

## Supplementary Information

### Catalytic Amination of Lactic acid using Ru-Zeolites

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#### **Section I - Experimental**

##### **I.1 Materials**

The zeolite samples were supplied from Zeolyst: BEA 12.5 (CP814E), BEA 150 (CP811C-300), FAU 15 (CBV720) and ZSM-5 40 (CBV8014). Commercial catalysts were sourced from Alfa Aesar: Ru/Al<sub>2</sub>O<sub>3</sub> 5wt% and Ru/C 5wt% reduced. Hexamineruthenium(III) chloride Ru(NH<sub>3</sub>)<sub>6</sub>Cl<sub>3</sub> (98%) and potassium nitrate were provided by Acros. Ruthenium (III) chloride hydrate RuCl<sub>3</sub> (99.99%) was supplied by Alfa Aesar. D,L-lactic acid was provided by Fluka Analytical and the ammonia solution (28-30 wt%) was provided by Sigma Aldrich (Emsure).

##### **I.2 Ru-zeolite catalyst preparation**

Ruthenium zeolites were prepared through two methods, ion exchange (IE) using Ru(NH<sub>3</sub>)<sub>6</sub>Cl<sub>3</sub> or wetness impregnation (IMP) using RuCl<sub>3</sub>.

The ion exchange method required several cation exchanges before introduction the ruthenium (NH<sub>4</sub><sup>+</sup>, Na<sup>+</sup>, and Cs<sup>+</sup>). The NH<sub>4</sub><sup>+</sup> exchanged was performed by mixing the zeolite with an aqueous solution of ammonia (0.015M) at room temperature for 16h (200 mL.g<sup>-1</sup>). The Na<sup>+</sup> form was obtained from the NH<sub>4</sub><sup>+</sup> zeolite via two successive ion-exchange steps at room temperature of 16h each, using 100 mL of 1M aqueous solution of NaCl per 1 g of dry zeolite. The obtained Na<sup>+</sup> zeolite was transformed into the Cs<sup>+</sup> form by two successive room temperature ion-exchange steps (48h and 72h) with a 0.1M aqueous solution of cesium acetate (25 mL.g<sup>-1</sup>). After each exchange step, the zeolite powder was recuperated via centrifugation, washed with distilled water, and further air-dried at 60°C. Finally, the zeolite supports were loaded with 2-3 wt.% Ru ion exchange by adding 1g of Cs<sup>+</sup> zeolite to 100 mL aqueous solution containing the required of ruthenium precursor Ru(NH<sub>3</sub>)<sub>6</sub>Cl<sub>3</sub>. After 24h zeolite powder was filtered, washed once with distilled water, and dried at 60°C.

Impregnated samples were prepared using RuCl<sub>3</sub> and the commercial form of the zeolite. A calculated amount of RuCl<sub>3</sub> (1-5 wt% by metal) was dissolved in distilled water before the zeolite powder was

added (1 g of zeolite to 4 mL of water). The resulting suspension was mixed thoroughly overnight. The sample was brought to dryness under reduced pressure and constant agitation before any pre-treatment was carried out.

### **I.3 Catalyst activation**

Prior to activation, the zeolite powder was pressed, crushed and sieved between 250 and 500  $\mu\text{m}$ . Activation was carried out in a quartz U-tube under a flow of  $\text{N}_2$  and  $\text{H}_2$ . The sample was heated to 200°C at 2°Cmin<sup>-1</sup> under  $\text{N}_2$  and held for 5 min. The sample was then heated to 350°C at 3°Cmin<sup>-1</sup> under  $\text{N}_2$  and held for 2h to ensure the sample was dry. Finally, the sample was heated to 400°C at 5°Cmin<sup>-1</sup> and held for 2h under  $\text{H}_2$  to reduce the ruthenium.

### **I.4 Lactic acid amination to Alanine**

Reactions were carried out in a 12 mL pressure reactor. A solution of 1.5 mL to 2.5 mL of ammonia containing 0.1 mM to 20 mM of lactic acid was mixed with 50 mg of catalyst. The reactor was flushed with nitrogen before being filled with 10 bar of  $\text{H}_2$  at 25°C. Reactions were performed at 110-220°C for 2-22 h. Product distribution was determined through <sup>1</sup>H NMR spectroscopy, detailed below.

To test dissolution of zeolites, the above procedure was followed for 4h under 1.5 ml ammonia solution, 10 bar  $\text{H}_2$  and 220°C (no lactic acid) using the parent H-BEA(12.5) zeolite. The zeolite was dried overnight at 80°C before further analysis was carried out.

For the recyclability test, the above procedure was followed using 2 mmol lactic acid, 1.5 ml ammonia solution (14-15 wt%), 10 bar  $\text{H}_2$  and 220°C. The catalyst was recovered, washed with  $\text{H}_2\text{O}$  and dried at 80°C before being reused.

## **I.5 Characterisation tools and Analysis methods**

### **I.5.1 ICP**

The elemental analysis was performed using an inductively coupled plasma-atomic emission spectrometer (ICP-AES, PerkinElmer Optima 3300 DV) with signals for Ru, Al, and Si at 267.9, 308.2, and 251.6 nm, respectively. Prior to ICP-AES measurements, 10 mg of the zeolite sample were dissolved in 0.4 mL hydrofluoric acid and 0.2 mL aqua regia. After few hours, the solution was neutralized with 5 mL boric acid solution (0.49 M) and further diluted to 20 mL in deionized water. A sample was taken of the solution and diluted 25 times in 0.42 M aqueous nitric acid ( $\text{HNO}_3$ ) solution. Calibration curve for Ru standards was plotted using 5 solutions with the following concentrations: 0.01, 0.02, 0.03, 0.04, and 0.05 ppm.

