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Electronic Supplementary Information

Glycerol acetins: Fuel additive synthesis by acetylation and esterification of glycerol using cesium phosphotungstate catalyst

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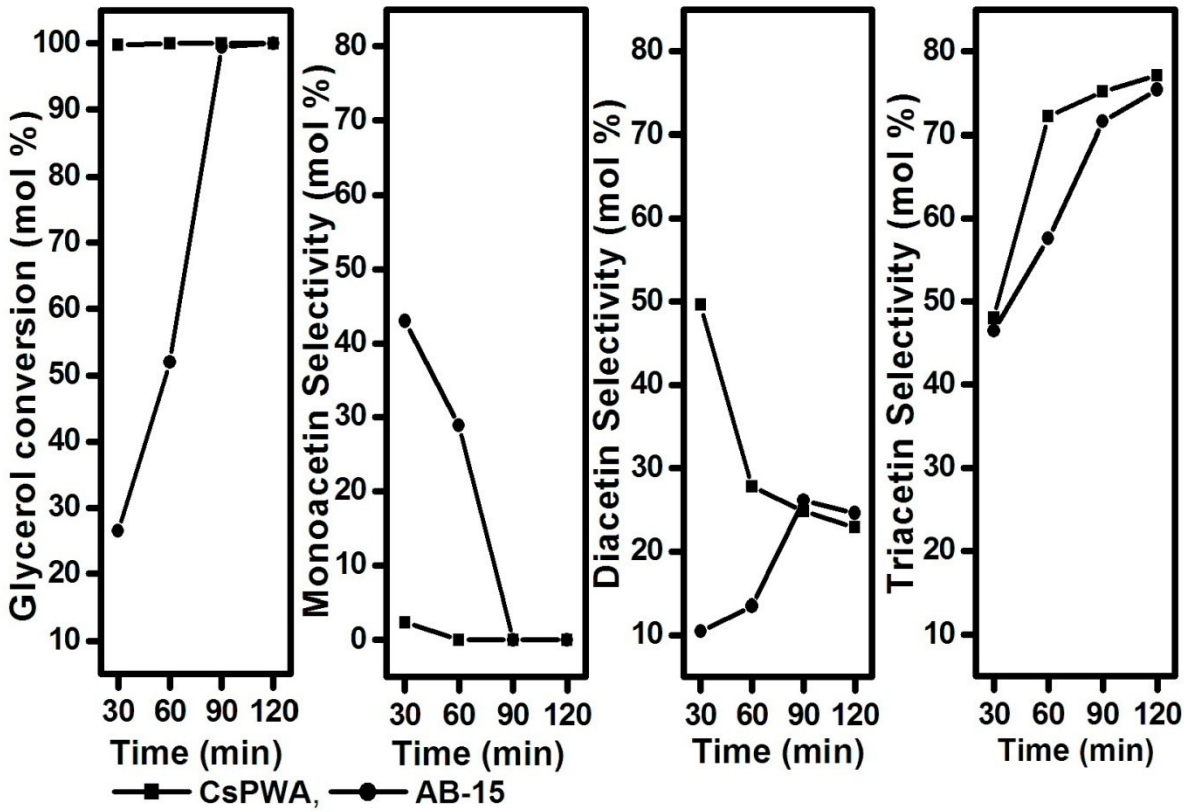
Fig. S1. Comparison of CsPWA and AB-15 catalysts for acetylation of glycerol with acetic anhydride.
Reaction conditions: Glycerol : Acetic anhydride = 1 : 3, