## Catalytic activity and stability of hydrophobic Mg-Al hydrotalcites in the continuous aqueous-phase isomerization of glucose into fructose

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Figure S1. Separation of the hydrophobic HT to the top of the glucose solution



(A)



(B)

Figure S2. XRD pattern (A) and TG and DSC curves (B) of the HT



(A)



(B)

Figure S3. XRD pattern (A) and TG and DSC curves (B) of the HT-CO<sub>3</sub>



(A)



(B)

Figure S4. XRD pattern (A) and TG and DSC curves (B) of the HT-R

| Catalyst           | Sbet, $m^2 g^{-1}$ | Adsorbed water, wt. % |
|--------------------|--------------------|-----------------------|
| HT                 | 8                  | 9.5                   |
| HT-CO <sub>3</sub> | 32                 | 15.7                  |
| HT-R               | 37                 | -                     |

Table S1. Data on the specific surface area of the hydrotalcites and amount of water physically adsorbed by the hydrotalcites.



**Figure S5.** Time dependency of glucose consumption (closed symbols) and fructose accumulation (open symbols) in the presence of the HT (triangles), HT-CO<sub>3</sub> (squares) and HT-R (circles). Reaction conditions: 1 wt.% glucose solution (30 mL), 90  $^{\circ}$ C, 500 rpm, mass of the catalyst is written on the graphs.



**Figure S6.** Results of the hot filtration test of HT. Solid and dashed lines refer to kinetics of glucose consumption before and after filtration, respectively. Reaction conditions: 1 wt.% glucose solution (30 mL), 3 g of catalyst, 90 °C, 500 rpm.

**Table 2S.** Concentration of  $Mg^{2+}$  detected in the reaction solution after experiments over HT-R and HT-CO<sub>3</sub>. Reaction conditions: 1 wt.% glucose solution (30 mL), 90 °C, 500 rpm, 24 h.

|                  | Concentration of Mg <sup>2+</sup> (mg L <sup>-1</sup> ) in |      |  |
|------------------|--|------|--|
|                  | the presence of  |      |  |
| Catalyst mass, g | HT-CO <sub>3</sub>   | HT-R |  |
| 0.03             | 20   | -    |  |
| 0.1              | 29   | 59   |  |
| 1                | 96   | 201  |  |

**Table S3.** Accumulation of the by-products during isomerization of glucose into fructose. Batch reaction conditions: 30 mL of aqueous solution of glucose, 2 g of a catalyst, 90 °C, stirring 500 rpm. Continuous reaction conditions: 180 mL, 12 g of HT, 90 °C, 430 rpm.

|       | Batch       | Batch       | Continuous       | Continuous     | Continuous     | Continuous       | Continuous     | Continuous     |
|-------|-------------|-------------|------------------|----------------|----------------|------------------|----------------|----------------|
|       |             |             | mode $(t = 8 h)$ | mode (t = $24$ | mode(t = 43 h) | mode $(t = 8 h)$ | mode (t = $24$ | mode (t = $43$ |
|       |             |             |                  | h)             |                |                  | h)             | h)             |
|       | 1% Glu      | 10% Glu     | 1% Glu           | 1% Glu         | 1% Glu         | 10% Glu          | 10% Glu        | 10% Glu        |
| Time, | S           | S           | S                | S              | S              | S                | S              | S              |
| h     | (DHA/GA/LA) | (DHA/GA/LA) | (DHA/GA/LA)      | (DHA/GA/LA)    | (DHA/GA/LA)    | (DHA/GA/LA)      | (DHA/GA/LA)    | (DHA/GA/LA)    |
| 4     | 3/0/0       | -           | 0/0/0            | 0/0/0          | 0/0/0          | -                | -              | 4/3/0          |
| 8     | 4/3/0       | 2/1/0       | -                | 0/0/0          | -              | 1/0/0            | 1/2/0          | -              |
| 21    | -           | -           | 0/0/0            | -              | 10/8/0         | 2/0/0            | -              | 2/2/0          |
| 24    | 6/5/0       | 3/2/0       | 0/0/0            | 0/0/0          | 12/8/0         | 2/0/0            | 1/2/0          | 5/3/0          |
| 28    | -           | -           | 0/0/0            | -              | 16/10/0        | -                | 1/2/0          |                |
| 32    | 6/6/0       | 4/3/0       | -                | 0/0/0          | -              | 2/0/0            | 2/2/0          | 5/3/0          |
| 45    | -           | 5/4/1       | 0/0/0            | 4/0/0          | 10/4/0         | 0/0/0            | -              | 4/3/0          |
| 48    | 7/7/1       | -           | 0/0/0            | -              | 7/3/0          | -                | 1/2/0          | 4/3/0          |
| 50    | -           | -           | 0/0/0            | 4/0/0          | 7/5/0          | 0/0/0            | 2/2/0          | -              |
| 54    | -           | -           | -                | 2/0/0          | -              | 0/0/0            | 1/1/0          | 4/3/0          |
| 70    | -           | -           | 0/0/0            | 4/0/0          | 5/4/0          | 0/0/0            | 1/1/0          | 3/3/0          |
| 73    | -           | -           | 0/0/0            | -              | 5/2/0          | -                | -              | 3/3/0          |
| 77    | -           | -           | -                | -              | 5/2/0          | -                | 1/1/0          | 4/3/0          |
| 93    | -           | -           | -                | -              | -              | 0/0/0            | -              | 4/3/0          |
| 97    | -           | -           | -                | -              | -              | 0/0/0            | -              | 4/3/0          |



