Supplementary Information

A practical approach for enhanced biodiesel production using organic modified montmorillonites as efficient heterogeneous hybrid catalysts

Lijuan He[a], Long Chen[a], Yingxia Nie[a], Minglu He[b], Guixiang Wu[b], Yan Li[b], Hanjing Tian[c]*, Heng Zhang[a]*

[a]National Key Laboratory of Green Pesticide, State-Local Joint Laboratory for Comprehensive Utilization of Biomass, Center for Research & Development of Fine Chemicals, Guizhou University, Guiyang, Guizhou 550025, China

[b]School of Chemistry and Chemical Engineering, Guizhou University, Guiyang 550025, Guizhou, China

[c]School of Materials and Architectural Engineering, Guizhou Normal University, Guiyang, Guizhou 550025, China

* Correspondence should be addressed to Heng Zhang: hzhang23@gzu.edu.cn; tianhj@gznu.edu.cn.

Characterization of catalyst

X-ray diffraction (XRD) was utilized to identify the crystal textures of the samples, and the instrument model was Bruker D8 Advance, using Cu kα radiation with λ = 0.15 nm and 2θ range from 5 ° to 90 °. Fourier transform infrared (FT-IR) spectra of the catalysts were measured by NICOLET iS50 with tested ranging was 4000-400 cm^{-1}, and spectral information was recorded by KBr and carbon catalytic mixed tablet pressing method. X-ray photoelectron spectroscopy (XPS) was conducted on a Thermo Scientific™ K-Alpha™+ spectrometer equipped with a monochromatic Al Kα X-ray source (1486.68 eV) operating at 100 W. Samples were analysed under vacuum (P < 10^{-8} mbar) with a pass energy of 150 eV (survey scans) or 50 eV (high-resolution scans). All peaks would be calibrated with C1s peak binding energy at 284.60 eV for adventitious carbon. Thermogravimetric analysis was conducted on (Netzsch TG 209F1, Germany), and the system was programmed to heat up from room temperature to 800 °C at 10 °C/min under nitrogen gas at 50 mL/min with a constant flow rate. Scanning electron microscope (SEM) characterization was conducted on an electron microscope (Quanta FEG 250). TEM (transmission electron microscope), STEM-HAADF (high-angle annular dark-field scanning transmission electron microscopy) images, and corresponding element mapping were obtained utilizing a JEM-2100F instrument.

N_2-physical adsorption-desorption characterization, the specific surface area, and pore size of the sample were detected by Micromeritics ASAP 2460 chemisosorbent instrument. The samples were vacuumed at 120 °C for 5 h and tested at the temperature of liquid nitrogen (-196 °C), the specific surface area was BET, and the pore size distribution was calculated by the BJH formula. Ammonia temperature-programmed desorption (NH_3-TPD) was analyzed with the AutoChem 2920 apparatus. By the pretreatment method of keeping at 120 ℃ for 5 h under He gas purging atmosphere and then cooling to room temperature, NH_3 was quantitatively adsorbed on the sample as the probe molecule, and then the adsorbed NH_3 was desorbed with He gas as the desorption medium under the continuous heating condition of 50-500 ℃.

Biodiesel yield calculation method

Biodiesel yield was determined using gas chromatography (GC, Agilent 7890 B), and the specific GC analysis information was expressed as follows: inlet temperature = 523 K, detector temperature = 523 K, split ratio = 20:1, oven temperature programmed = 453 K, ramp rate of 15 K min^{-1} to 513 K and maintained for 8 min at 513 K, injection volume = 1 μL, flow rate of nitrogen carrier gas = 45 mL/min; flow rate of air = 450 mL/min; and flow rate hydrogen = 40 mL/min.

Heptadecanoic acid methyl ester (C17:0) was utilized as an internal standard, and the mass of FAMEs formed and yield of biodiesel were calculated according following formals:

$$\text{Weight of FAMEs in product} = \frac{\left(\sum A\right) - A_{C17:0}}{A_{C17:0}} \times m_{C17:0}$$

$$\text{Biodiesel yield} = \frac{\text{Weight of FAMEs in product}}{\text{Weight of feedstock taken}}$$

Wherein, $\sum A$ denotes the total peak areas of FAMEs. $A_{C17:0}$ and $m_{C17:0}$ represent the peak and mass of internal standard respectively.

Table and Figure Captions:

Table S1. Textural, acid properties and corresponding biodiesel yield of different catalysts.

Table S2. The design matrix includes experimental variables (A-D) and biodiesel yield.

