# Catalytic conversion of biomass-derived levulinic acid to valerate esters as oxygenated fuels using supported ruthenium catalysts

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## 1. Experimental

#### **Catalyst characterization**

Nitrogen adsorption/desorption isotherms were measured by a Micromeritics ASAP 2020 analyzer at 77 K. The surface area was determined using Barrett-Emmet-Taller (BET) method and the average pore size, pore volume and pore size distributions were determined by Barret-Joyner-Halenda (BJH) method.

X-ray power diffraction (XRD) patterns of SBA-SO<sub>3</sub>H and Ru/SBA-SO<sub>3</sub>H were recorded on an X'pert (PANalytical) diffractometer at 40 kV and 40 mA, using Ni-filtered Cu-K $\alpha$  radiation. 2 $\theta$  range was  $0.5^{\circ} \sim 10^{\circ}$ .

Transmission electron microscopy (TEM) microphotographs were performed on a JEOL-2010 electron microscope operating at 200 kV. The samples were suspended in methanol.

X-ray photoelectron spectra (XPS) were acquired with a Thermo Scientific Escalab 250-X-ray photoelectron spectrometer equipped with a hemispherical electron analyzer and an Al K $\alpha$  X-ray source. All binding energies were referenced to the C 1s line at 284.8 eV.

The amount of the sulphur and metal loading were determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES, Thermo-Jarrell ASH-Atom Scan Advantage) based on the sulphur and metal content. The pretreatment of the samples were pretreated by alkali fusion or HF dissolution method.

The amount of acid sites of the catalysts were determined by the sulphur content and XPS of S 2p, Hammett titration and acid-base titration. The indicators of Hammett titration were crystal violet and anthraquinone.

## 2. Results

Catalysts	Amount of acid sites / mmol g <sup>-1</sup>	$D_p/ {\rm \AA}$	$V_p / cm^3 g^{-1}$	$S_{BET}/m^2 g^{-1}$
SBA-15	-	42.2	0.50	622
SBA-SO <sub>3</sub> H-1	0.18	48.3	0.73	723
SBA-SO <sub>3</sub> H-2	0.40	43.7	0.62	689
SBA-SO <sub>3</sub> H-3	0.49	39.1	0.56	638
SBA-SO <sub>3</sub> H-4	1.20	37.3	0.49	601
Ru/SBA-SO <sub>3</sub> H-4 <sup>b</sup>	1.14	31.7	0.39	506

Table S1. Textural properties of supports and catalyst <sup>a</sup>

a. Amount of acid sites were determined by Hammett titration; b. 5 wt% Ru.

Table S2. The amount of acid sites of the catalysts determined by different methods

Catalyst	S content <sup>a</sup> (mmol g <sup>-1</sup> )	Amount of acid sites $(H_0 \le 0.8, \text{ mmol g}^{-1})^{b}$	Amount of acid sites (mmol g <sup>-1</sup> ) <sup>c</sup>
SBA-SO <sub>3</sub> H-4	1.50	1.20	1.11
Ru/SBA-SO <sub>3</sub> H-1	0.18	0.17	0.16
Ru/SBA-SO <sub>3</sub> H-2	0.43	0.39	0.36
Ru/SBA-SO <sub>3</sub> H-3	0.54	0.46	0.42
Ru/SBA-SO <sub>3</sub> H-4	1.43	1.14	1.05
Ru/C-SO <sub>3</sub> H	0.69	0.66	0.62
Ru/HZSM-5	-	0.28	0.29
$Ru/SBA-SO_3H-4^d$	0.77	0.08	0.06

a. The S contents were detected by ICP element analysis;

b. The amount of acid sites were determined by Hammett titration;

c. The amount of acid sites were determined by acid-base titration;

d. Ru/SBA-SO<sub>3</sub>H-4 was used once under the optimized reaction conditions.

Table S3. The acid strength of the catalysts determined by Hammett titration <sup>a</sup>

Catalyst	$H_0 \leq -8.2 \pmod{g^{-1}}$	$H_0 \leq 0.8 \pmod{g^{-1}}$
SBA-SO <sub>3</sub> H-4	0	1.20
Ru/SBA-SO <sub>3</sub> H-1	0	0.17
Ru/SBA-SO <sub>3</sub> H-2	0	0.39
Ru/SBA-SO <sub>3</sub> H-3	0	0.46
Ru/SBA-SO <sub>3</sub> H-4	0	1.14
Ru/C-SO <sub>3</sub> H	0	0.66
Ru/HZSM-5	0	0.28

a. The indicators of Hammett titration were crystal violet and anthraquinone.

