

## Supporting information

### Selective hydroconversion of levulinic acid to $\gamma$ -valerolactone or 2-methyltetrahydrofuran over silica-supported cobalt catalyst

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## Experimental

### Cobalt dispersion

The hydrogen adsorption method, developed by Bartholomew<sup>1</sup> was applied to determine the cobalt dispersion. The same instrument was used as that for the H<sub>2</sub>-TPR measurements. First, the catalyst was reduced *in-situ* at 450 °C in a 20 cm<sup>3</sup>min<sup>-1</sup> H<sub>2</sub> flow for 1 h, flushed with N<sub>2</sub> for 0.5 h at this temperature and cooled to 100 °C. The N<sub>2</sub> flow was changed then for flow of 9.0 vol% H<sub>2</sub>/N<sub>2</sub> gas mixture to flush the catalyst sample for one additional hour, cooled further to 50 °C, exposed again to a flow of N<sub>2</sub>, and heated up to 400 °C at a rate of 10 °Cmin<sup>-1</sup>. The composition of the reactor effluent was monitored using TCD detector. The amount of the hydrogen, retained at 100 °C was calculated from the integrated area of the H<sub>2</sub>-TPD curves. The dispersion (D) of Co metal was calculated dividing the number of chemisorbed hydrogen atoms by the number of zero valent Co atoms (Co<sup>0</sup>). The amount of Co<sup>0</sup> was estimated from the H<sub>2</sub>-TPR curve of the sample. It was assumed that the amount of H<sub>2</sub> consumed in the reduction process up to 450 °C is equivalent with the amount of Co<sup>0</sup> in the sample. The average metal particle diameter (d) was calculated assuming spherical geometry as  $d = 6.59 \times s / D$ ; where *s* stands for the surface density of Co atoms on the surface of cobalt metal particles (14.6 atoms nm<sup>-2</sup>) (Table S1).

## Results

**Table S1** Characterization of the silica-supported cobalt catalysts reduced in H<sub>2</sub> at 450 °C for 1 h.

| Catalyst                   | Co content | SSA <sup>a</sup><br>m <sup>2</sup> g <sup>-1</sup> | Amount of Lewis sites <sup>b</sup><br>μmolg <sub>cat</sub> <sup>-1</sup> | H <sub>2</sub> uptake <sup>c</sup><br>μmolg <sub>cat</sub> <sup>-1</sup> | Dispersion <sup>d</sup><br>% | Reduction degree <sup>e</sup><br>% | Average Co <sup>0</sup> diameter (d, nm) |     |
|----------------------------|------------|--|--|--|------------------------------|------------------------------------|--|-----|
|                            | wt%        |  |  |  |                              |                                    | H <sub>2</sub> -TPD <sup>f</sup>         | XRD |
| Co/SiO <sub>2</sub> (4.6)  | 4.6        | 178 (179)  | 14.4   | 8.1  | 2.6                          | 92                                 | 37                                       | 25  |
| Co/SiO <sub>2</sub> (8.1)  | 8.1        | 175 (179)  | 19.1   | 15.5   | 2.5                          | 89                                 | 38                                       | 27  |
| Co/SiO <sub>2</sub> (13.3) | 13.3       | 157 (179)  | 36.9   | 16.4   | 1.5                          | 86                                 | 64                                       | 42  |

<sup>a</sup> Specific Surface Area (SSA) determined by the Brunauer-Emmett-Teller (BET) method (SSA of the support is given in parentheses).

<sup>b</sup> Determined by pyridine adsorption followed by FT-IR spectroscopy. The amount of Lewis acid sites was calculated from the integrated absorbance of the 1450 cm<sup>-1</sup>-pyridine band in the spectrum obtained by degassing the wafer at 200 °C after pyridine adsorption. For the calculation, the integrated molar extinction coefficient of 2.22 cm μmol<sup>-1</sup> was used.<sup>2</sup>

<sup>c</sup> Determined by H<sub>2</sub>-TPD method. In order to obtain H<sub>2</sub>-TPD curve the catalyst was reduced *in-situ* at 450 °C in a 20 cm<sup>3</sup>min<sup>-1</sup> H<sub>2</sub> flow for 1 h, then flushed with N<sub>2</sub> for 0.5 h at this temperature and cooled then to 100 °C. After that N<sub>2</sub> was changed for 9.0 vol% H<sub>2</sub>/N<sub>2</sub> mixture and flushed for 1.0 h, then cooled to 50 °C, exposed to a flow of N<sub>2</sub>, and then heated up to 400 °C at a rate of 10 °Cmin<sup>-1</sup>. During last step the composition of the effluent was monitored by TDC and the signal was recorded (not shown here).

