Electronic Supplementary Material (ESI) for Reaction Chemistry & Engineering.

Supporting information

Highly effective production of levulinic acid and γ-valerolactone through self-circulation of solvent in continuous process

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Computational formula

The conversion of Furfural alcohol (FOL) and the yields or selectivity of the products were quantified according to the following equations:

$$\text{Conversion (\%)} = \frac{\text{Mole of FOL converted (mol)}}{\text{Mole of FOL fed (mol)}} \quad 100$$

$$\text{Selectivity (\%)} = \frac{\text{Mole of product produced (mol)}}{\text{Mole of FOL converted (mol)}} \quad 100$$

$$\text{Yield (\%)} = \text{Selectivity (\%)} \times \text{Conversion (\%)}$$

BET anslysis

Table S1. Textural properties of the samples obtained from BET analysis.

Sample	S_{BET} (m^2/g)	S_{mic} (m^2/g)	V_{tot} (cm^3/g)	V_{mic} (cm^3/g)
ZSM-5	350.9	307.0	0.236	0.152
β	496.7	379.6	0.527	0.186
Y	646.9	603.8	0.368	0.298
USY	636.4	598.8	0.377	0.294
MCM-22	463.1	336.1	0.665	0.164

S_{BET} is the specific surface area; S_{mic} and V_{mic} were calculated by t-plot method.

BET anslysis

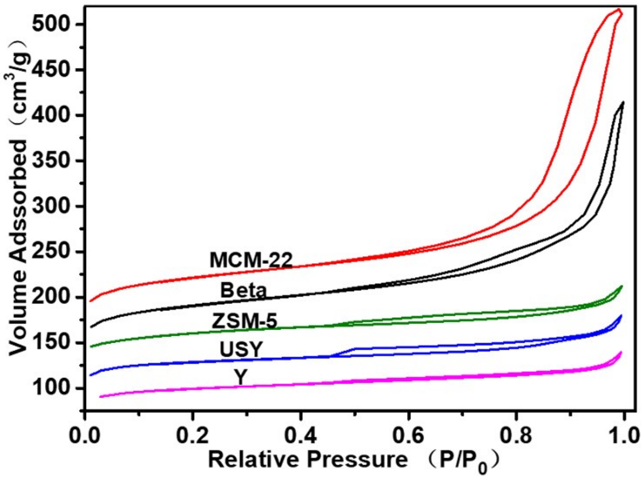

Figure S1. N_2 adsorption–desorption isotherms of the catalysts

NH_3-TPD analysis

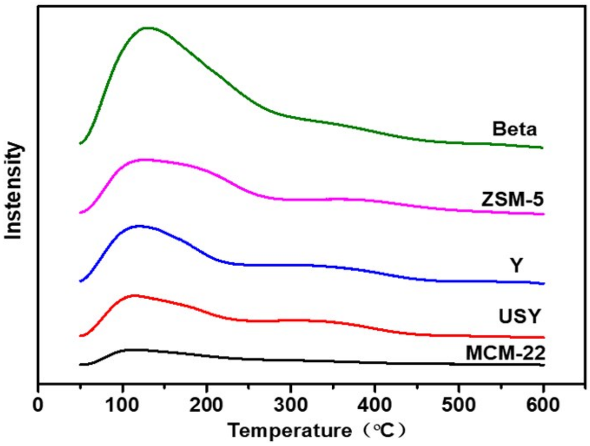

Figure S2. Typical NH_3 - TPD profiles of catalytic materials.