### **I.5.2 <sup>1</sup>H-NMR spectroscopy**

<sup>1</sup>H-NMR spectra were recorded on a Bruker Avance 300 MHz spectrometer with a BBI 5 mm probe.  $\text{D}_2\text{O}$  (Sigma-Aldrich) solvent was used.

The chemical shifts used to identify the products are given below:

<u>Lactic Acid</u>	<u>Alanine</u>	<u>Ethanol</u>	<u>Propionic acid</u>	<u>Propanamide</u>
1H (q) 4.10 ppm	1H (q) 3.75 ppm	2H (q) 2.95 ppm	2H (q) 2.19 ppm	2H (q) 2.08 ppm

### I.5.3 XRD

The structure and crystallinity of the zeolites were confirmed by X-ray powder diffraction (P-XRD) on a high-throughput STOE STADI P Combi diffractometer in transmission mode with focusing Ge(111) monochromatic X-ray inlet beams ( $\lambda = 1.5406 \text{ \AA}$ , Cu K $\alpha$  source).

### I.5.4 N<sub>2</sub> physisorption

Porosity was measured by nitrogen physisorption (Tristar II 3020, micrometrics) at -196°C on dried samples (16 h at 300°C under N<sub>2</sub>). The relative nitrogen pressure was varied between 0.01 and 0.99 ( $p/p_0$ ). The  $t$ -plot method (Harkins and Jura) was used to determine micropore volumes on the adsorption branch.

### I.5.5 STEM-EDS

Transmission electron microscopy (TEM) of the samples was performed with an aberration corrected JEOL ARM200F Microscope operating at an acceleration voltage of 200 kV and equipped with a cold FEG. Dark-field imaging was performed in Scanning TEM (STEM) mode with an annular dark-field (ADF) detector. Energy Dispersive X-ray (EDX) spectroscopy analysis of Si, O, Al, and Ru in the samples was carried out utilizing a Centurio EDX detector with a solid angle of 0.98 steradians from a 100 mm<sup>2</sup> detection area. The samples were prepared via drop-casting a sonicated particle suspension on a holey carbon-coated TEM grid (Cu, 400 mesh, Agar Scientific).

### I.5.6 XPS

XPS measurements were carried out on a SSI X probe spectrometer (model SSI 100, Surface Science Laboratories, Mountain View, CA) equipped with a monochromatized Al-K $\alpha$  radiation (1486 eV). The sample powders, pressed in small stainless troughs of 4 mm diameter, were placed on an insulating home-made ceramic carousel. The pressure in the analysis chamber was around 10–6 Pa. The analysed area was  $\sim 1.4 \text{ mm}^2$  and the pass energy was set at 150 eV. The Si2p peak of silicon was fixed to 103.5 eV to set the binding energy scale. Data treatment was performed with the CasaXPS program (Casa Software Ltd, UK); spectra were decomposed with the least squares fitting routine provided by the software with a Gaussian/Lorentzian (85/15) product function or specific asymmetric shapes for the Ru 3d doublet (Ru[0] : LF(0.8,1.25,500,180) and Ru[IV] : LF(0.25,1,45,280) taking into account Ru 3d<sub>5/2</sub>-3d<sub>3/2</sub> splitting of 4.17 eV).

### I.5.7 Data calculation

At the end of the reaction, a 0.2 mL sampling was taken and dried in a mild flow of N<sub>2</sub> to remove the water solvent. Once dried, the sample was dissolved in 500 μL mL of D<sub>2</sub>O, shaken till homogeneous, transferred to and NMR tubes and measured on a Bruker Avance-400 MHz NMR-spectrometer. Analyzing the products distribution was done by integrating the area below the respective peaks of each component and comparing their ratio by considering the number of H counted in each peak (i.e., **Lactic acid**: 1H at 4.10 ppm, **Alanine**: 1H at 3.75ppm, **Ethanol**: 2H at 2.95ppm, **Propionic acid**: 2H at 2.19ppm and **Propanamide**: 2H at 2.08ppm). Thus, the total area was calculated as follow:

$$\text{Total Area} = A_{\text{Lactic acid}}/1 + A_{\text{Alanine}}/1 + A_{\text{EtOH}}/2 + A_{\text{Propionic acid}}/2 + A_{\text{Propanamide}}/2$$

and the contribution of each species was considered from its ratio over the total area. The selectivity towards alanine was estimated from the ratio of the yield of alanine over the conversion of lactic acid ( $\text{selectivity}_{(\text{alanine})} = \text{yield}_{(\text{alanine})}/\text{conversion}$ ). Finally, the TON was calculated from the number of moles of alanine produced by each mole of Ru (by considering all Ru atoms in the zeolite being equally active in the reaction). This relative species NMR method is not the most accurate but offered decent and consistent results across all experiments. This method was found to be relatively trustworthy as i) few (coke) or adsorbed species are found in the zeolite (See Fig. S2: ca. 5 wt% for 50 mg of zeolite working on 2 mmol of LA in the optimized conditions) which is negligible versus the initial amount of substrate [but this method would be less accurate on the 0.1 mmol Fig. 1 screening reactions]; ii) no noticeable gaseous products formed (pressure after and before reaction same) iii) no noticeable solid (not NMR solvent soluble) side products were seen; and iv) our analysis on the benchmark catalyst (Ru/Al<sub>2</sub>O<sub>3</sub>) gave similar results as those reported in literature.

