Supporting Information

Polyoxometalate-MgF_2 hybrids as heterogeneous solid acid catalysts for efficient biodiesel production

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Table Captions:

Table S1 The amount of carbon in fresh and spent $Mg_{20}F_{39}$TPA-1.0 catalysts[a].

Table S2 The optimization of reaction conditions on the (trans)esterfication of Jatropha oil to biodiesel over $Mg_{20}F_{39}$TPA-1.0 catalyst.

Table S3 Comparison of catalysts performance in simultaneous esterification and transesterification.

Figure Captions:

Fig. S1 EDS spectra of (a) MgF_2, (b) $Mg_{20}F_{39}$TPA-1.2, (c) $Mg_{20}F_{39}$TPA-1.0, (d) $Mg_{20}F_{39}$TPA-0.8 and (e) $Mg_{20}F_{39}$TPA-0.6.

Fig. S2 FTIR spectra of (a) TPA, (b) $Mg_{20}F_{39}$TPA-0.6, (c) $Mg_{20}F_{39}$TPA-0.8, (d) $Mg_{20}F_{39}$TPA-1.0 and (e) $Mg_{20}F_{39}$TPA-1.2.

Fig. S3 NH_3-TPD profiles of (a) TPA, (b) $Mg_{20}F_{39}$TPA-1.2, (c) $Mg_{20}F_{39}$TPA-1.0, (d) $Mg_{20}F_{39}$TPA-0.8, (e) $Mg_{20}F_{39}$TPA-0.6 and (f) MgF_2.

Fig. S4 CO_2-TPD profiles of MgF_2.

Fig. S5 (a) N_2-adsorption isotherms and (b) pore size distribution of $Mg_{20}F_{39}$TPA-1.0.

Fig. S6 TG curves of $Mg_{20}F_{39}$TPA-1.0 in N_2.

Fig. S7 The leaching test of $Mg_{20}F_{39}$TPA-1.0 (9/1 methanol/oleic acid molar ratio, 5 wt% catalyst, 80 ºC at different reaction times of 1-5 h).

Fig. S8 Reusability of $Mg_{20}F_{39}$TPA-1.0 catalyst during oleic acid to methyl oleate conversion (9/1 methanol/oleic acid molar ratio, 5 wt% catalyst, 50 ºC at different reaction times: (1) 60 min, (2) 60 min, (3) 60 min, (4) 80 min and (5) 80 min).

Table S1

The amount of carbon in fresh and spent $Mg_{20}F_{39}$TPA-1.0 catalysts[a].

Catalyst	C content (wt%)
$Mg_{20}F_{39}$TPA-1.0 (fresh)	0.24
$Mg_{20}F_{39}$TPA-1.0 (reused 3th)	3.70

[a]Quantified by elemental analysis.

Table S2

The optimization of reaction conditions on the (trans)esterfication of *Jatropha* oil to biodiesel over $Mg_{20}F_{39}$TPA-1.0 catalyst.

No.	Temperature (ºC)	Methanol/oil molar ratio	Catalyst dosage (wt%)	Time (h)	Yield (%)
1	120	20:1	6	8	49 ± 1.5
2	120	25:1	8	10	51 ± 0.9
3	120	30:1	10	12	62 ± 0.8
4	130	20:1	8	12	90 ± 1.8
5	130	25:1	10	8	73 ± 0.6
6	130	30:1	6	10	72 ± 0.7
7	140	20:1	10	10	75 ± 1.4
8	140	25:1	6	12	68 ± 1.2
9	140	30:1	8	8	89 ± 1.8
k_1	54	71	63	70	
k_2	78	64	77	66	
k_3	77	74	70	73	
R	24	10	14	7	

CE[a]	130	30:1	8	12	93 ± 0.7

[a]CE, Confirmation experiment.

Table S3

Comparison of catalysts performance in simultaneous esterification and transesterification.

Catalyst	Acidity[a]	T	t	M/O	CA	Conversion[e]	Yield[f]
	[mmol/g]	(°C)	(h)		(wt%)	(%)	(%)
Amberlyst 15	4.71	80[b]	4[b]	9:1[b]	1.1[bd]	71 ±	37 ±
		(130[c])	(12[c])	(30:1[c])	(1.7[cd])	1.8%	0.6%
Nafion NR50	0.80	80[b]	4[b]	9:1[b]	6.5[bd]	79 ±	45 ±
		(130[c])	(12[c])	(30:1[c])	(10.1[cd])	0.9%	1.2%
$Mg_{20}F_{39}$TPA-1.0	1.01	80[b]	4[b]	9:1[b]	5.0[b]	95 ±	93 ±
		(130[c])	(12[c])	(30:1[c])	(8.0[cd])	0.6%	0.7%

T — temperature, t — time, M/O — molar ration of methanol to oil (oleic acid, Jatropha oil), CA — catalyst amount

[a] Quantified by acid-base titration.