<sup>d</sup> Dispersion  $D = (\text{hydrogen uptake, } \mu\text{mol/g}_{\text{cat}}) / [(\text{bulk Co content, } \mu\text{molg}_{\text{cat}}^{-1}) \times (\text{reduced fraction of Co content})]$ .

<sup>e</sup> Reduction degree at 450 °C calculated from the H<sub>2</sub>-TPR curve.

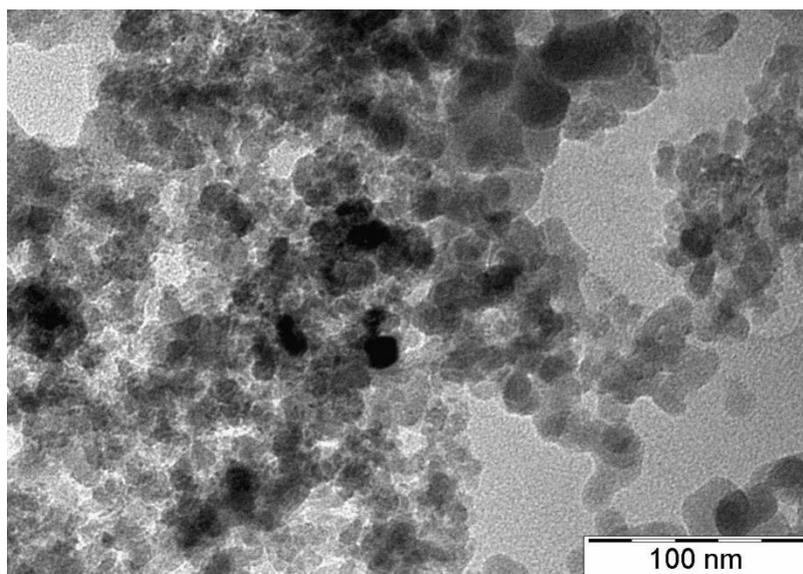
<sup>f</sup> Calculated from  $d = 6.59 \times s / D$ ; *s* = site density (14.6 atoms·nm<sup>-2</sup>).

**Table S2** Rate of GVL formation from LA over selected noble metals and non-noble metals supported over carbon or oxides.