## Section II – Figures and Tables

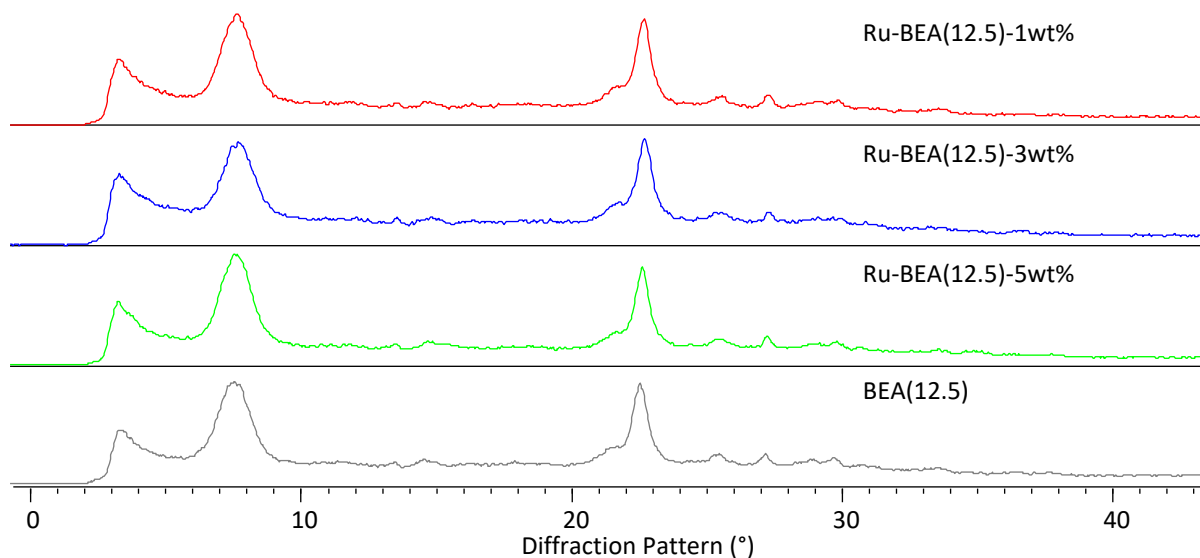


Figure S1: XRD patterns for Ru-BEA(12.5) catalysts with varying Ru loading.

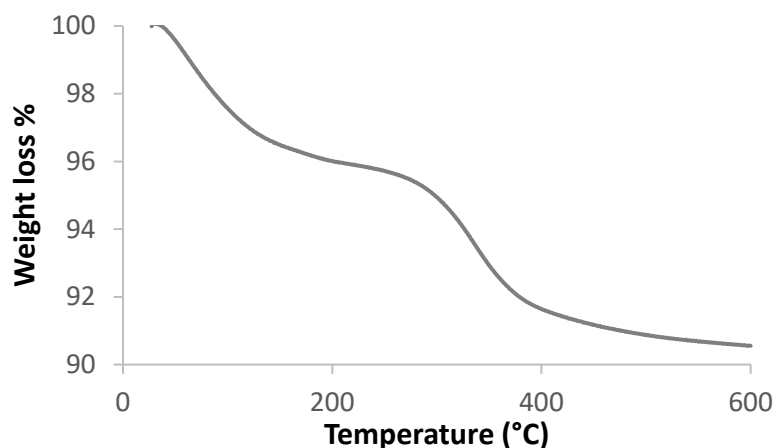


Figure S2: TGA data on spent catalyst (3% Ru-BEA 12.5) after one cycle in optimized conditions (2 mmol LA). Prior to measurement, the spent catalyst was filtrated from solution and washed 3 times with water (1ml/10mg) and further dried under air at 100°C. Measurement were performed under O<sub>2</sub> flow with a T° ramp of 5°C/min. Around 5% coke has formed. These organic species are thus not included in the product and conversion distribution estimations of the liquid phase by NMR (see I.5.7).

Table S1: ICP analysis of catalyst to determine Ru leaching. Reaction was done with 50 mg catalyst at 220°C reaction temperature.

Catalyst	Ru wt% before reaction	Ammonia concentration / wt% in H <sub>2</sub> O	Reaction time	Ru wt% after reaction	Percentage Ru leached
Ru/C	5	28-30	22	0.8	84
Ru/Al <sub>2</sub> O <sub>3</sub>	5	28-30	22	0.4	92
Ru/BEA(12.5) – IE	2.2	28-30	22	1.9	14
Ru/BEA(12.5) - IMP	5	28-30	22	0.2	96

Ru/BEA(150) - IMP	5	28-30	22	1.9	62
Ru/BEA(12.5) - IMP	5	14-15	4	0.5	90
Ru/BEA(12.5) - IMP	5	7-8	4	1.1	78
Ru/C	5	14-15	4	0.7	86
Ru/BEA(12.5) - IMP	1	14-15	4	0.5	50
Ru/BEA(12.5) - IMP	3	14-15	4	1.5	50
Ru/BEA(12.5) - IMP	3	14-15	3x 4h cycles	1.2	54

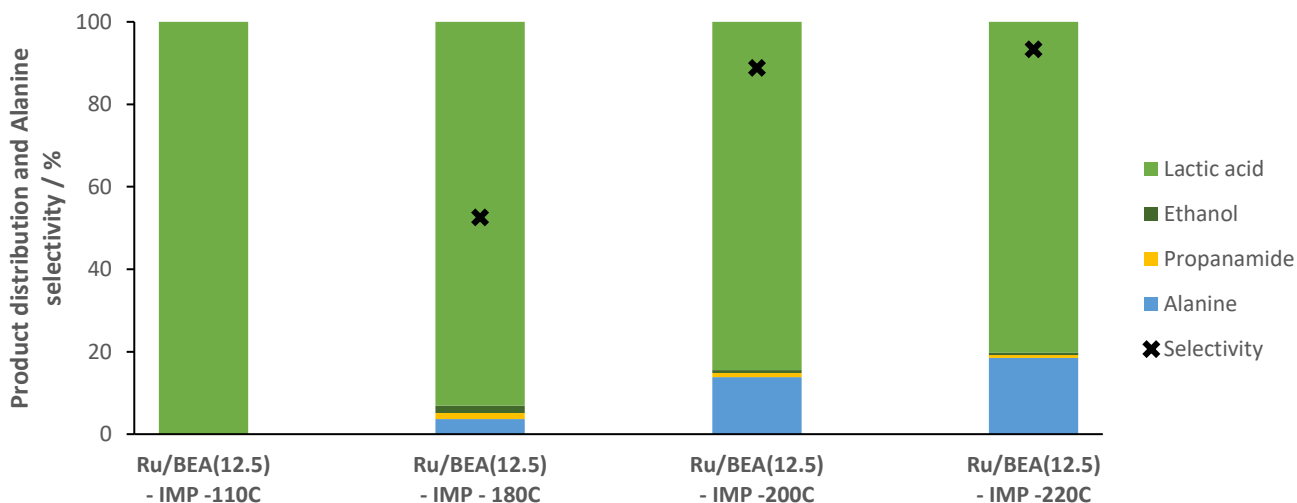


Figure S3: Comparing the reactivity of ruthenium impregnated BEA (12.5) – 5wt% at different temperatures. Reaction conditions: 50 mg catalyst, 2 mmol lactic acid, 1.5 ml NH<sub>3</sub> in water (28-30 wt%), 10 bar H<sub>2</sub>, 4h, and temperature varied between 110 and 220°C.

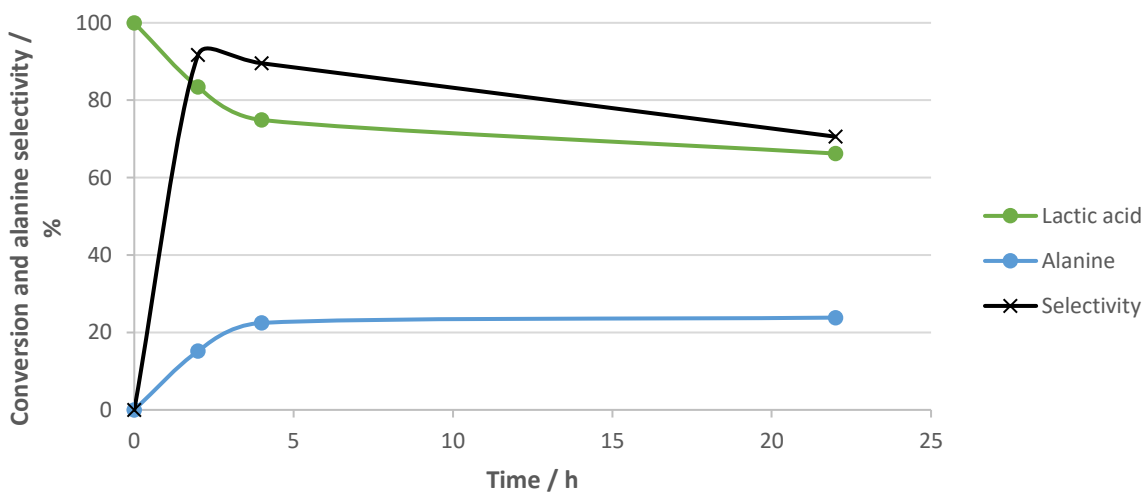


Figure S4: Comparing the reactivity of ruthenium impregnated BEA (12.5) – 5wt% at different times. Reaction conditions: 50 mg catalyst, 0.01 mmol lactic acid, 2.5 ml NH<sub>3</sub> in water (28-30 wt%), 10 bar H<sub>2</sub>, 2-22 h, and 220°C.

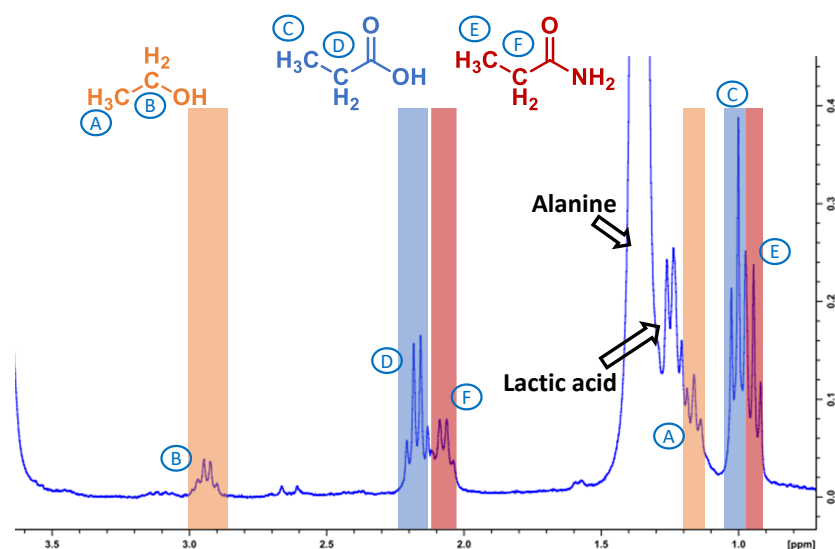


Figure S5: Alanine conversion (44%) under the reaction conditions into lactic acid (23%), ethanol (6%), propionic acid (11%), and propenamide (4%). Reaction conditions: 50 mg 5% IMP Ru-BEA12.5 catalyst, 2 mmol alanine, 1.5 ml NH<sub>3</sub> in water (28-30 wt%), 10 bar H<sub>2</sub>, 2 h, and 220°C.