Investigation of reaction conditions

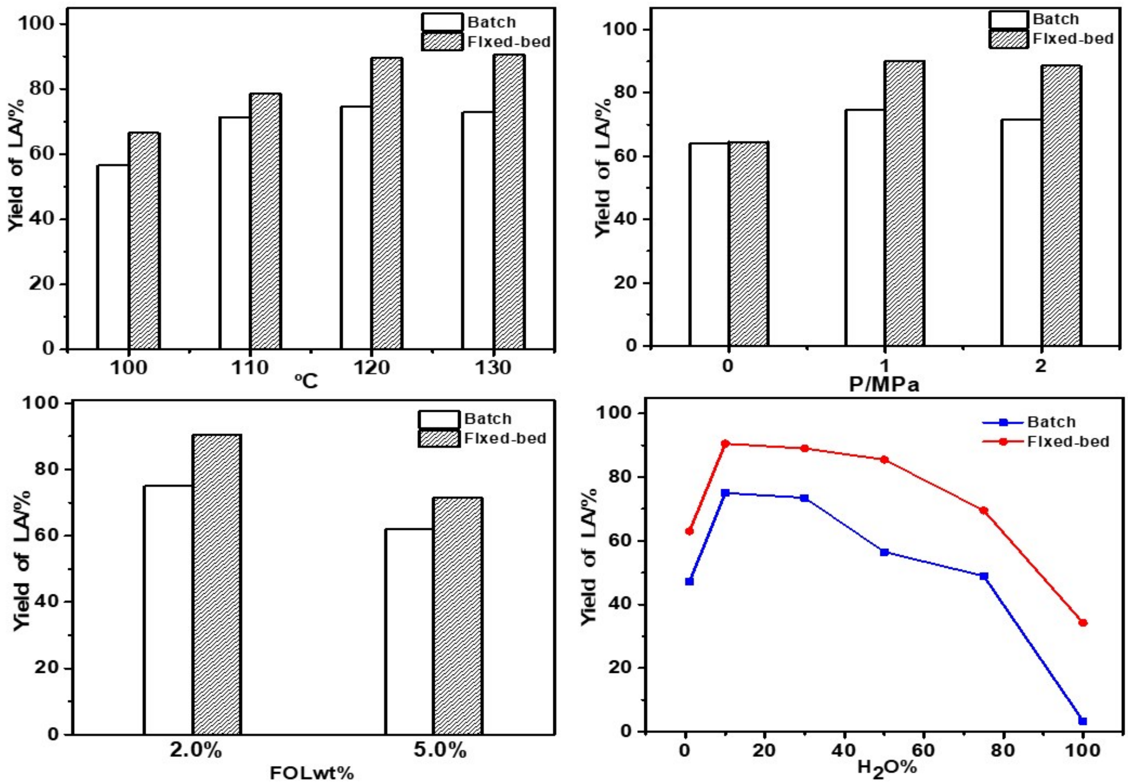

Figure S3. The effects of reaction parameters on LA yield. Conditions: Batch: 40min. Fixed-bed: 5.0g Cat; Liquid hourly space velocity (LHSV)=0.024h^{-1}; v_{gas}= 25ml/min.

Various reaction parameters such as temperature, pressure and so on were investigated, then the reaction results in the batch and fixed-bed reactors were systematically compared. As is shown in Figure S1, the yield of levulinic acid (LA) in the fixed-bed reactors was always higher than the yield in the batch reactors. In addition, the reaction results of two reactors have the same change trends when changing the reaction conditions. LA yield increased firstly with the temperature increasing, the reaction system tends to be stable when further increasing the reaction temperature to 130 °C. Reaction pressure is also a key parameter in the hydration of FOL, although an increase in the reaction pressure resulted in higher yield of levulinic acid, LA yield was similar at 1 MPa and 2 MPa, indicating that the reactions are not sensitive to pressure changes at P≥1.0MPa. The effects of FOL concentration on LA yield were also evaluated in two reactors, and yield of LA was significantly decreased with FOL concentration increases. In view of the above results, considering the reaction conditions and other aspects of the impact, 130 °C, 1 MPa was chosen as the optimum reaction parameters.

Water plays a crucial role in the formation of LA because it is an important participant in the hydrolysis of FOL. The effect of water content ranged from 1wt%-100wt% was then systematically evaluated with γ- valerolactone (GVL) as reaction solvent. It can be seen from the data that the yield of LA increased firstly followed by a gradual decrease when water content increased. FOL has the particularity to polymerization in acidic aqueous solutions leading to low yield of LA. [1] The formation of polymers can be alleviated through hydrogen bonding and shielding effects by adding of organic solvents. [2] In short, despite the fact that excess H_2O is unfavorable for obtaining high yield of LA, it is indispensable for the conversion of FOL.

TG-MS analysis

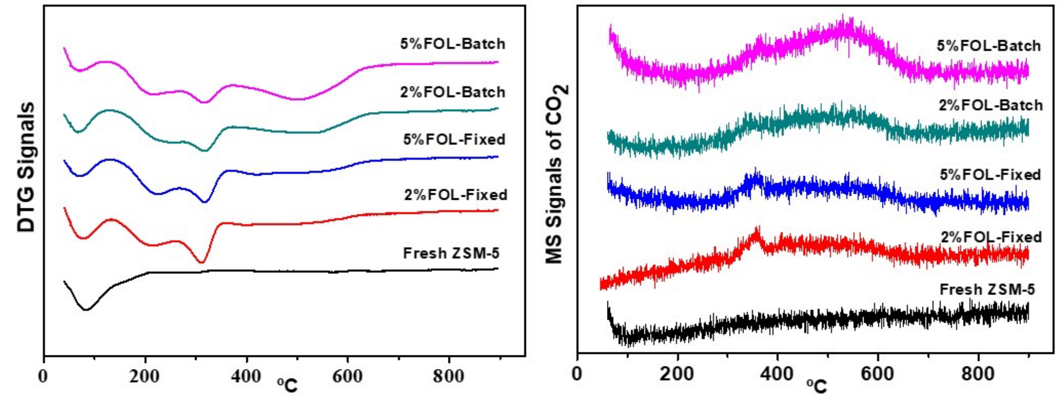

Figure S4. DTG curves of HZSM-5 in different reaction models recorded at 10℃/min and MS singles of CO_2. Reaction time is setted as 40min and 300min respectively for catalysts in the autoclaves and the fixed-bed reactors, all samples were dried in 100˚C for 120min before analysis of TGA.