Table S3. Properties of biodiesel produced from *Jatropha curcas* L. oil.

Fig. S1. The typical GC graph of biodiesel sample.

Fig. S2. The relative parity of the biodiesel yield and predicted value.

Fig. S3. The relationship between reaction time and biodiesel yield at different temperatures using (a) ILs-OMt-0.6, (b) Amberlyst-15, (c) Mt.

Fig. S4. Computational energy diagrams for esterification reaction of FFAs with methanol via H^+ and no catalyst pathway.

Fig. S5. (a) XRD patterns, (b) BET curves, (c) FT-IR, and (d) XPS spectrum of ILs-OMt-0.6 before and after reuse.

Table S1. Textural, acid properties and corresponding biodiesel yield of different catalysts.

Entry	Catalyst	S_{BET} (m^2/g)	V_{pore} (cm^3/g)	D_{mean} (nm)	Strong acid site (mmol/g)	Weak/moderate acid site (mmol/g)	Total acid site (mmol/g)	Biodiesel yield (%)
1	Mt	118.39	0.17	9.24	0.32	0.23	0.55	17.26%
2	OMt-0.6	98.85	0.16	9.54	0.35	0.30	0.65	20.03%
3	ILs-OMt-0.4	86.54	0.14	10.69	0.60	0.64	1.25	86.25%
4	ILs-OMt-0.6	80.41	0.13	12.28	0.83	0.81	1.63	96.45%
5	ILs-OMt-0.8	77.36	0.12	12.21	0.85	0.94	1.78	93.61%

Reaction conditions: reaction temperature=80 ℃, reaction time=6 h, catalyst dosage=6 wt%, molar ratio of methanol/OA=15:1.

Table S2. The design matrix includes experimental variables (A-D) and biodiesel yield.

Run	CD (A) /wt.%	T (B) /°C	t (C) /h	M/OA (D)	Yield /%
1	0.06	80	8	12	91.73
2	0.06	80	6	15	96.32
3	0.08	60	6	15	78.92
4	0.06	100	4	15	86.24
5	0.08	80	6	12	85.64
6	0.06	60	6	12	77.48
7	0.06	80	6	15	96.41
8	0.04	80	8	15	87.49
9	0.06	100	6	18	96.00
10	0.06	100	6	12	84.73
11	0.06	80	4	18	94.67
12	0.04	80	6	18	85.49
13	0.06	60	4	15	82.27
14	0.06	100	8	15	92.20
15	0.04	80	4	15	90.79
16	0.08	100	6	15	88.40
17	0.06	60	8	15	82.49
18	0.08	80	4	15	89.67
19	0.08	80	8	15	93.50
20	0.06	80	6	15	96.37
21	0.08	80	6	18	94.06
22	0.06	80	8	18	95.10
23	0.06	80	6	15	96.39
24	0.06	60	6	18	78.13
25	0.04	100	6	15	86.46
26	0.06	80	6	15	96.43
27	0.04	60	6	15	73.07
28	0.06	80	4	12	85.13
29	0.04	80	6	12	86.09

T-reaction temperature, t-reaction time, CD-catalyst dosage, M/OA-methanol/oleic acid molar ratio.

Table S3. Properties of biodiesel produced from *Jatropha curcas* L. oil.

Properties	ASTM D6751	EN 14214	Prepared *Jatropha curcas* L. biodiesel
Flash point (℃)	93 min	120 min	147
Acid value (mg KOH/g)	0.50 max	0.50 max	0.17
Density (20.00 ℃, $kg \cdot m^{-3}$)	-	860-900	879.98
Cetane number	47 min	51 min	55.53
Water content (mg/kg)	-	500 max	traces
Oxidative stability (110.00 ℃, h)	3 min	6 min	8
Kinematic viscosity (mm^2/s, 40.00 ℃)	1.90-6.00	3.50-5.00	4.27
Free glycerin (%)	0.02 max	0.02 max	0.02
Total glycerin (%)	0.24 max	0.25 max	0.15