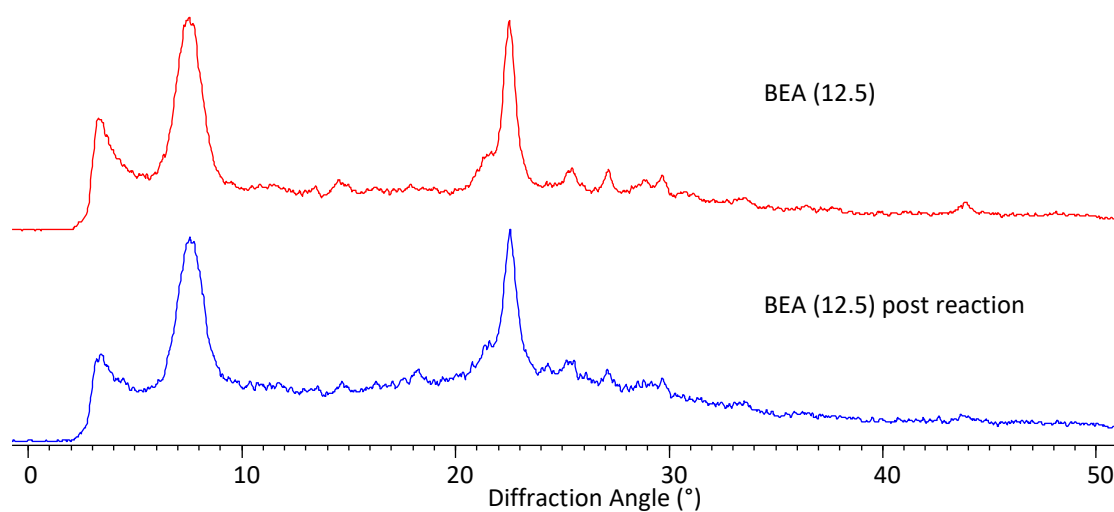


Figure S6: XRD patterns of BEA (12.5) before and after dissolution test. Reaction was carried out in a batch reactor: 50mg catalyst, 1.5 mL NH<sub>3</sub> in water (28-30wt%), 10 bar H<sub>2</sub>, 220°C for 4h. Some loss in crystallinity is observed.

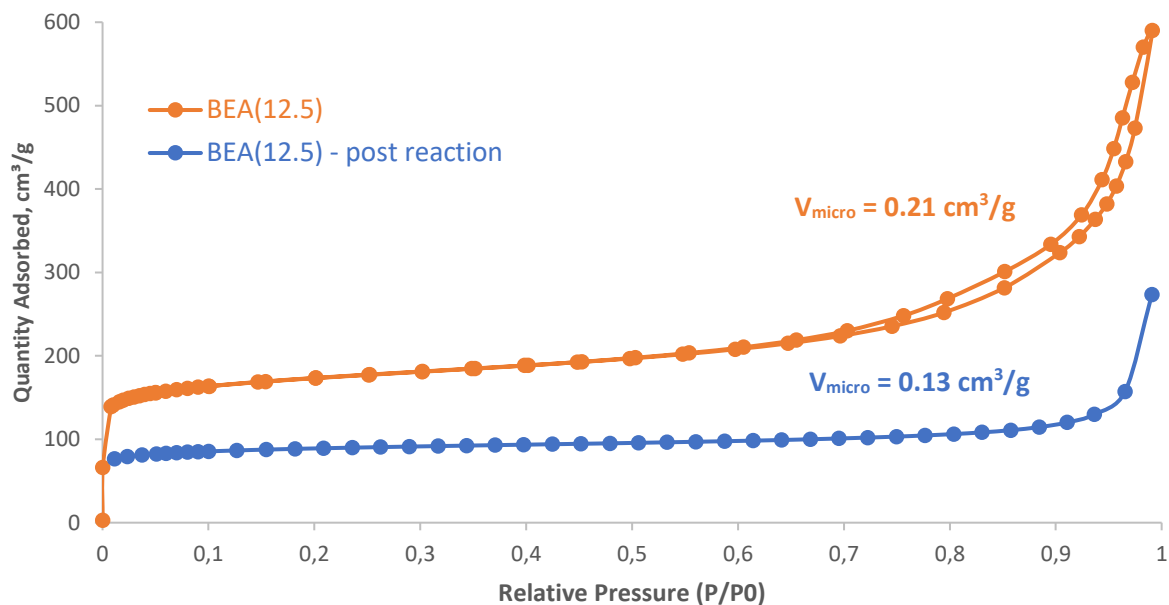


Figure S7: N<sub>2</sub> physisorption data on BEA(12.5) before and after a substrate-free reaction which was carried out in a batch reactor: 50mg catalyst, 1.5 mL NH<sub>3</sub> in water (28-30wt%), 10 bar H<sub>2</sub>, 220°C for 4h. A decrease in microporous surface area is observed. V<sub>micro</sub>: microporous volume.