In the mass spectrometry of CO_2, decomposition peaks at around 350 ˚C and 550˚C can be attributed to the release of CO_2, and the size of the peak area in the mass spectrum of CO_2 is related to the amount of polymers deposited on the surface of the catalysts. Obviously, the polymers deposited on the catalysts in the fixed bed reactors were obviously less than that of the counterpart in the fixed bed reactors. In addition, as the FOL concentration increases, the reaction was more prone to polymerization.

71 ## Investigation of catalysts doses in the autoclaves

72 **Table S2.** The effects of catalyst doses in the autoclaves

Entry	m_{cat}/g	Time/min	Conversion/%	Yield of LA/%
1	0.1	40	99.6	66.6
2	0.2	40	99.9	75.0
3	0.4	40	99.9	75.5

Conditions: 15mL reaction solution (2wt%FOL+88wt%GVL+10wt%H_2O); 130°C; 1.0MPa; 40min.

Diagram of the direct conversion of FOL to GVL

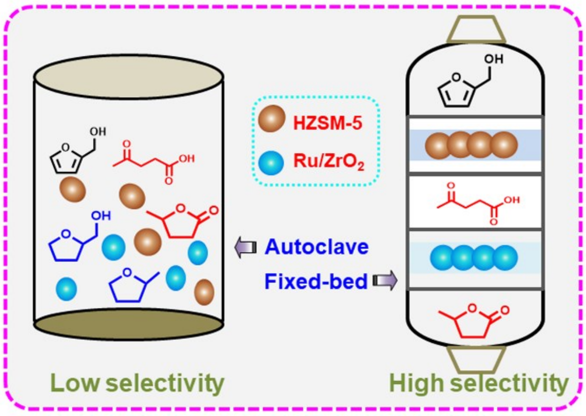

Figure S5. Diagram of the direct conversion of FOL to GVL in different reactors.

HPLC analysis

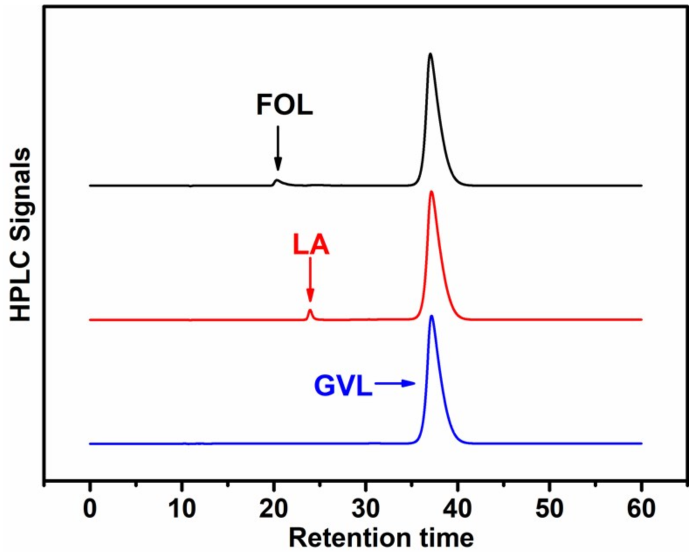

Figure S6. High Performance Liquid Chromatography of reaction mixtures at different reaction stage in the fixed-bed reactors. Black line: reaction substrates; Red line: production of LA from FOL in the fixed-bed reactors, 130℃; 2.0 MPa; 5.0g HZSM-5; v (H_2) = 25mL/min; LHSV=0.024h^{-1}; Blue line: production of GVL from FOL through "solvent self-circulation", 130℃; 2.0MPa; 5.0g HZSM-5 + 4.0gRu/ZrO_2; v (H_2) = 25mL/min; LHSV=0.024h^{-1}.

Notes and references

[1] a)T. Kim, R. S. Assary, C. L. Marshall, D. J. Gosztola, L. A. Curtiss, P. C. Stair, *ChemCatChem* **2011**, *3*, 1451-1458; b)T. Kim, R. S. Assary, H. Kim, C. L. Marshall, D. J. Gosztola, L. A. Curtiss, P. C. Stair, *Catalysis Today* **2013**, *205*, 60-66

[2] G. Falco, N. Guigo, L. Vincent, N. Sbirrazzuoli, *Polymers* **2018**, *10*, 529