Efficient aqueous hydrogenation of levulinic acid to γ-valerolactone over highly active and stable ruthenium catalyst

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The supporting information includes:

S1 Experimental details

Figures S1 to S8

Tables S1-S3

S1 Experimental details

S1.1 Materials

Levulinic acid (LA, 99%), 3-aminopropyltriethoxysilane (KH550, 99%) were purchased from Aladdin Chemistry Co. Ltd. (Shanghai, China). RuCl$_3$.3H$_2$O, γ-valerolactone (GVL, 98 %), γ-Al$_2$O$_3$ was purchased from the Aluminum Co., Ltd, of China, anhydrous ethanol was purchased from Sinopharm Chemical Reagent Co., Ltd..

S1.2 Method

1.2.1 Surface modification of γ-Al$_2$O$_3$. 3-aminopropyltriethoxysilane (KH550) was chosen as the organosilane agent to modify the surface of γ-Al$_2$O$_3$. The modification procedure is described as follows: 0.05 mol γ-Al$_2$O$_3$ was placed in a 500 mL flask containing 120 mL anhydrous ethanol. 20 mmol KH550 were slowly added by means of a syringe under stirring. The mixture was refluxed at 100 °C for 48 h. After cooling down to room temperature, the product was filtered and washed several times with anhydrous ethanol to remove unreacted KH550 and dried in a vacuum at 100 °C for 12 h.

1.2.2 Preparation of immobilized Ru-NH$_2$-γ-Al$_2$O$_3$ catalyst. Immobilized Ru catalysts was synthesized by refluxing 180 mL anhydrous ethanol solution of RuCl$_3$•3H$_2$O (0.5937 mmol) with 2.94 g KH550-modified-γ-Al$_2$O$_3$ support. After refluxing for 24 h, the Ru catalyst was filtered and washed several times with anhydrous ethanol, and dried in a vacuum at 80 °C for 12 h. Prior to the reactions, the catalysts were reduced in a quartz tube at 250 °C for 2 h in 1atm H$_2$, and removed into the

autoclave under hydrogen. The reaction solution for preparing i-Ru-NH$_2$-Al$_2$O$_3$ catalyst before and after refluxing was illustrated in Figure S8.

1.2.3 Preparation of Ru/γ-Al$_2$O$_3$ catalyst. The catalyst was prepared by the wet impregnation method. γ-Al$_2$O$_3$ was dried at 100 °C overnight before the wet impregnation. The dried support was impregnated with an aqueous solution containing RuCl$_3$·3H$_2$O at room temperature (25 °C) for 24 h, then dried at 100 °C for 20 h. Ru/γ-Al$_2$O$_3$ catalyst was calcined in air at 400 °C for 4 h to remove the chloride. Prior to the reactions, the catalysts were reduced in a quartz tube at 250 °C for 2 h in 1 atm H$_2$, and removed into the autoclave under hydrogen.

1.2.4 Catalytic test. All experiments were performed in a batch reactor (30 mL) with a magnetic stirrer. Typically, LA and water were added in a vessel, and then the Ru-based catalyst (0.1 g) was added. Before each run the vessel was sealed and flushed with H$_2$ to exclude the air for five times. After reactions, the vessel was cooled down. The reaction products were centrifuged for 10 min and then filtered with a 0.45 μm syringe filter to obtain a clear solution prior to analysis. The samples were analyzed by HPLC (Agilent 1260) with a Shodex SH-1821 capillary column (300 mm×8 mm×0.6 μm). Standard solutions were used to obtain the calibration curves to calculate concentrations of the compounds by the external standard method. The catalyst was recycled as described by the following procedure: at the end of the each run, the catalyst was separated from the reaction mixture by high rate of centrifugation, thoroughly washed with water for three times, and then reused as the catalyst for the next run under the identical conditions.