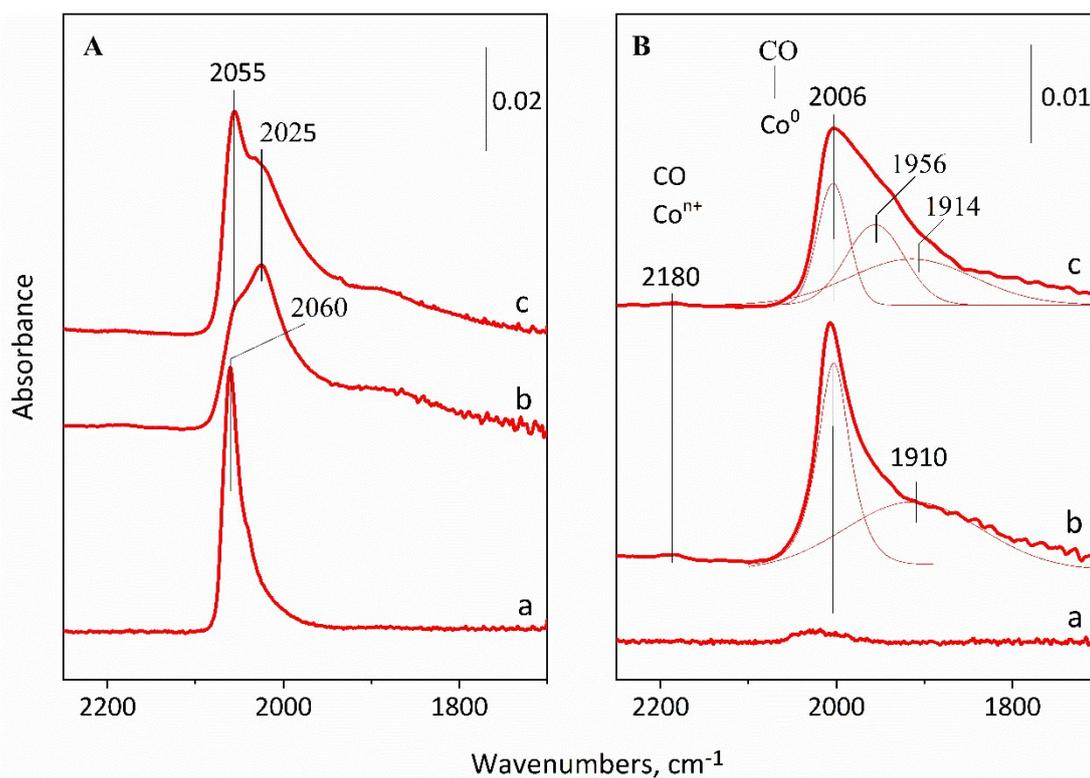
| Catalysts  | Conditions   | LA conv. % | GVL sel. % | Rate <sub>GVL</sub> $\mu\text{mol g}_{\text{cat}}^{-1} \text{s}^{-1}$ | Ref.  |
|--|--|------------|------------|---|---|
| 5wt%Ru/C   | 265°C, <b>1 bar</b> ,<br>WHSV: 0.512 $\text{g}_{\text{LA}} \text{h}^{-1} \text{g}_{\text{cat}}^{-1}$<br>fixed-bed  | 100.0      | 98.6       | 1.25  | Upare et al. cited in the MS as Ref. 62     |
| 2wt%Ru/HAP   | 275°C, <b>1 bar</b> ,<br>GHSV: 2.616 $\text{ml s}^{-1} \text{g}_{\text{cat}}^{-1}$<br>fixed-bed  | 92.2       | 99.8       | 88.8  | <sup>a</sup> Kumar et al.                   |
| 5wt%Ni/HAP   | 275°C, <b>1 bar</b> ,<br>GHSV: 2.616 $\text{ml s}^{-1} \text{g}_{\text{cat}}^{-1}$<br>fixed-bed  | 21.0       | 65.0       | 13.1  | <sup>a</sup> Kumar et al.                   |
| 5wt%Cu/HAP   | 275°C, <b>1 bar</b> ,<br>GHSV: 2.616 $\text{ml s}^{-1} \text{g}_{\text{cat}}^{-1}$<br>fixed-bed  | 32.2       | 74.8       | 23.2  | <sup>a</sup> Kumar et al.                   |
| 20wt%Ni/SiO <sub>2</sub>                           | 270°C, <b>1 bar</b><br>GHSV: 19.5 $\text{ml s}^{-1} \text{g}_{\text{cat}}^{-1}$<br>10% LA in water,<br>fixed-bed   | 15.7       | 90.6       | 136.2   | Kumar et al. cited in the MS as Ref. 57     |
| 10wt%Ni/TiO <sub>2</sub>                           | 275°C, <b>1 bar</b><br>GHSV: 9.74 $\text{ml s}^{-1} \text{g}_{\text{cat}}^{-1}$<br>fixed-bed   | 17.3       | 78.3       | 0.77  | Peddakasu et al. cited in the MS as Ref. 70 |