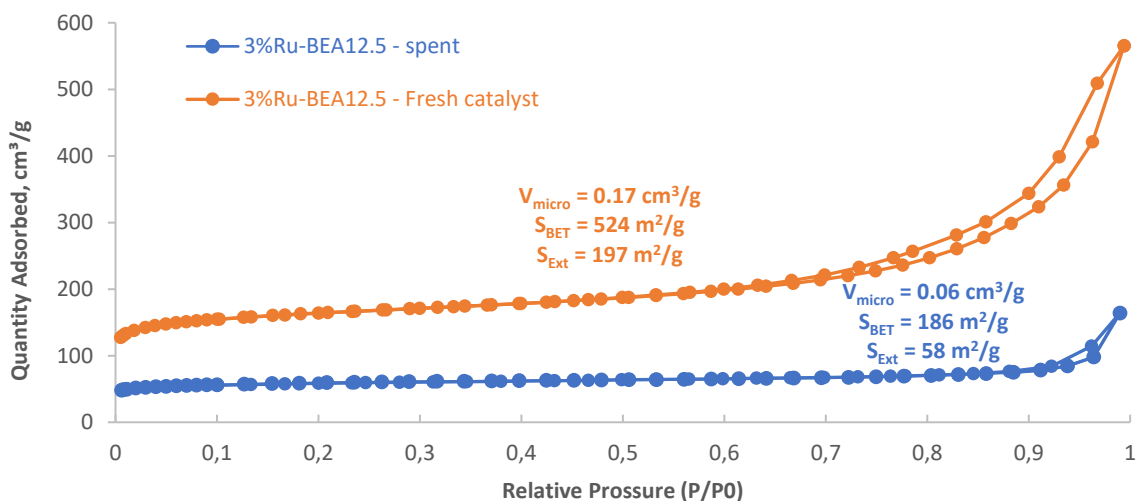


Figure S8: N<sub>2</sub> physisorption data on spent BEA(12.5) after 3 catalytic cycles (Fig. 3 main manuscript). Reaction conditions: 50mg catalyst (sample weight in cycle 1), 2 mmol lactic acid, 1.5 mL NH<sub>3</sub> in water (14-15wt%), 10 bar H<sub>2</sub>, 220°C for 4h. V<sub>micro</sub>: microporous volume, S<sub>BET</sub>: BET surface area, and S<sub>Ext</sub>: external surface area.



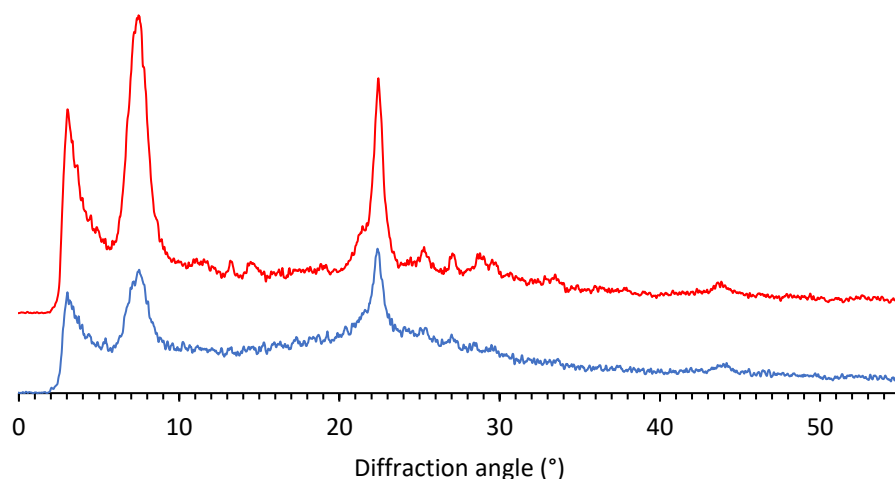


Figure S9: XRD pattern comparing activated catalyst (red) and spent catalyst (blue). Reaction conditions: 50 mg catalyst, 2 mmol lactic acid, 1.5 ml NH<sub>3</sub> in water (14-15 wt%), 10 bar H<sub>2</sub>, and 220°C. Catalyst had 2 cycles at 4h each.

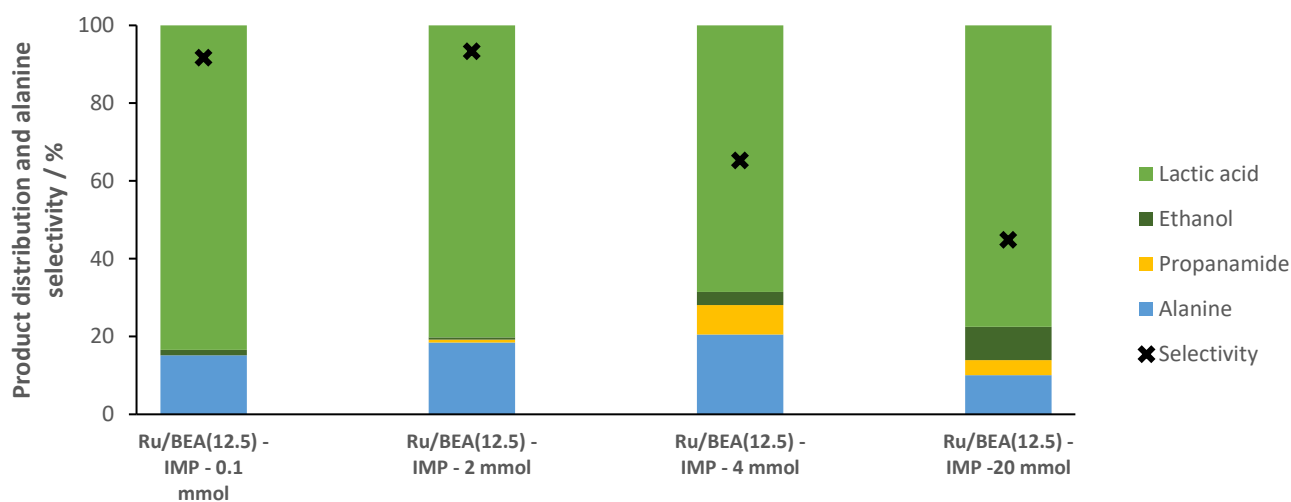


Figure S10: Comparing the reactivity of ruthenium impregnated BEA (12.5) – 5wt% at different lactic acid concentrations. Reaction conditions: 50 mg catalyst, 0.5-20 mmol lactic acid, 1.5 ml NH<sub>3</sub> in water (28-30wt%), 10 bar H<sub>2</sub>, 4h, and 220°C.