The computational formula

The conversion of LA and the selectivity of the products (GVL) were quantified according to the following equations:

$$Conversion = \frac{mol\ of\ LA(inlet) - mol\ of\ LA(outle}{mol\ of\ LA(inle} \times 100\%$$

$$Selectivity = \frac{mol\ of\ one\ produ}{mol\ of\ all\ products} \times 100\%$$

Turnover frequency (TOF), the number of converted molecules per active site and hour, is calculated on the basis of surface Ru atoms, which is estimated with the total loadings of Ru(determined by ICP-OES).

$$TOF = \frac{Number\ of\ LA\ molecular\ converte}{(Number\ of\ surface\ Ru\ atoms) \times (reaction\ time, h)}$$

The calculation method of the carbon balance was calculated by the following equation:

$$Carbon\ balance\% = \frac{mol\ (carbon\ product + carbon\ remained\ substrate)(out}{mol\ carbon\ (in)\ (substrate)} \times 100\%$$

S1.3 Catalyst characterizations

Fourier transforms infrared spectroscopy (FTIR)

The FT-IR spectra were measured on a BRUKER TENSOR27 FTIR spectrophotometer (Bruker, Germany), equipped with a deuterium triglycine sulfate (DTGS) detector. The powder samples were mixed with KBr and pressed into

translucent disks at room temperature. The spectra were recorded in the range of 400-4000 cm^{-1}.

X-ray diffraction (XRD)

Powder X-ray diffraction (XRD) patterns were obtained on a D8 ADVANCE A25 X-ray diffractometer (Germany), with Cu Kα radiation at 30 kV and 10 mA. The X-ray patterns were recorded in 2θ values ranging from 5° to 80° with a scanning speed of 4 °/min.

N$_2$ adsorption-desorption isotherms of the catalysts

BET surface area was measured at -196°C using a Micromeritics ASAP 2420 instrument after degassing at 100°C to remove physically adsorbed impurities for 8h in vacuum.

High-resolution transmission electron microscopy (HRTEM).

TEM and HRTEM measurements were performed with a field-emission transmission electron microscopy (FETEM, JEM-2011F) operating at 200 kV voltages. The reduced samples were suspended in ethanol with an ultrasonic dispersion for 30 min and deposited on copper grids coated with amorphous carbon films.

The mean diameter of Ru NPs was determined using the following equation[1]:

$$d_{p\ HRTEM} = \frac{\Sigma n_i \cdot d_i^3}{\Sigma n_i \cdot d_i^2}$$

Herein，d_i represents the mean of a specific range of Ru particle diameters, n_i represents the number of particles within that range, and $d_{p\ HRTEM}$ is the average particle size.

Induced coupled plasma-optical emission spectrometry (ICP-OES)

The content of Ru in the catalysts was determined by an induced coupled plasma-

optical emission spectrometry (PerkinElmer Optima 2100 DV).

X-ray photoelectron spectroscopy (XPS)