| 10wt%Ni-2wt%Nb/TiO <sub>2</sub>                    | 275°C, <b>1 bar</b><br>GHSV: 9.74 $\text{ml s}^{-1} \text{g}_{\text{cat}}^{-1}$<br>fixed-bed   | 25.3       | 99.0       | 1.21  | Peddakasu et al. cited in the MS as Ref. 70 |
| Co/SiO <sub>2</sub> (8.1)                          | 250°C, <b>1 bar</b> ,<br>WHSV: 4.0 $\text{g}_{\text{LA}} \text{h}^{-1} \text{g}_{\text{cat}}^{-1}$<br>fixed-bed  | 40.8       | 44.6       | 1.97  | this study                                  |
| Co/SiO <sub>2</sub> (8.1)                          | 200°C, <b>30 bar</b> ,<br>WHSV: 4.0 $\text{g}_{\text{LA}} \text{h}^{-1} \text{g}_{\text{cat}}^{-1}$<br>fixed-bed   | 51.2       | 98.0       | 5.55  | this study                                  |
| 0.5wt%Ru/C   | 150°C, <b>45 bar</b> ,<br>WHSV: 30 $\text{g}_{\text{feed}} \text{h}^{-1} \text{g}_{\text{cat}}^{-1}$<br>LA <sub>conc.</sub> : 1.1 $\text{molL}^{-1}$ (H <sub>2</sub> O)<br>fixed-bed | 92         | 78         | 9,2   | <sup>b</sup> Piskun et al.                  |
| 0.5wt%Ru/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub> | 150°C, <b>45 bar</b> ,<br>WHSV: 30 $\text{g}_{\text{feed}} \text{h}^{-1} \text{g}_{\text{cat}}^{-1}$<br>LA <sub>conc.</sub> : 1.1 $\text{molL}^{-1}$ (H <sub>2</sub> O)<br>fixed-bed | 26         | 62         | 2,33  | <sup>b</sup> Piskun et al.                  |
| 1wt%Ru/TiO <sub>2</sub>                            | 150°C, <b>45 bar</b> ,<br>WHSV: 30 $\text{g}_{\text{feed}} \text{h}^{-1} \text{g}_{\text{cat}}^{-1}$<br>LA <sub>conc.</sub> : 1.1 $\text{molL}^{-1}$ (H <sub>2</sub> O)<br>fixed-bed | 26         | 54         | 2,49  | <sup>b</sup> Piskun et al.                  |

