (ESI)

### Production of bio-derived ethyl lactate on GaUSY zeolites prepared by post-synthetic galliation

Pierre Y. Dapsens, Martin J. Menart, Cecilia Mondelli\* and Javier Pérez-Ramírez\*

*Institute for Chemical and Bioengineering, Department of Chemistry and Applied Biosciences, ETH Zurich, Wolfgang-Pauli-Strasse 10, CH-8093 Zurich, Switzerland. Fax: +41 44 6331405 Tel: +41 44 6337120; E-mails: cecilia.mondelli@chem.ethz.ch; jpr@chem.ethz.ch.*

#### Catalyst preparation

The FAU-type zeolites employed throughout this study (CBV600, CBV712, CBV720, CBV760, and CBV780) were purchased from Zeolyst International and used as received for post-synthetic modification. The latter comprised alkaline treatment in aqueous 0.2 M NaOH (30 cm<sup>3</sup> per gram of dried zeolite) containing different concentrations (0-0.05 M) of Al(NO<sub>3</sub>)<sub>3</sub> or Ga(NO<sub>3</sub>)<sub>3</sub> (both purchased from Sigma, 99.9%) at 338 K for 30 min in an Easymax<sup>TM</sup> 102 reactor (Mettler Toledo). The resulting materials were converted into the protonic form by three consecutive ion-exchanges in an aqueous solution of ammonium nitrate (0.1 M NH<sub>4</sub>NO<sub>3</sub>, 6 h, 298 K, 100 cm<sup>3</sup> per gram of dried zeolite) followed by calcination in static air at 823 K (5 K min<sup>-1</sup>) for 5 h. A sample of the ATGa4 zeolite (particle size = 0.2-0.4 mm) was further steamed in a fixed-bed reactor (13 mm i.d.) under flowing water vapour in N<sub>2</sub> (30 cm<sup>3</sup> min<sup>-1</sup> N<sub>2</sub>, partial H<sub>2</sub>O pressure 300 mbar) during 6 h at 823 K. All of the samples were used in the catalytic tests in their protonic form. Gallium (III) oxide (Strem Chemicals, 99.998%) was used as received.

#### Catalyst characterisation

The content of Si, Al, and Ga in the catalysts was determined by inductively coupled plasma optical emission spectroscopy (ICP-OES) in a Horiba Ultra 2 instrument equipped with a photomultiplier tube detector. Prior to the measurements, the materials were dissolved in aqueous 3.0 M NaOH under heating at 343 K for 3 h. Nitrogen sorption was performed at 77 K in a Quantachrome Quadrasorb-SI gas adsorption analyser on degassed samples (10<sup>-1</sup> mbar, 573 K, 3 h). Powder X-ray diffraction (XRD) was conducted in a PANalytical X'Pert PRO-MPD diffractometer. Data were recorded in the 5-70° 2θ range with an angular step size of 0.05° and a counting time of 7 s per step. Infrared (IR) spectroscopy of adsorbed pyridine was performed in a Bruker IFS 66 spectrometer equipped with a liquid N<sub>2</sub>-cooled MCT detector. Self-supporting zeolite wafers (5 tons cm<sup>-2</sup>, 20 mg, 1 cm<sup>2</sup>) were pretreated at 10<sup>-3</sup> mbar and 693 K for 4 h. After cooling down to room temperature, the samples were saturated with pyridine vapour and then evacuated at room temperature for 15 min and subsequently at 473 K for 30 min. Spectra were recorded in the 4000-650 cm<sup>-1</sup> range at 4 cm<sup>-1</sup> resolution by co-addition of 32 scans. High-resolution magic angle spinning <sup>71</sup>Ga nuclear magnetic resonance (MAS NMR) spectroscopy was measured in a Bruker AVANCE 700 NMR spectrometer equipped with a 4-mm probe head and 4-mm ZrO<sub>2</sub> rotors at 213.5 MHz. Spectra were acquired using a spinning speed of 10 kHz, 20000 accumulations, 1 μs pulses, a recycle delay of 0.02 s, and a Ga(NO<sub>3</sub>)<sub>3</sub> reference. Transmission electron microscopy (TEM) imaging was undertaken with a FEI Tecnai F30 microscope operated at 300 kV (field emission gun). The samples were prepared by depositing a few droplets of zeolites suspension in methanol on a carbon-coated copper grid, followed by evaporation at room temperature.