X-ray photoelectron spectroscopy (XPS) was measured on an AXIS ULTRA DLD (Kratos U.K.) spectrometer with Al Kα radiation and a multichannel detector. Prior to each test, the sample was reduced at 250℃ in 1 atm H_2 for 2 h. The obtained binding energies were calibrated using the C_{1s} peak at 284.6 eV as the reference. The experiment error was given within ±0.1eV.
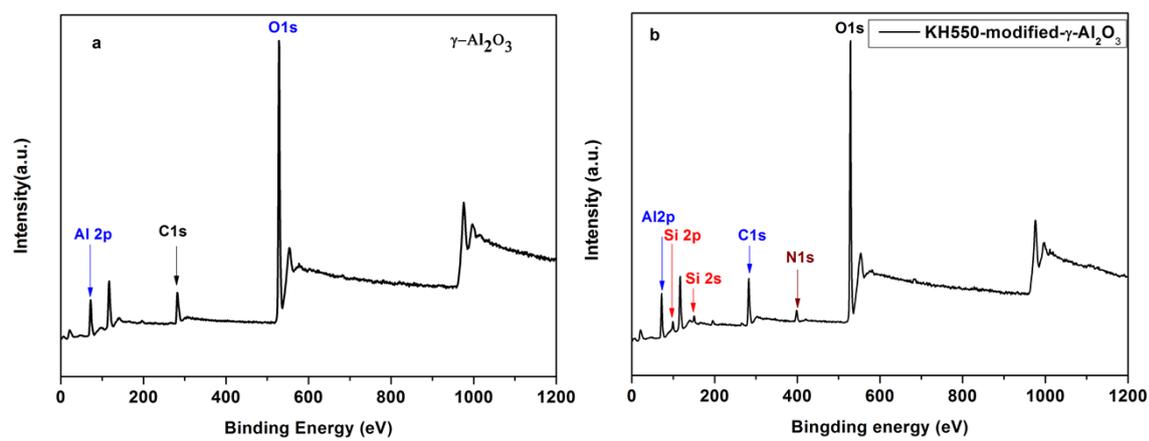
Figure S1 Full range XPS spectrum of (a) γ-Al$_2$O$_3$ (b) KH550-modified-γ-Al$_2$O$_3$
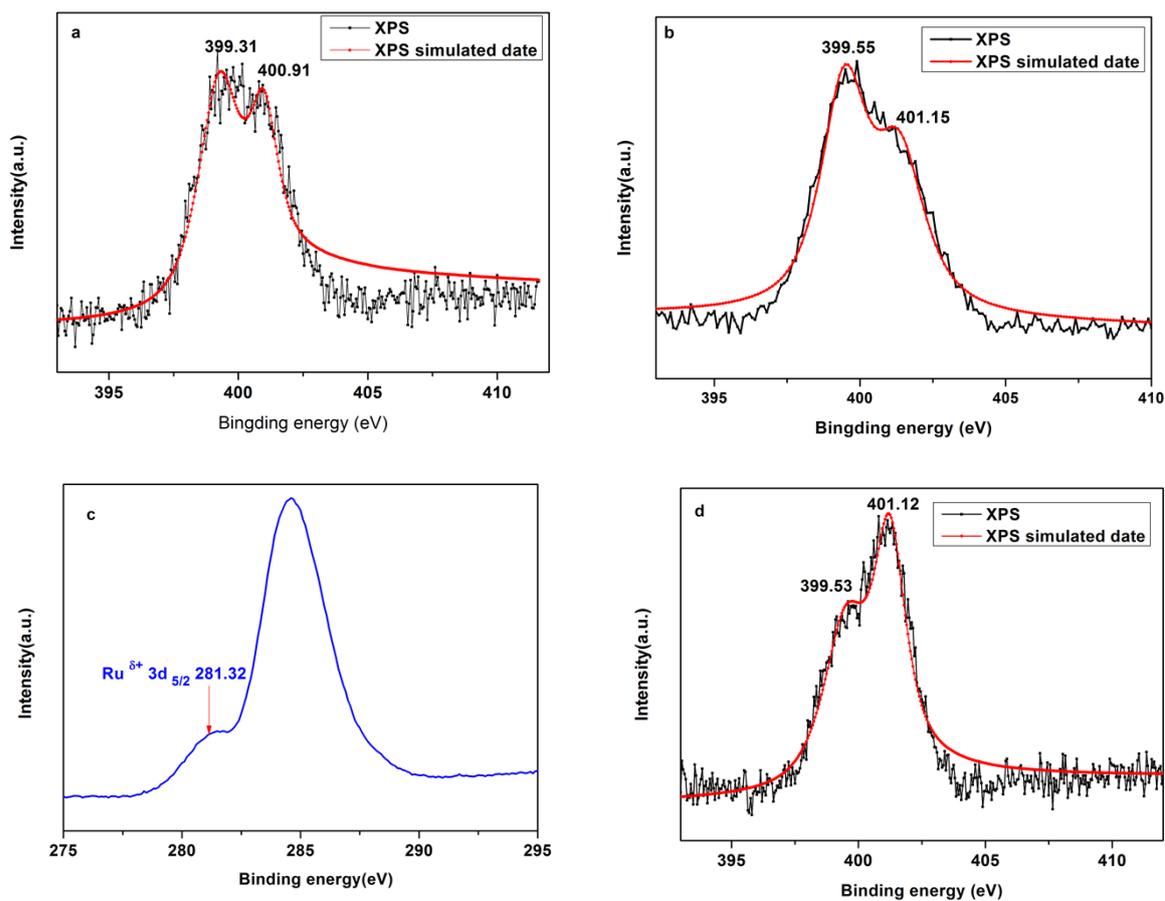
Figure S2. XPS spectra of (a) N1s in KH550-modified-γ-Al$_2$O$_3$ (b) N1s in fresh Ru-NH$_2$-γ-Al$_2$O$_3$ (c) Ru3d$_{5/2}$ in fresh Ru-NH$_2$-γ-Al$_2$O$_3$ (d) N1s in reduced Ru-NH$_2$-γ-Al$_2$O$_3$
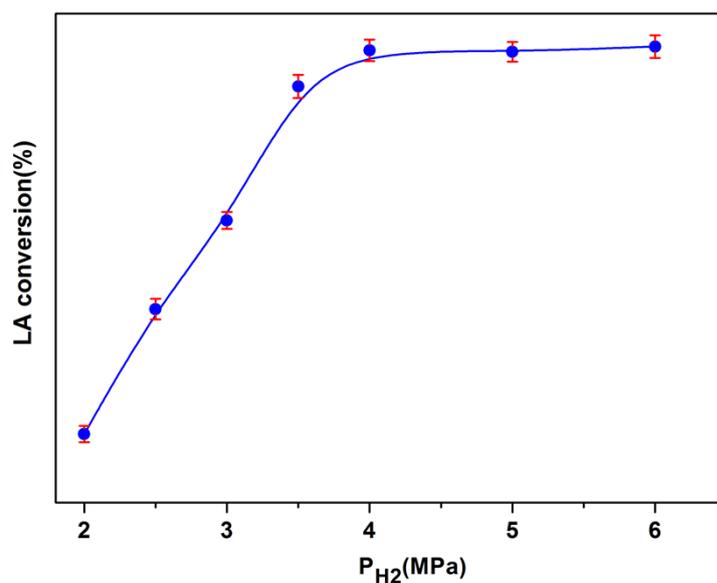
Figure S3. The effect of hydrogen pressure on LA conversion