Entry	Temp / K	Initial hydrogen pressure / MPa	Solvent	Ru loading	LA conversion (%)	Selectivity to EV and VA(%)
1	423	2	ethanol	1%	90	2
2	423	4	water	5%	95	3
3	423	6	THF	10%	94	3
4	503	2	water	10%	90	75
5	503	4	THF	1%	89	65
6	503	6	ethanol	5%	95	80
7	553	2	THF	5%	95	39
8	553	4	ethanol	10%	96	31
9	553	6	water	1%	97	32

## Table S4. Factorial design of experimental conditions and corresponding results

**Table S5.** The leaching of Ru and S determined by ICP-AES of the reaction mixture after reaction <sup>a</sup>

Catalyst	Ru leaching (%)	S leaching (%)
Ru/SBA-SO <sub>3</sub> H-4	3.1%	45.7

a. Reaction conditions: 4 mmol of LA, 0.2 g of Ru/SBA-SO<sub>3</sub>H-4 (5 wt% Ru), 10 mL of ethanol, 6 h, 4 MPa  $H_2$  and 513 K.



Fig. S1  $N_2$  adsorption isotherms at 77 K on SBA-SO<sub>3</sub>H-4 and Ru/SBA-SO<sub>3</sub>H-4



Fig. S2 BJH pore size distributions for SBA-SO<sub>3</sub>H-4



Fig. S3 BJH pore size distributions for Ru/SBA-SO<sub>3</sub>H-4



Fig. S4 X-ray diffraction patterns of SBA-SO<sub>3</sub>H-4 and Ru/SBA-SO<sub>3</sub>H-4



Fig. S5 TEM micrographs of SBA-SO<sub>3</sub>H-4 (left) and Ru/SBA-SO<sub>3</sub>H-4 (right) (scale bar 90 nm)



Fig. S6 XPS Ru 3d spectra for Ru/SBA-SO<sub>3</sub>H-4



Fig. S7 XPS S 2p spectra for Ru/SBA-SO<sub>3</sub>H-4



Fig. S8 X-ray diffraction patterns of Ru/SBA-SO<sub>3</sub>H-4 used at 553 K

## 3. Discussion

#### **Catalyst characterization**

Table S1 summarizes the structural parameters containing the BET surface area ( $S_{BET}$ ), pore size ( $D_p$ ) and pore volume ( $V_p$ ) of SBA-15, SBA-SO<sub>3</sub>H-x and Ru/SBA-SO<sub>3</sub>H-4.

The N<sub>2</sub> adsorption isotherms for SBA-15-SO<sub>3</sub>H-4 and Ru/SBA-SO<sub>3</sub>H-4 (Fig. S1) were consistent with Type IV isotherms, which are characteristic of mesoporous materials. Compared with unfunctionalized SBA-15, the incorporation of sulfonic acid groups increased the mean mesopore diameter, the pore volume and BET surface area as reported earlier. On the other hand, the increase of the sulfonic acid loading decreased the mean mesopore diameter, the pore volume and BET surface area as a reslut of the sulfonic acid groups tethered to the walls of the mesoporous silica. It was interesting to note that the impregnation of 5 wt% Ru on the SBA-SO<sub>3</sub>H caused a decrease in the above properties.

The small angle XRD spectra of SBA-SO<sub>3</sub>H-4 and Ru/SBA-SO<sub>3</sub>H-4 were showed in Fig. S4. The solid acid SBA-SO<sub>3</sub>H-4 had a very strong angle diffraction peaks in the range of 0.8  $\sim 0.9^{\circ}$  corresponded to the (100) surface. Two weak (110) and (200) diffraction peaks between 1.3° and 1.8° disappeared, indicating that the degree of order was reduced due to the introduction of the sulfonic acid group as reported <sup>1</sup>. It was obvious that the XRD patterns of Ru/SBA-SO<sub>3</sub>H-4 were similar to those of SBA-SO<sub>3</sub>H-4, but a slight decrease of the intensity of the (100) diffraction peaks was observed to show a further decline of the degree of order.

Fig. S5 presented the TEM micrographs of SBA-SO<sub>3</sub>H-4 and Ru/SBA-SO<sub>3</sub>H-4. The images clearly showed the ordered mesoporous structure in SBA-SO<sub>3</sub>H and Ru/SBA-SO<sub>3</sub>H, corroborating the results given by XRD and N<sub>2</sub> adsorption. In particular, a high dispersion of Ru was embedded in the ordered silica matrix, with no aggregates being formed. Furthermore, it seemed that the surface morphology of the supports was not modified after the introduction of Ru.

The XPS spectrum of S 2p exhibited only one peak of 169.00 eV in the binding energy range from 156 eV to 175 eV, indicating that mercapto groups were completely oxidized to sulfonic groups by hydrogen peroxide and sulfonic groups had not been reduced during the reduction of the catalyst under H<sub>2</sub>. This finding was in agreement with the result of Stucky et al.<sup>1</sup> Ru(0) and Ru(IV) were detectable in XPS spectrum of Ru 3d in Fig. S6.

Three different methods were used to determine the amount of acid sites (two direct methods of Hammett titration and acid-base titration and one indirect method combining the sulfur content and XPS of S 2p) and the comparisons of the results obtained from three methods were also listed in Table S2.

# References

[1] (a) D. Margolese, J. A. Melero, S. C. Christiansen, B. F. Chmelka and G. D. Stucky, *Chem. Mater.*, 2000, **12**, 2448; (b) J. A. Melero, G. D. Stucky, R. van Grieken and G. Morales, *J. Mater. Chem.*, 2002, **12**, 1664.