<sup>a</sup> V. V. Kumar, G. Naresh, M. Sudhakar, J. Tardio, S. K. Bhargava, A. Venogupal, *Appl. Catal. A*, 2015, **505**, 217-223.

<sup>b</sup> A. S. Piskun, J. E. de Haan, E. Wilbers, H. H. van de Bovenkamp, Z. Tang, H. J. Heeres, *ACS Sus. Chem. Eng.* 2016, **4**, 2939–2950.

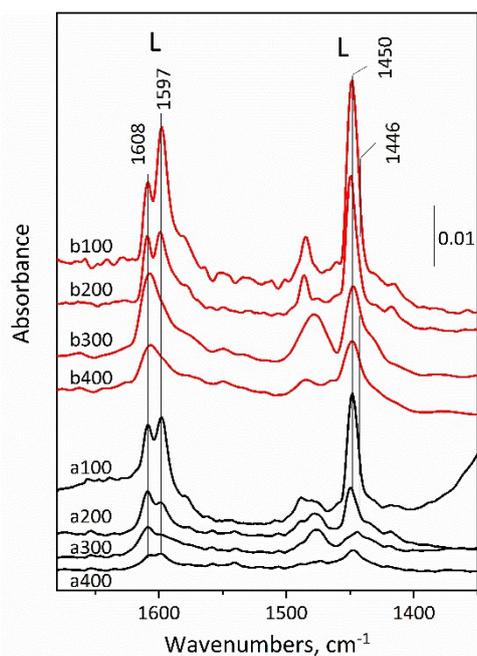


**Fig. S1** TEM image of the reduced Co/SiO<sub>2</sub>(8.1) catalyst.

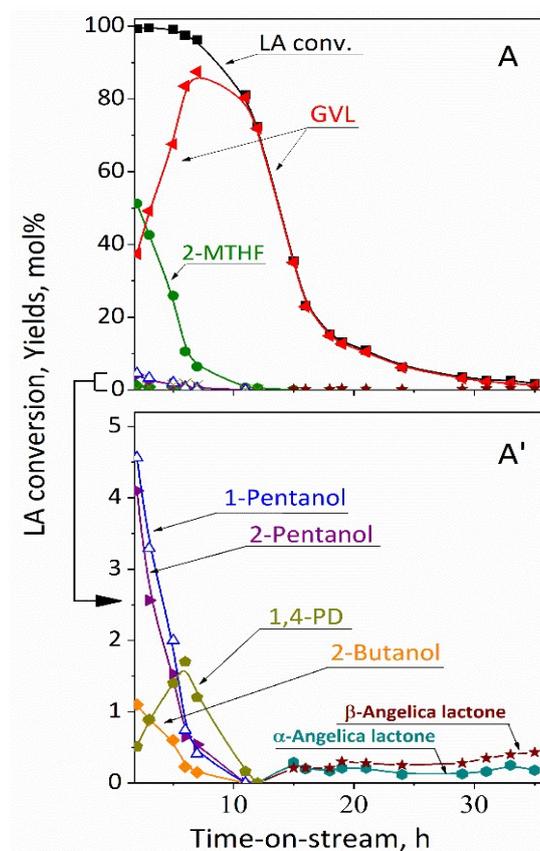


**Fig. S2** FT-IR spectra of CO adsorbed on the reduced silica-supported Co catalysts (a) Co/SiO<sub>2</sub>(4.6), (b) Co/SiO<sub>2</sub>(8.1), (c) Co/SiO<sub>2</sub>(13.3)) at room temperature after (A) having been contacted with CO at 5 mbar for 10 min and (B) subsequent evacuation in high vacuum for 10 min. The samples were in-situ reduced by H<sub>2</sub> flow at 450 °C for 1h. After reduction, the catalysts were degassed by evacuation, cooled to room temperature, and CO was introduced into the IR cell. The thin lines under the curves give the component bands obtained using a peak fitting computer program.

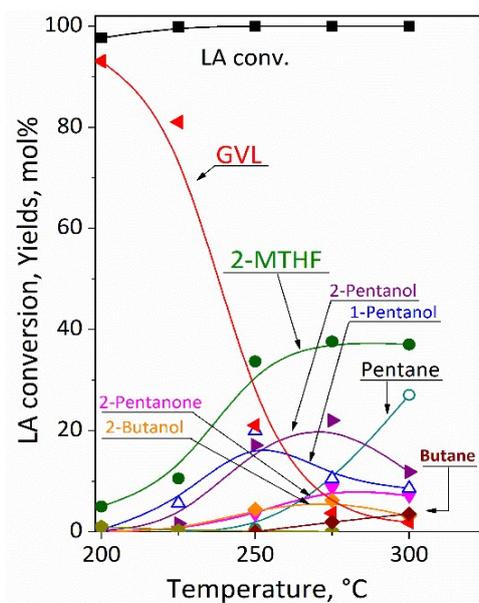
In Fig. S2 the spectra of CO chemisorbed on the three reduced Co/SiO<sub>2</sub> catalysts at room temperature are shown in the presence of (A) excess carbon monoxide and (B) after evacuation in high vacuum. Upon evacuation the doublet having maxima at about 2055 and 2025 cm<sup>-1</sup> changed to a single band with a maximum at about 2006 cm<sup>-1</sup> with shoulder(s) at lower wavenumbers (1956 and 1914 cm<sup>-1</sup>) in the spectra of the catalysts of higher Co content (Fig. S2A and B). In case of the Co/SiO<sub>2</sub>(4.6) sample the CO almost completely desorbed from the surface during evacuation. The narrow band with a maximum about 2060 cm<sup>-1</sup> disappeared and only a very weak band of linearly-bound CO remained (Fig. S2A,a and B,a). Absorption bands that are at 20 or 50 cm<sup>-1</sup> higher frequency than the frequency of the band obtained from the linearly-bound CO may be an indication for adsorption site metal atoms that are adjacent to oxygen atoms that can be located either on the metal particles itself or on the surface of the oxide support.<sup>3</sup> Others assigned the two bands in the 2100 to 2000 cm<sup>-1</sup> region to CO species of the M(CO)<sub>n</sub> type where n > 1.<sup>4</sup> Our XRD, TPR and FT-IR results indicated that the reduction of silica-supported Co catalysts was not complete at 450°C. This finding supports the first assignment.



**Fig. S3** FT-IR spectra of pyridine (Py) adsorbed on  $\text{Co}_3\text{O}_4/\text{SiO}_2(4.6)$  (spectra a100-a400) and  $\text{Co}_3\text{O}_4/\text{SiO}_2(13.3)$  (spectra b100-b400) reduced in  $\text{H}_2$  flow at 450 °C. Pre-treated samples were contacted with Py vapor at 5 mbar, 200 °C for 30 min, cooled to 100 °C and evacuated for 30 min. Evacuation was repeated at temperatures increased in 100 °C intervals. After evacuation spectra were recorded at room temperature. Label [L] indicate the characteristic bands for Py bonded to Lewis-acid sites.