Reaction conditions: 0.1 g 2 wt% r-Ru-NH$_2$-γ-Al$_2$O$_3$, 12 g 16.7 wt% LA/water solution, T=40 °C, t=2 h,

As shown in Figure S3, an increasing in the hydrogen pressure from 2 MPa to 4 MPa enhanced the catalyst activity. No obvious enhancement was observed on the catalytic activity when the hydrogen pressure exceeds 4 MPa, indicating that the conversion of LA is independent of the hydrogen pressure when the pressure exceeds 4 MPa. Similar saturation kinetics has been observed for related hydrogenations using homogeneous Ru-catalyst systems[2]. Accordingly, the optimum hydrogen pressure (4 MPa) was chosen for the effective conversion of LA.
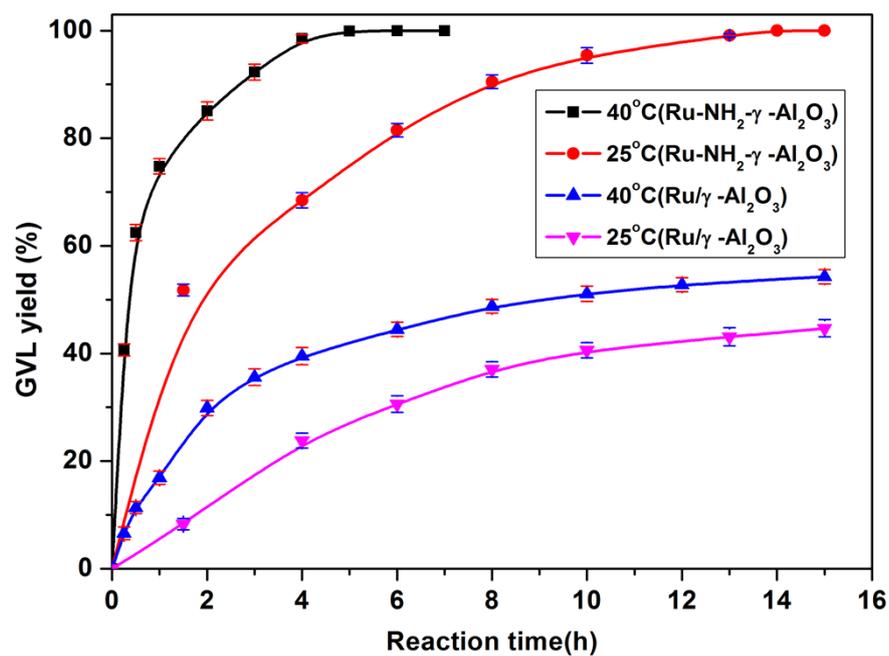
Figure S4. GVL yield as a function of the reaction time over reduced Ru-NH$_2$-γ-Al$_2$O$_3$ and Ru/γ-Al$_2$O$_3$. Reaction conditions: Cat. 0.1 g, LA 2 g, H$_2$O 10 g, H$_2$= 4.0 MPa

Figure S5. The stability of r-Ru-NH$_2$-γ-Al$_2$O$_3$ catalyst at room temperature