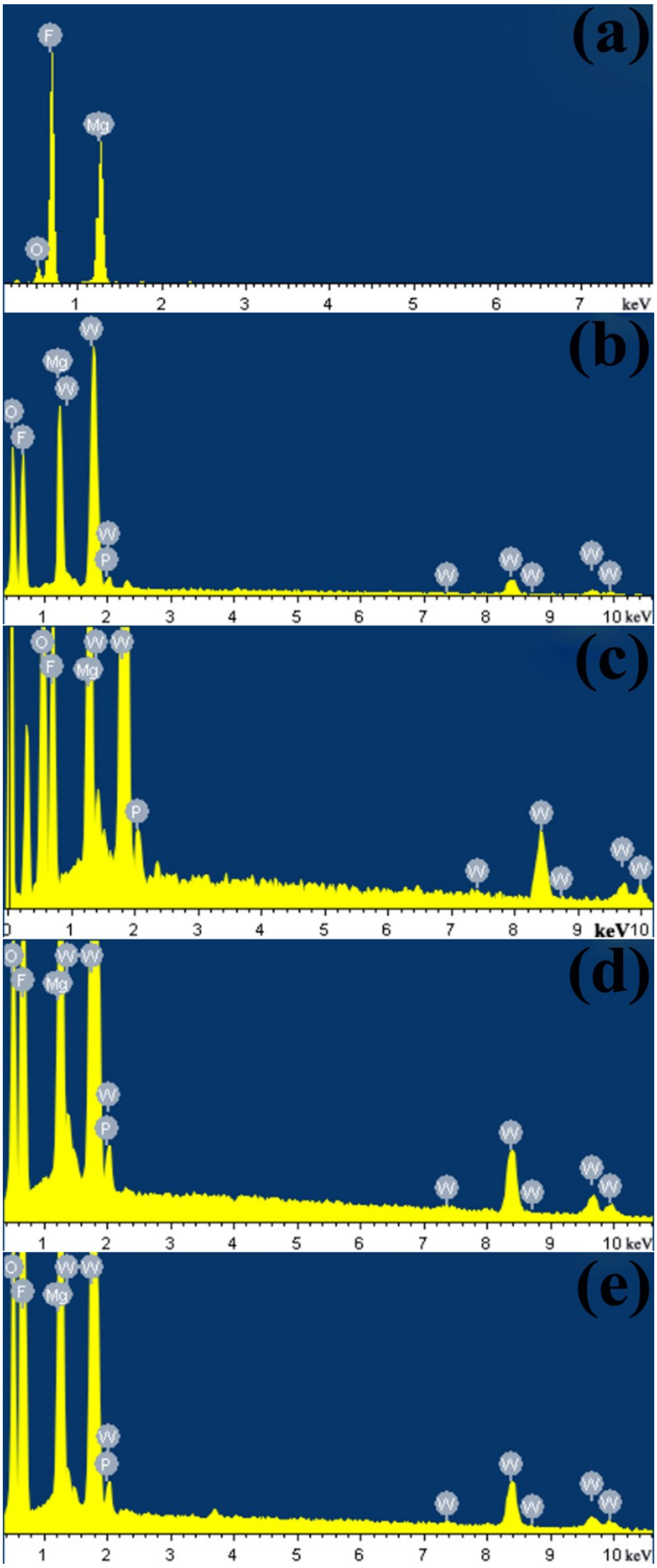
[b] Reaction conditions of oleic acid esterification.

[c] Reaction conditions of simultaneous esterification and transesterification.

[d] Equaled to the acid density of 5 or 8 wt% $Mg_{20}F_{39}$TPA-1.0.

[e] Conversion of oleic acid.

[d] Yield of biodiesel from Jatropha oil.



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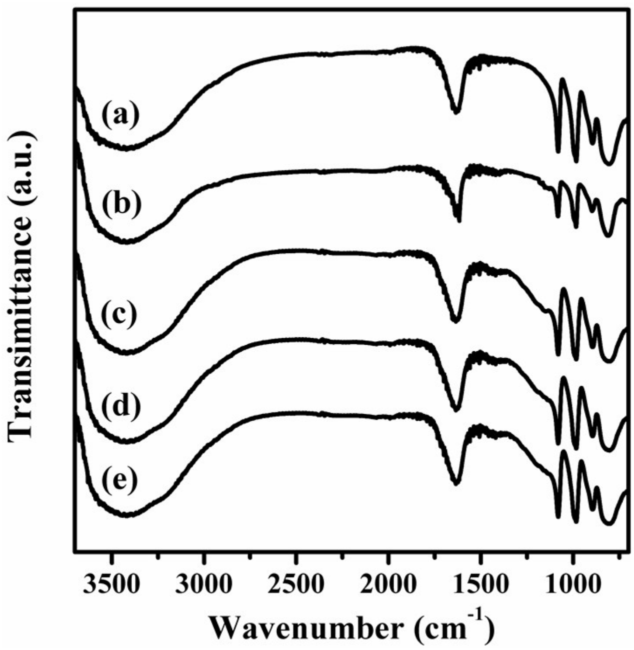