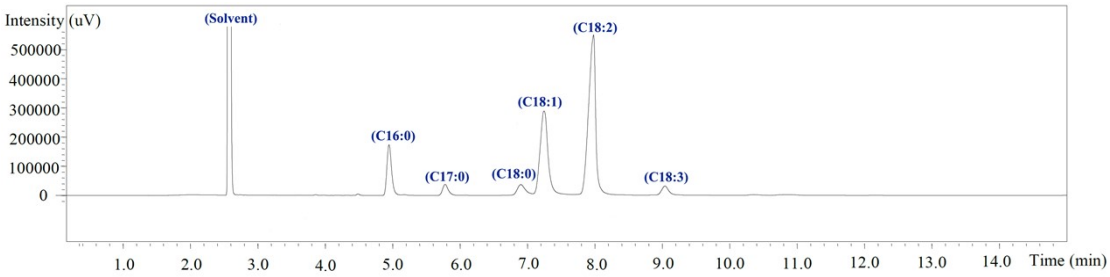
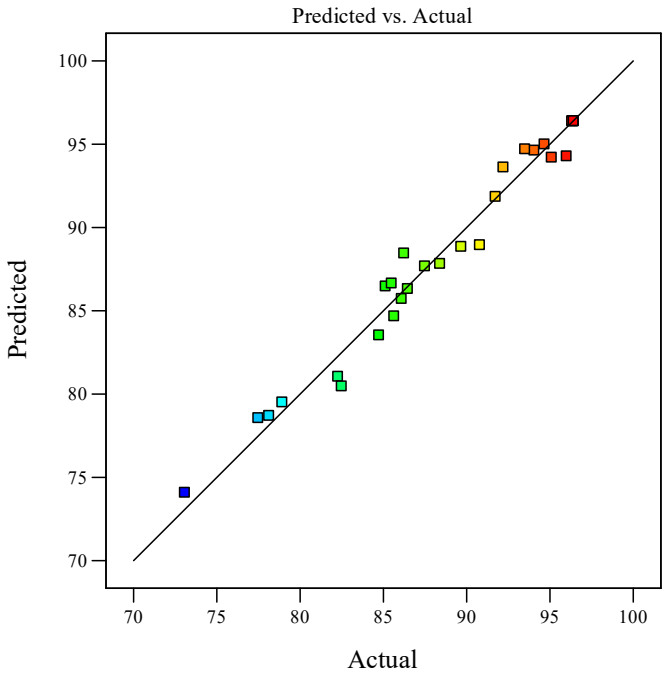


Fig. S1. The typical GC graph of biodiesel sample.



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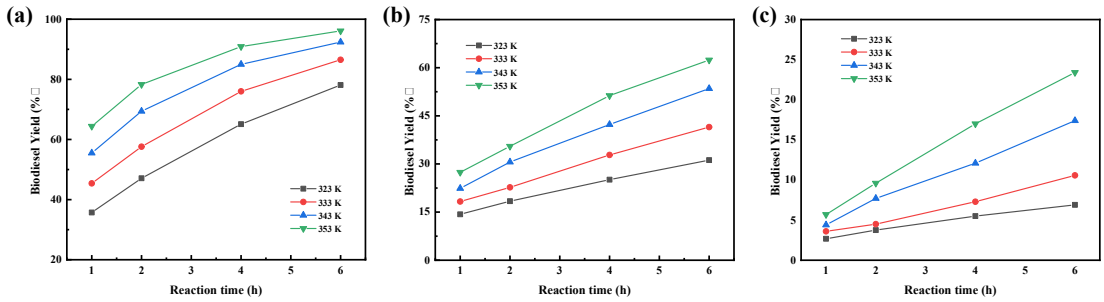

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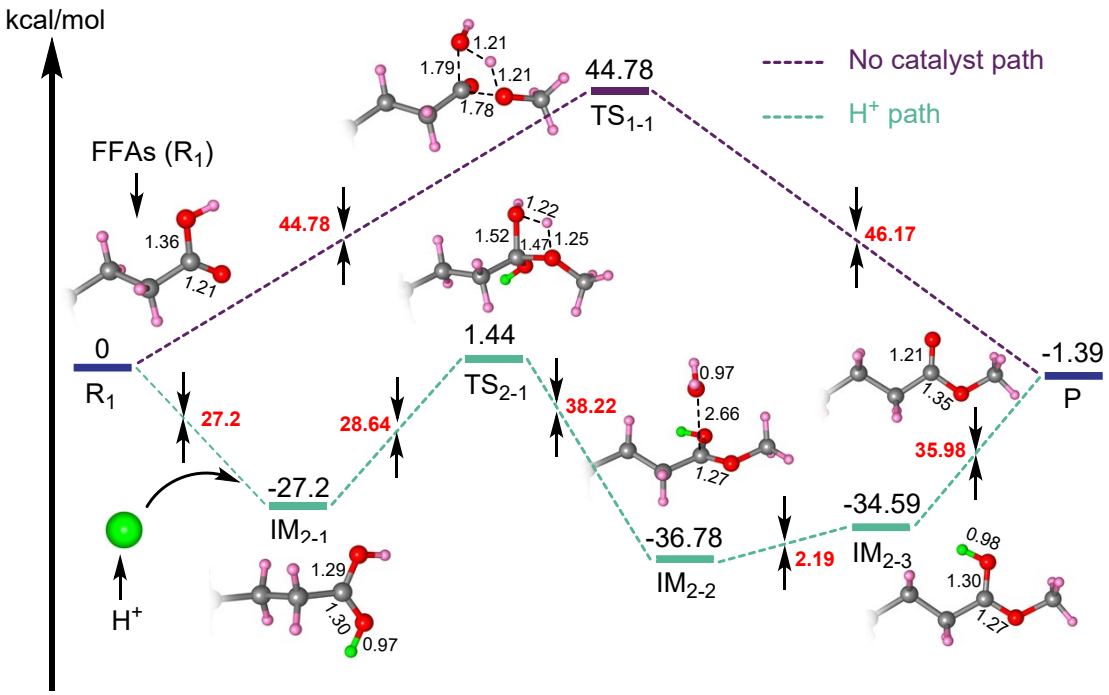