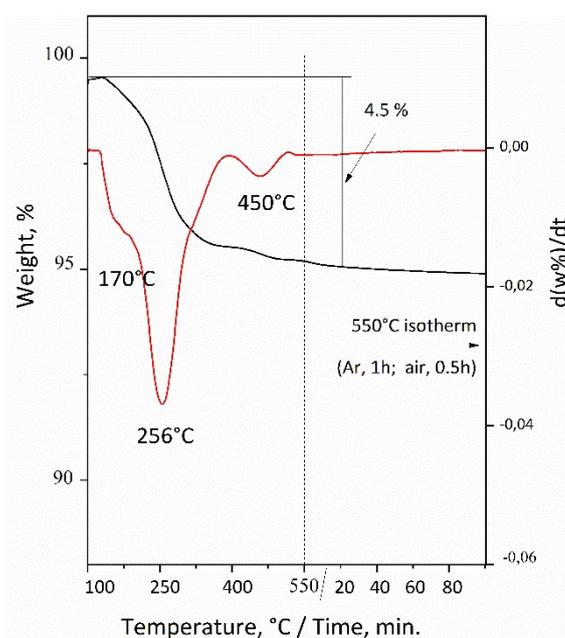
**Fig. S4** LA conversion and product yields on  $\text{Co}/\text{SiO}_2(4.6)$  catalyst (A, A') as a function of time-on-stream (TOS) at 200 °C, 30 bar total pressure, and  $1.0 \text{ g}_{\text{cat}}/\text{g}_{\text{LA}}^{-1}\text{h}$  space time of LA. The  $\text{H}_2/\text{LA}$  ratio was 12. Figure (A') shows a section of figure (A) enlarged.



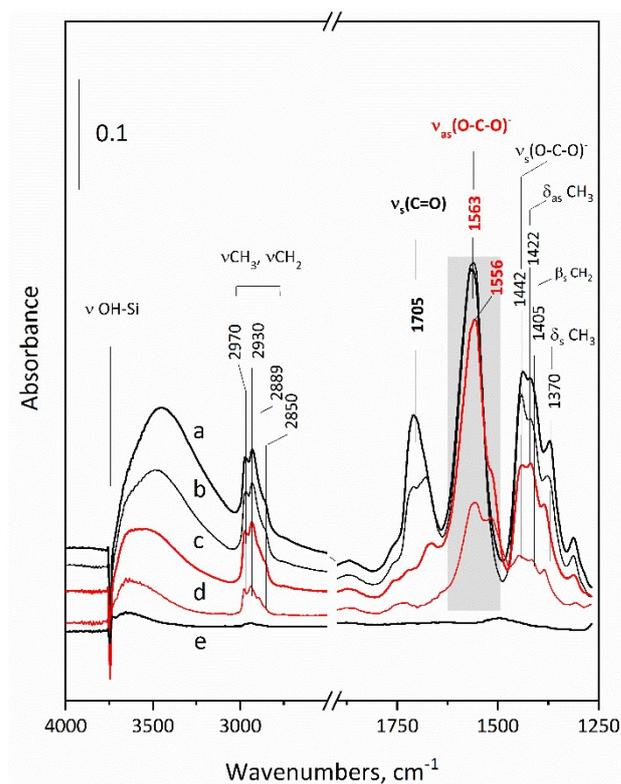
**Fig. S5** LA conversion and product yields on Co/SiO<sub>2</sub>(8.1) catalyst as a function of temperature at 30 bar total pressure, and 1.0 g<sub>cat</sub>/g<sub>LA</sub><sup>-1</sup>h space time of LA. The H<sub>2</sub>/LA ratio was 12. After achieving the steady state at 200°C, shown in Fig. 7, the temperature was increased up to 300 °C in 25 °C intervals.