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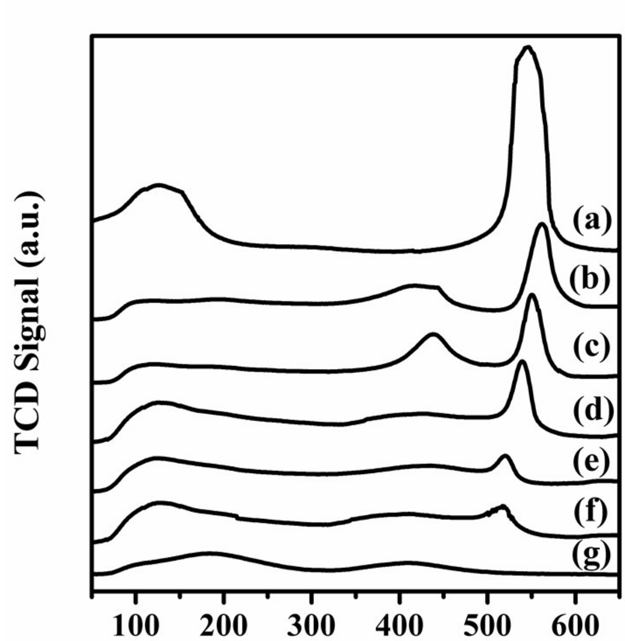

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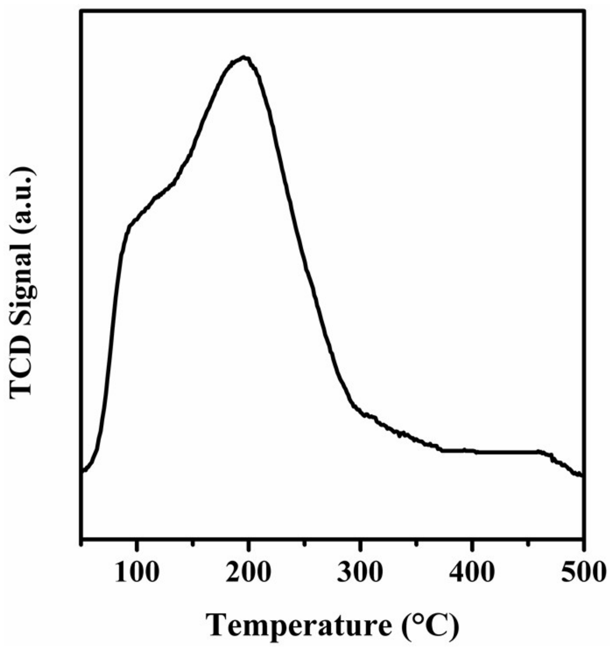

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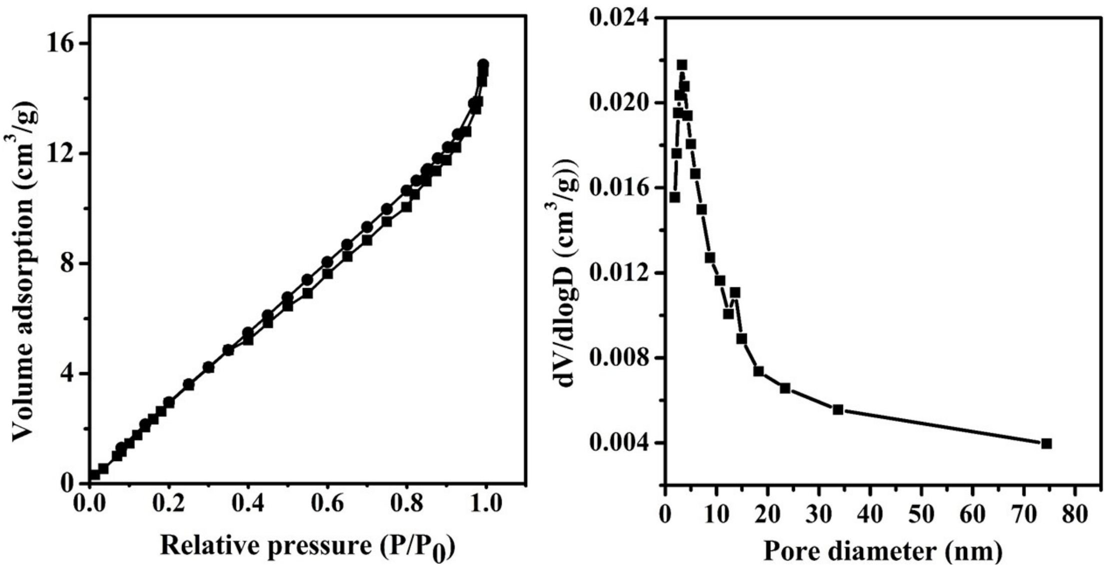