Reaction conditions: Cat. 0.1 g, LA 2 g, H$_2$O 10 g, H$_2$= 4.0 MPa, T=25 °C t=8 h
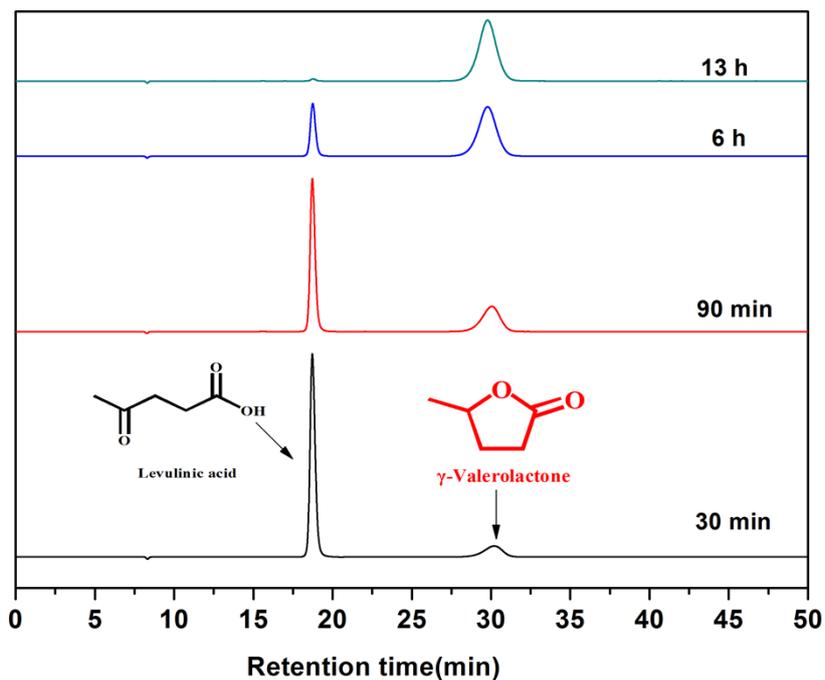
Figure S6 the GC charts of LA hydrogenation to GVL over r-Ru-NH$_2$-γ-Al$_2$O$_3$

Reaction conditions: Cat. 0.1 g, LA 2 g, H$_2$O 10 g, H$_2$= 4.0 MPa, T=25 °C
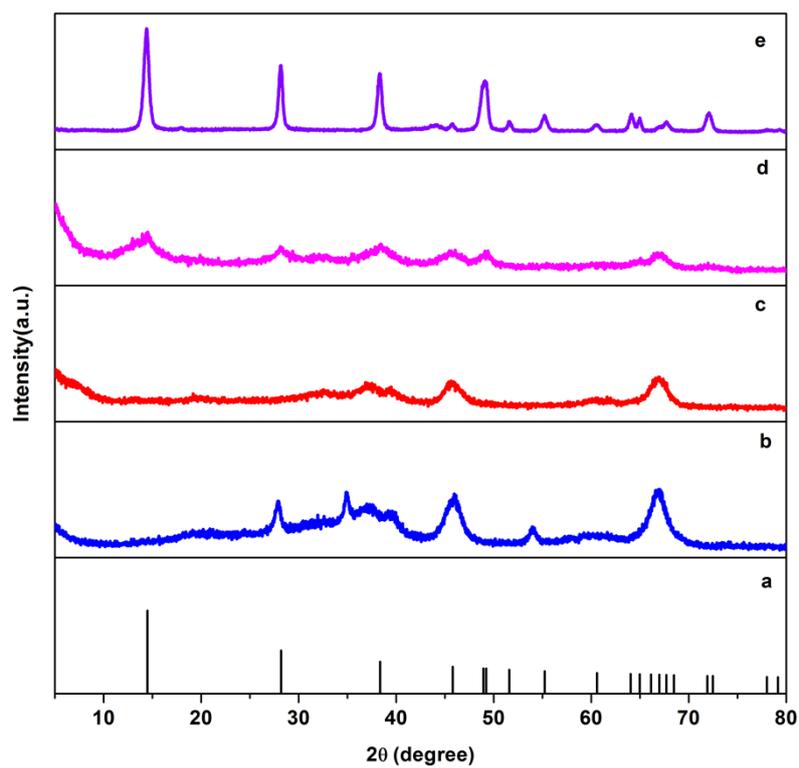
Figure S7 XRD patterns of (a) γ-AlOOH (b) Fresh Ru/γ-Al$_2$O$_3$ (c) Fresh Ru-NH$_2$-γ-Al$_2$O$_3$ (d) Ru-NH$_2$-γ-Al$_2$O$_3$ spent for 10 runs (e) Ru/γ-Al$_2$O$_3$spent for 2 runs
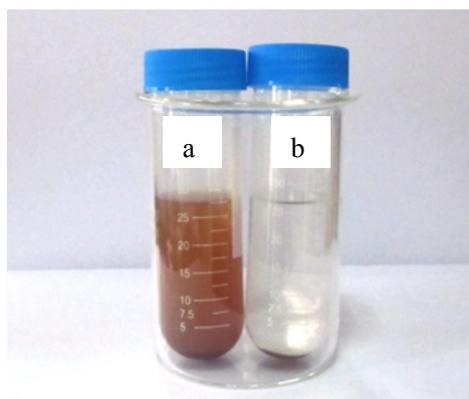
Figure S 8 The reaction solution for preparing i-Ru-NH$_2$-Al$_2$O$_3$ before (a) and after (b)