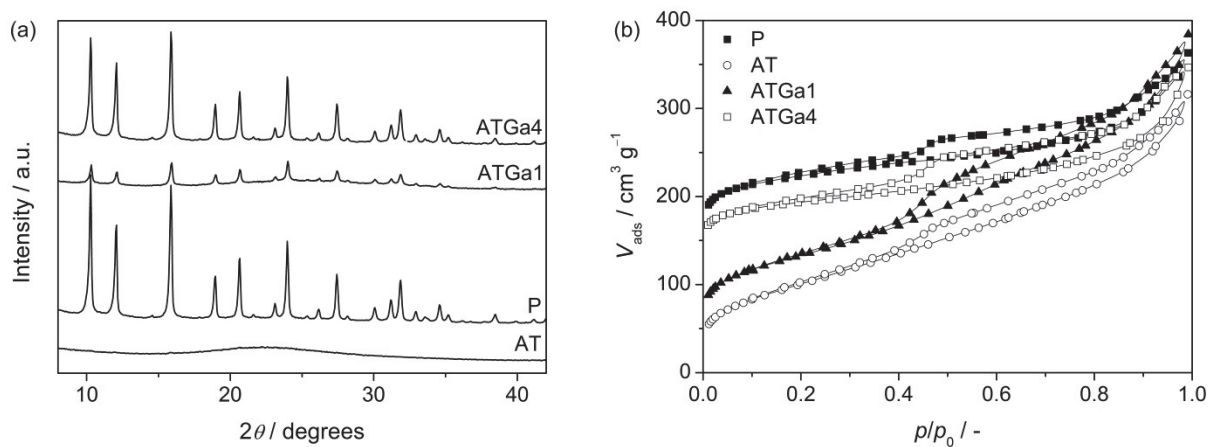
## Catalytic tests

Catalytic tests were carried out batch-wise in 15-cm<sup>3</sup> thick-walled glass vials (Ace, pressure tubes, front seal) dipped in an oil bath at 363 K under autogenous pressure. The internal temperature recorded during the reactions was 358 K. The vials were loaded with 120 mg of dihydroxyacetone (DHA, Sigma-Aldrich, 97%, dimer), 80 mg of catalyst, and 3.88 g of ethanol (99.9%, Scharlau). The mixture was allowed to react under vigorous magnetic stirring for 24 h. After this time, the reaction was quenched in an ice bath and the catalyst removed by means of a Chromafil Xtra 0.25 µm syringe filter. The unconverted DHA was isolated by high-performance liquid chromatography (HPLC) in a Merck LaChrom system equipped with a Biorad Aminex HPX-87H column heated at 308 K, using an aqueous eluent of 0.005 M H<sub>2</sub>SO<sub>4</sub> (pH 2) flowing at 0.6 cm<sup>3</sup> min<sup>-1</sup>. Quantification was obtained by integration of its UV-Vis absorbance band at 272 nm using methyl ethyl ketone as an internal standard. The produced ethyl lactate (EL) and pyruvic aldehyde diethyl acetal (PADA) were analysed using a gas chromatograph (GC, HP 6890) equipped with an HP-5 capillary column and a flame ionization detector. A He carrier gas flow rate of 4.3 cm<sup>3</sup> min<sup>-1</sup> (pressure = 1.4 bar) and an injection size of 0.3 µL were used. The initial temperature of 328 K was held for 2 min before heating to 473 K (30 K min<sup>-1</sup>). The yield of EL was determined using iso-octane as an internal standard, while that of PADA was determined utilising the response factor calculated for pyruvic aldehyde dimethyl acetal, since PADA was not commercially available. The conversion of DHA was calculated as the moles of DHA reacted divided by the moles of DHA fed, while the yields of EL and PADA were calculated as the moles EL and PADA formed, respectively, divided by the moles of DHA fed. Pyruvaldehyde and 1,1,2,2-tetraethoxypropane were identified as the other by-products by HPLC and GC-MS (GC, HP 6890, MS, HP 5973), respectively, but they were not quantified. No coke formation was detected. Reusability tests were performed at the above-described conditions. Between each run, the used catalyst was calcined in flowing air at 823 K (5 K min<sup>-1</sup>) for 2 h. The testing of each catalyst was repeated three times. The experimental error for the reported conversion and selectivity values is ±1%.