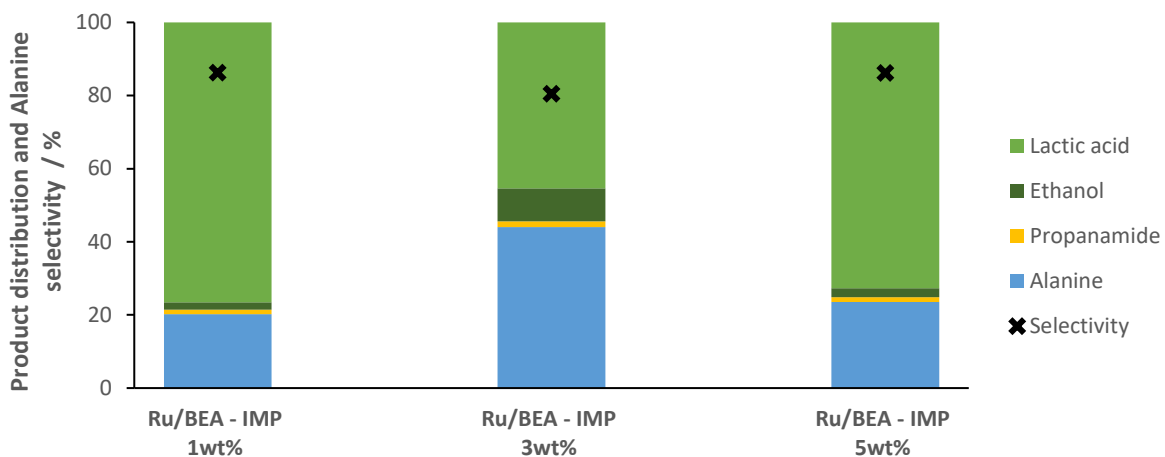


Figure S11: Comparing the reactivity of ruthenium impregnated BEA (12.5) at different Ru loadings. Reaction conditions: 50 mg catalyst, 2 mmol lactic acid, 1.5 ml  $\text{NH}_3$  in water (14-15 wt%), 10 bar  $\text{H}_2$ , 4 h, and 220°C.

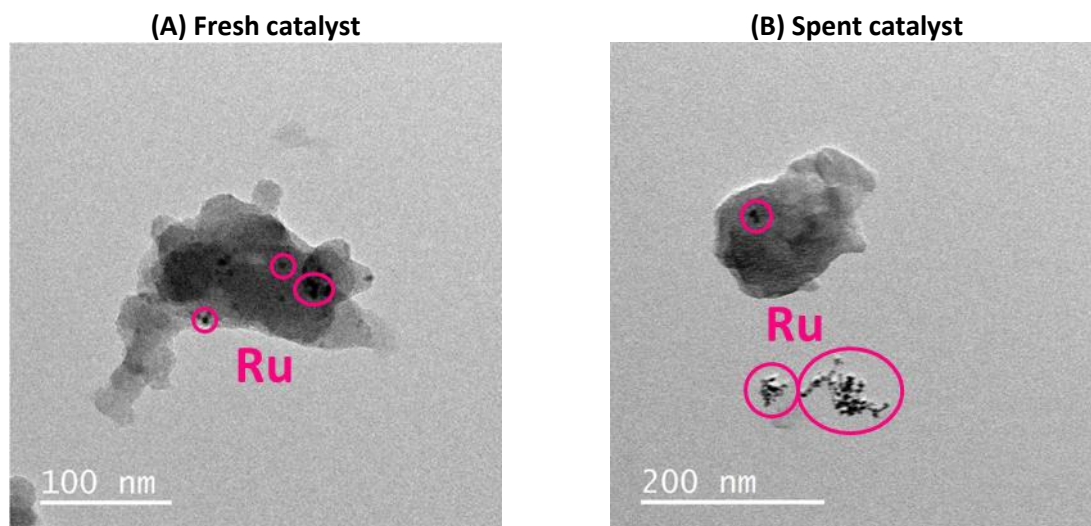


Figure S12: TEM images for (A) Ru/BEA – 3wt% catalyst before reaction (fresh catalyst – after activation) and (B) after reaction (spent catalyst). A selection of Ru particles is encircled in both images. Reaction conditions: 50 mg catalyst, 2 mmol lactic acid, 1.5 mL  $\text{NH}_3$  in water (14-15 wt%), 10 bar  $\text{H}_2$ , 220 °C for 4h.

