## Steering the Ester and gamma-Valerolactone Selectivities in Levulinic Acid Hydrogenation

Gayatri B. Kasar<sup>[a, b]</sup>, Nandan S. Date<sup>[a]</sup>, P.N. Bhosale<sup>[b]</sup>, Chandrashekhar V. Rode<sup>[a]</sup> \*

[a] Chemical Engineering and Process Development Division, CSIR-NCL, Dr. Homi Bhabha Road, Pashan, Pune-411008

[b]Materials Research Laboratory, Department of Chemistry, Shivaji University, Kolhapur-416004, India

## **# Supporting Information**

## Table of contents:

- Table S1: CO<sub>2</sub>-TPD table
- Table S2: NH<sub>3</sub>-TPD table
- Table S3: Results for LA esterification
- Figure S1: XPS spectra of Lanthanum 3d 3/2 in 20% Co/La<sub>2</sub>O<sub>3</sub>, (a) Fresh and (b) Used
- Figure S2: XPS spectra Oxygen 1s (a) Fresh, (b) Used
- Figure S3: EDX spectrum for 20% Co/La<sub>2</sub>O<sub>3</sub>
- Figure S4: Ammonia TPD analysis of (a) 20% Co/La<sub>2</sub>O<sub>3</sub>, (b) 20% Cu/La<sub>2</sub>O<sub>3</sub>, (c) 20% Ni/La<sub>2</sub>O<sub>3</sub>
- Figure S5: Py-IR spectra of catalysts
- Figure S6: CT profile of Levulinic acid esterification
- Figure S7: Effect of solvent on selectivity pattern
- Figure S8: Effect of reaction time (a) without water, (b) with water
- Figure S9: Catalyst magnetic properties

| Sr.No. | Catalyst                                | Total CO <sub>2</sub><br>desorbed | Temperature range-wise desorption CO <sub>2</sub><br>(mmol g <sup>-1</sup> ) |           |           |
|--------|---|-----------------------------------|--|-----------|-----------|
|        |   | (mmol g <sup>-1</sup> )           | 30-260°C   | 260-460°C | 460-760°C |
| 1      | $La_2O_3$                               | 3.115                             |  | -         | 3.115     |
| 2      | $Co_3O_4$                               | 0.131                             | 0.112  | 0.012     | 0.007     |
| 3      | Fresh Co/La <sub>2</sub> O <sub>3</sub> | 2.321                             | 0.320  | 1.344     | 0.657     |
| 4      | Used Co/La <sub>2</sub> O <sub>3</sub>  | 5.444                             | 0.598  | 4.639     | 0.208     |
| 5      | Cu/La <sub>2</sub> O <sub>3</sub>       | 0.871                             | 0.048  | 0.708     | 0.114     |
| 6      | Ni/La <sub>2</sub> O <sub>3</sub>       | 0.924                             | 0.267  | 0.656     | 0         |

 Table S1: CO2-TPD table

 Table S2: NH<sub>3</sub>-TPD table

| Sr.No. | Catalyst                          | Total NH <sub>3</sub><br>desorbed | Temperature range-wise desorption NH <sub>3</sub><br>(mmol g <sup>-1</sup> ) |           |           |
|--------|-----------------------------------|-----------------------------------|--|-----------|-----------|
|        |                                   | (mmolg <sup>-1</sup> )            | 50-360°C   | 360-460°C | 460-660°C |
| 1      | Co/La <sub>2</sub> O <sub>3</sub> | 0.5001                            | 0.1774   | 0.2047    | 0.1180    |
| 2      | Cu/La <sub>2</sub> O <sub>3</sub> | 0.2245                            | 0.1122   | 0.0815    | 0.0308    |
| 3      | Ni/La <sub>2</sub> O <sub>3</sub> | 0.1771                            | 0.1256   | 0.0193    | 0.0322    |

| Sr.No | Catalyst                              | Conv, | Selectivity, % |      |
|-------|---------------------------------------|-------|----------------|------|
|       |                                       | %     | GVL            | MeLA |
| 1     | $La_2O_3$                             | 94    | 4.3            | 93   |
| 2     | 20% Co/La <sub>2</sub> O <sub>3</sub> | 96    | 9              | 91   |

 Table S3: Results for LA esterification

Reaction conditions: Levulinic acid, 5g; solvent, MeOH 100ml; catalyst, 0.5g; temperature, 200°C; H<sub>2</sub> pressure, 500 psi ; reaction time, 5 h.









Figure S3: EDX spectrum for 20% Co/La<sub>2</sub>O<sub>3</sub>



Figure S4: Ammonia TPD analysis of (a) 20% Co/La<sub>2</sub>O<sub>3</sub>, (b) 20% Cu/La<sub>2</sub>O<sub>3</sub>, (c) 20% Ni/La<sub>2</sub>O<sub>3</sub>



Figure S5: Py-IR spectra of catalysts



Figure S6: CT profile of Levulinic acid esterification



Reaction conditions: Levulinic acid, 5g; solvent, MeOH 100ml; catalyst, 0.5g; temperature, 200°C; reaction time, 5 h.



Figure S7: Effect of solvent on selectivity pattern

Reaction conditions: Levulinic acid, 5g; solvent, 100ml; catalyst, 0.5g; temperature, 200°C;  $H_2$  pressure, 500 psi; reaction time, 5 h.



Reaction conditions: Levulinic acid, 5g; solvent, 100ml; catalyst, 0.5g; temperature, 200<sup>0</sup>C; H<sub>2</sub> pressure, 500 psi.

Figure S9: Catalyst magnetic properties