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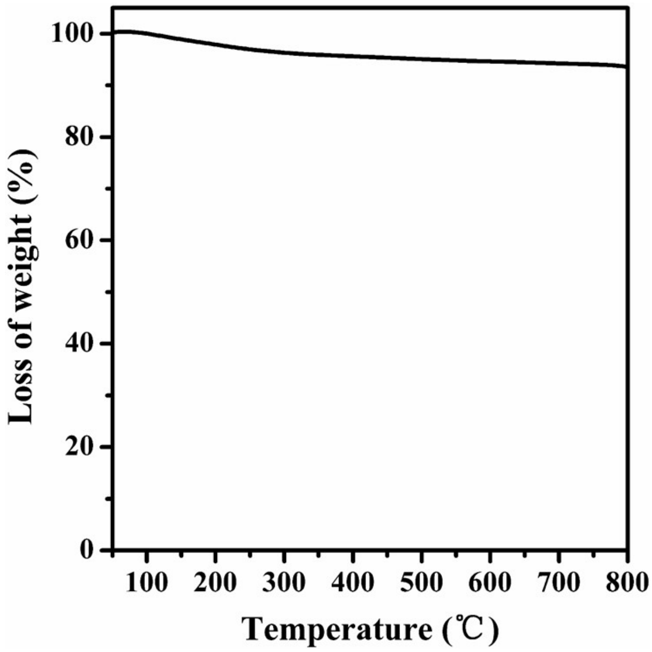

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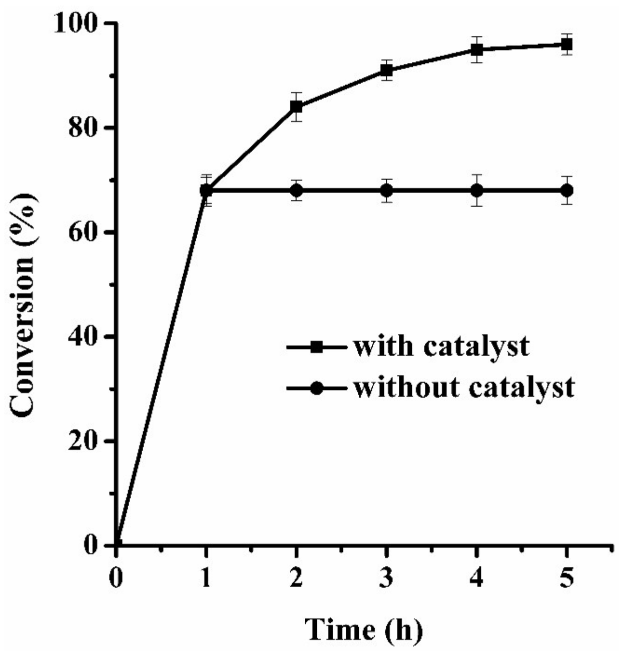

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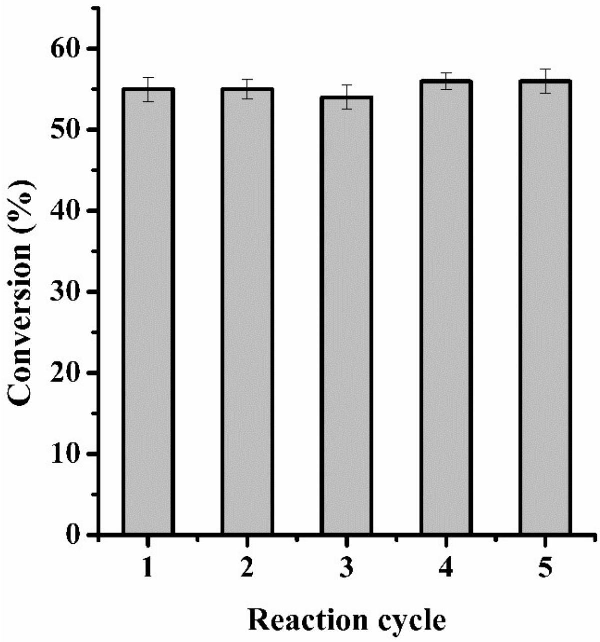

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