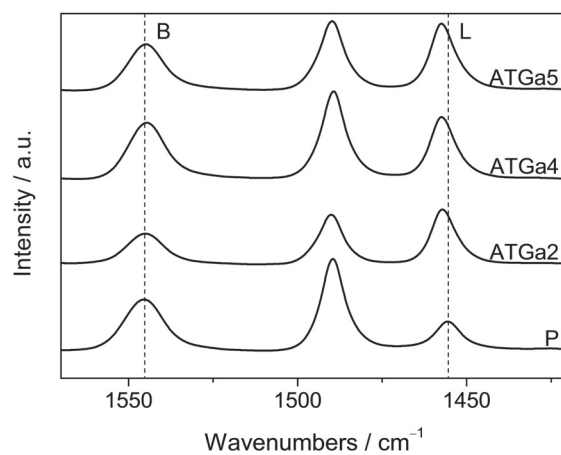
**Table S11** Characterisation of the parent and treated zeolites.

Catalyst <sup>d</sup>	Si/Al <sup>b</sup> (mol mol <sup>-1</sup> )	Yield <sup>c</sup> (%)	Crystallinity <sup>d</sup> (%)	$V_{\text{pore}}$ (cm <sup>3</sup> g <sup>-1</sup> )	$V_{\text{micro}}$ <sup>e</sup> (cm <sup>3</sup> g <sup>-1</sup> )	$S_{\text{meso}}$ <sup>e</sup> (m <sup>2</sup> g <sup>-1</sup> )	$S_{\text{BET}}$ <sup>f</sup> (m <sup>2</sup> g <sup>-1</sup> )
CBV600	2.6	100	100	0.36	0.24	83	675
CBV600-ATAI4	–	81	87	0.45	0.24	128	717
CBV600-ATGa4	–	75	95	0.43	0.28	96	778
CBV712	6	100	100	0.48	0.28	113	807
CBV712-ATAI4	–	85	80	0.47	0.25	132	732
CBV712-ATGa4	–	90	82	0.48	0.28	99	783
CBV720	17	100	100	0.56	0.29	128	842
CBV720-ATAI4	–	89	51	0.54	0.26	161	795
CBV720-ATGa4	–	94	88	0.54	0.24	137	730
CBV760	30	100	100	0.56	0.31	149	903
CBV760-ATAI4	–	90	35	0.48	0.25	130	727
CBV760-ATGa4	–	78	67	0.64	0.25	194	812
CBV780	40	100	100	0.54	0.30	139	859
CBV780-ATAI4	–	72	0	0.34	0.08	162	335
CBV780-ATGa4	–	70	0	0.51	0.09	258	479

<sup>a</sup>The suffixes ATAlx/ATGa<sub>x</sub> indicate alkaline treatment with 0.2 M aqueous NaOH (338 K, 30 min) in the presence of 0.0x M of Al(NO<sub>3</sub>)<sub>3</sub>/Ga(NO<sub>3</sub>)<sub>3</sub>. <sup>b</sup> According to the manufacturer's specifications. <sup>c</sup> Based on the amount of solid recovered after alkaline treatment, ion-exchange, and calcination. <sup>d</sup> Crystallinity derived from XRD. <sup>e</sup> Determined by the *t*-plot method. <sup>f</sup> Determined by the BET method.



**Fig. S11** (a) X-ray diffraction patterns and (b) N<sub>2</sub> isotherms of CBV720 in parent form and after different post-synthetic treatments. The samples' codes are described in the caption of Table S11.



**Fig. S12** Normalized IR spectra of adsorbed pyridine of CBV720 in parent form and selected ATGax samples. The samples' codes are described in the caption of Table S11.