**Figure S7.** Changes of pH during the reactions in the continuous set-up. Reaction conditions: 180 mL, 12 g of HT, 90 °C, 430 rpm. Glu is glucose, t is resident time.



**Figure S8.** Glucose isomerization in the presence of NaOH. Reaction conditions: 10 wt.% glucose, 180 mL, residence time is 24 h, 90 °C, 430 rpm. Yield of fructose at pH 7.5 (squares) and 8 (circles).

**Table S4**. Amount of by-products in the presence of NaOH as catalyst. Reaction conditions: 10 wt.% glucose, 180 mL, residence time is 24 h, 90 °C, 430 rpm.

|       | pH 7.5      | pH 8        |
|-------|-------------|-------------|
|       |             |             |
| time, | S           | S           |
| h     | (DHA/GA/LA) | (DHA/GA/LA) |
| 22    | 8/8/0       | 6/7/0       |
| 26    | 6/6/0       | 7/7/0       |
| 30    | 5/6/0       | 7/8/0       |
| 45    | 5/6/0       | -           |
| 48    | 5/7/0       | -           |



**Figure S9.** Consumption of 1M NaOH under continuous operation conditions. Reaction conditions: 10 wt.% glucose, 180 mL, residence time is 24 h, 90 °C, 430 rpm, pH is kept constant at 7.5 or 8 by addition of 1M NaOH.

| Entry | Glucose, % | Residence time, h | Mg <sup>2+</sup> , mg/L | Leached Mg, % <sup>a</sup> |
|-------|------------|-------------------|-------------------------|----------------------------|
| 1     | 1          | 8                 | 18                      | 1.9                        |
| 2     | 1          | 24                | 25                      | 0.9                        |
| 3     | 1          | 43                | 66                      | 1.1                        |
| 4     | 10         | 8                 | 26                      | 2.7                        |
| 5     | 10         | 24                | 63                      | 1.7                        |
| 6     | 10         | 43                | 96                      | 1.7                        |

**Table S5.** Leaching of Mg<sup>2+</sup> from the HT during continuous operation. Reaction conditions: 180 mL, 12 g of HT, 90 °C, 430 rpm.

<sup>a</sup> Estimation on Mg leached from the charged HT after 100 h time-on-stream











(C)

**Figure S10.** Characterization of the HT after use in the continuous set-up. Reaction conditions: 180 mL of the solution, 12 g of HT, 90 °C, 430 rpm, residence time 24 h. (A) XRD of the HT after 1wt.% glucose feed; (B) TG and DSC of the HT after 1wt.% glucose feed; (C) TG and DSC of the HT after 10wt.% glucose feed.



**Figure S11.** XRD patterns of HT-SDS (A) as-prepared and (B) after the catalytic test under the following reaction conditions: batch, 30 mL of 1 wt.% aqueous solution of glucose, 250 g of a catalyst, 90 °C, stirring 500 rpm.