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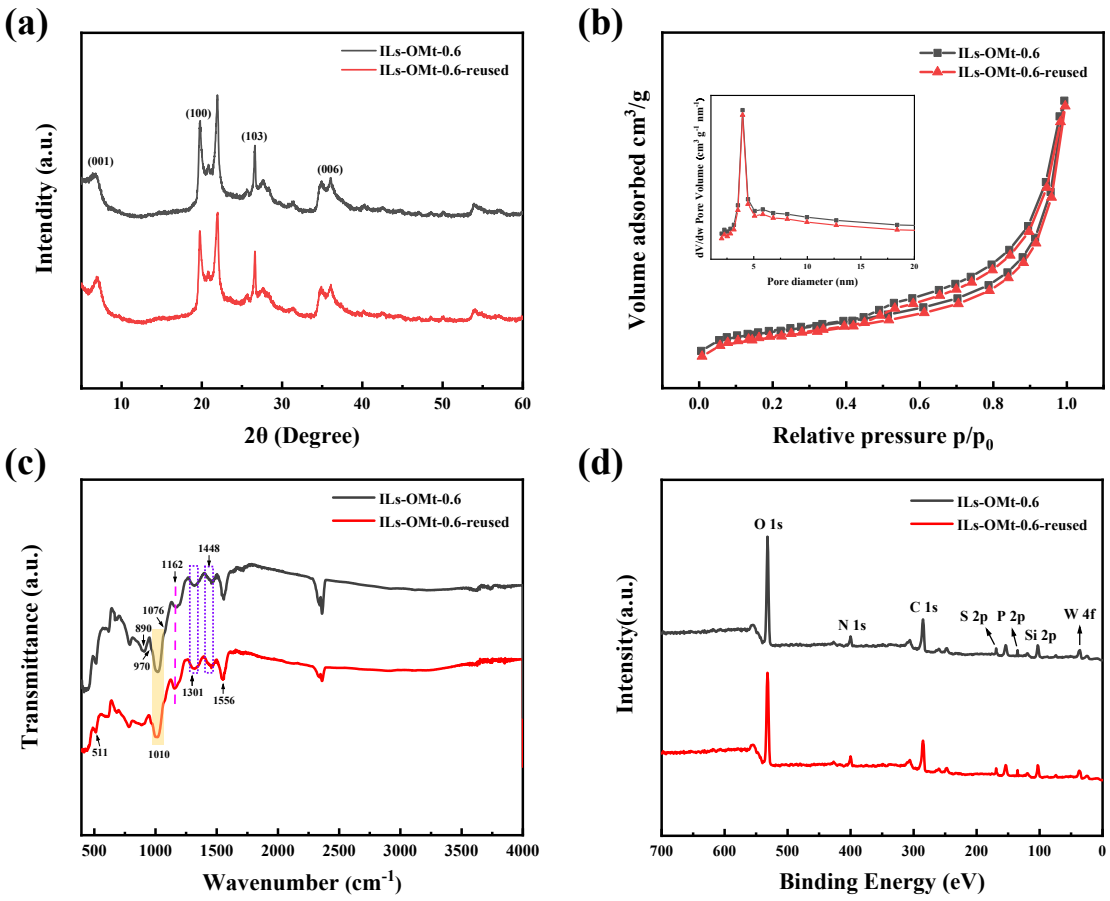

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