refluxing

Table S1 Physicochemical properties of catalysts

Entry	Catalyst	Ru (wt.%)[a]	Cl/Ru [b]	S_{BET} (m^2/g)[c]	D_{pore} (nm)[c]	V_{pore} (cm^3/g)[c]	d_{Ru}(nm)[d]
1	γ-Al$_2$O$_3$	-	-	275.78	5.87	0.58	-
2	Ru/γ-Al$_2$O$_3$	1.95	-	273.97	5.77	0.54	12.3
3	Ru-NH$_2$-γ-Al$_2$O$_3$	1.97	2.3	264.12	6.42	0.54	1.2

[a]: the content of Ru in the catalysts were detected by ICP-OES

[b]: composition of elements on the surface of catalysts measured by XPS

[c]: The BET surface area and pore volume were determined by N$_2$ physical adsorption

[d]: The sizes of Ru were calculated calculated by HRTEM for Ru/Al$_2$O$_3$ and r- Ru-NH$_2$-γ-Al$_2$O$_3$

Table S2 the content of Ru in the fresh and spent for 10 runs catalysts

Entry	catalyst	Ru content (wt.%)[a]	
		Fresh	Spent for 10 runs
1	r-Ru-NH$_2$-γ-Al$_2$O$_3$	1.97	1.94
2	Ru/γ-Al$_2$O$_3$	1.95	1.89

[a]: the content of Ru in the catalysts was determined by ICP-OES.

Table S3 The effect of HCOOH and H_2SO_4 on the activity of r-Ru-NH_2-γ-Al_2O_3

Entry	Catalyst	HCOOH	H_2SO_4	LA Conv.%	GVL Select.%
1	Ru/AC	-	-	71.4	99.9
2	r-Ru-NH_2-γ-Al_2O_3	-	-	85.1	99.9
3	r-Ru-NH_2-γ-Al_2O_3	0.10 M	-	85.9	99.9
4	r-Ru-NH_2-γ-Al_2O_3	0.25 M	-	84.7	99.9
5	r-Ru-NH_2-γ-Al_2O_3	0.50 M	-	85.4	99.9
6	r-Ru-NH_2-γ-Al_2O_3	-	0.05 M	84.8	99.9
7	r-Ru-NH_2-γ-Al_2O_3	-	0.10 M	81.9	99.9
8	r-Ru-NH_2-γ-Al_2O_3	-	0.25 M	79.2	99.9
9	r-Ru-NH_2-γ-Al_2O_3	-	0.50 M	76.1	99.9

Reaction conditions: 0.1 g 2 wt% Ru-catalyst, 12 g 16.7 wt% LA/water solution, T=40 ℃, H_2 4 MPa t=2 h, the carbon balance for each run exceeds 96%.

Notes and References

1 Abdelrahman, O. A.; Luo, H. Y.; Heyden, A.; Román-Leshkov Y.; Bond, J. Q. *J. Catal.* **2015** *329* 10-21.

2 M. Chalid, A. A.Broekhuis and H. J. Heeres, *J. Mol. Catal. A: Chem.* 2011,341, 14-21.