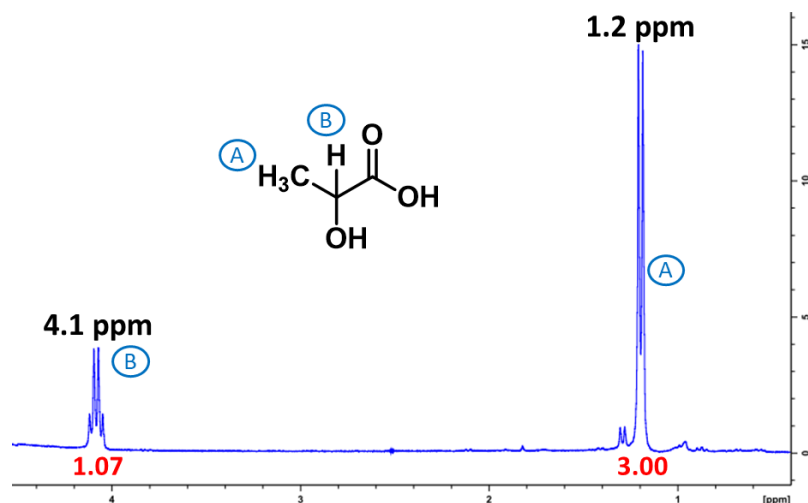


Figure S13: Lactic acid hydrogenation attempt. Reaction conditions: 50 mg 5% IMP Ru-BEA12.5 catalyst, 2 mmol lactic acid, 1.5 ml water (absence of NH<sub>3</sub>), 10 bar H<sub>2</sub>, 2 h, and 220°C.

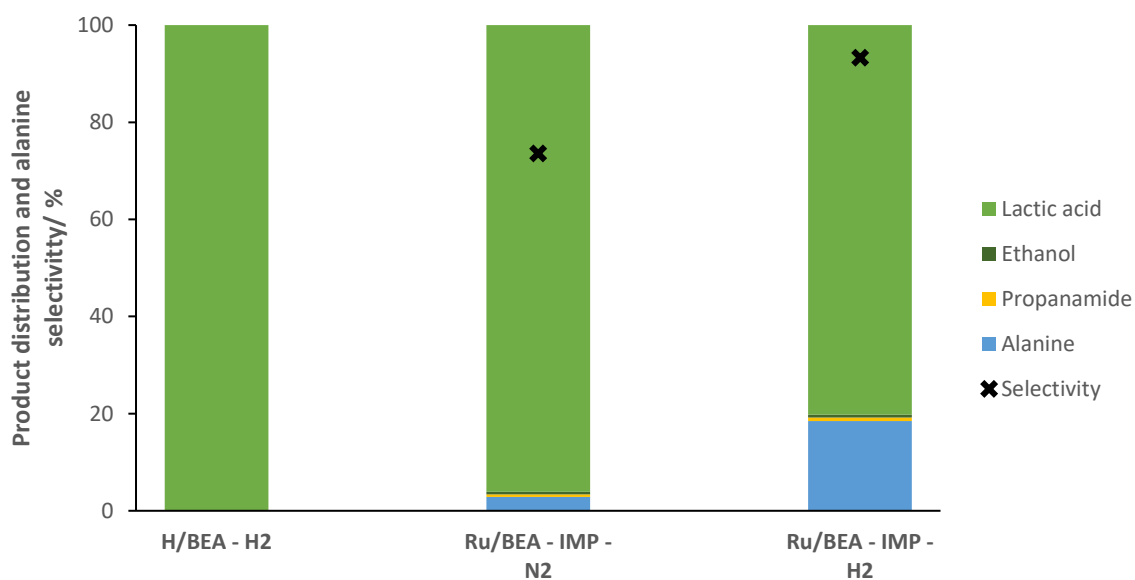


Figure S14: Comparing H/BEA with Ru/BEA (5wt%) under difference gasses. 10 bar of either N<sub>2</sub> or H<sub>2</sub> was used for the Ru/BEA(5wt%) reactions. The parent zeolite (H-BEA(12.5)) did not show any reactivity. Reaction conditions: 50 mg catalyst, 2 mmol lactic acid, 1.5 ml NH<sub>3</sub> in water (28-30 wt%), 10 bar H<sub>2</sub> or N<sub>2</sub>, 4 h, and 220°C.

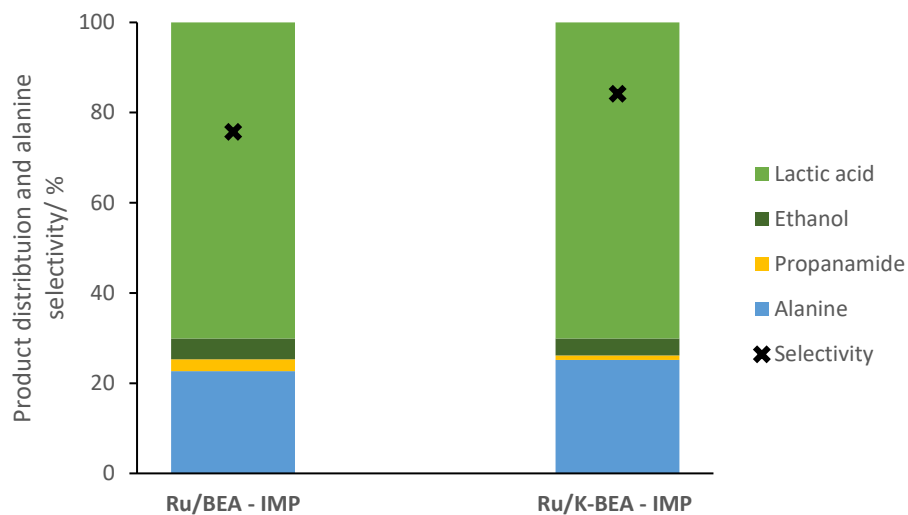


Figure S15: Comparing Ru/BEA (5wt%) with Ru/K-BEA (5wt%) where potassium was ion exchanged into the zeolite before Ru impregnation ( $K/Al = 0.6$ ) Reaction conditions: 50 mg catalyst, 2 mmol lactic acid, 1.5 ml  $NH_3$  in water (14-15 wt%), 10 bar  $H_2$ , 4 h, and 220°C.