### Characterization of the used catalysts

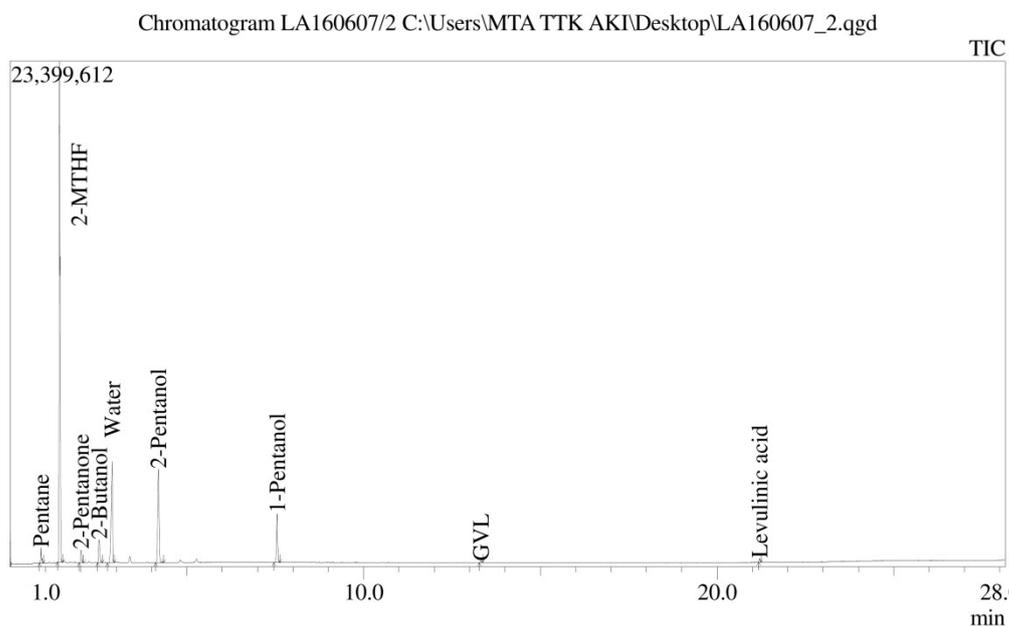
Thermogravimetric microbalance (Setaram TG 92) experiments were used for determination of the adsorbed carbonaceous species on the catalysts. After stopping LA feed the catalyst was cooled to RT. The catalyst was washed with ethanol at RT and dried at 60 °C. The washing solution was analyzed by GC-MS. 1,4-PD, GVL and LA were detected, their amount was about ~ 1 % of the catalyst weight. Both untreated and washed catalyst were placed into the microbalance and heated in Ar at a rate of 10 °Cmin<sup>-1</sup> up to 550 °C and kept them for 1 h at this temperature. After that, the flow of Ar was changed to air and the spent catalysts were left in the air flow for another 1 h. For treated catalysts, 4-5 % weight loss was detected in Ar flow up to 550 °C, no further mass change was observed during combustion at 550 °C (Fig. S6).



**Fig. S6** TG and DTG curve of the spent Co/SiO<sub>2</sub>(8.1) catalyst after LA conversion at 200 °C and 30 bar total pressure for 20 h (cf. Fig. 7A and A').



**Fig. S7** FT-IR difference spectra of adsorbed species retained by the spent Co/SiO<sub>2</sub>(8.1) catalyst after evacuation in high vacuum for 0.5 h at increasing temperatures from (a) 100 up to (e) 450 °C (a: 100 °C, b: 200 °C, c: 300 °C, d: 400 °C, e: 450 °C). Carboxylate bands are highlighted.



**Fig. S8** GCMS chromatogram of liquid phase product obtained at 5 hour of TOS at 225 °C, 30 bar total pressure and 1.0 g<sub>cat</sub>/g<sub>LA</sub>·h space time of LA.

## References

- 1 C. H. Bartholomew, *Catal. Lett.*, 1990, **7**, 27-52.
- 2 C. E. Emeis, *J. Catal.*, 1993, **141**, 347-354.
- 3 N. Sheppard, T.T. Nguyen, in „Advances in Infrared and Raman Spectroscopy”, Vol. 5 (Eds. R.J.H. Clark, R.R. Hester), Heyden, London, 1980, Ch. 2. p. 136.
- 4 M. J. Heal, E. C. Leisegang, R. G. Torrington, *J. Catal.*, 1978, **51**, 314-325.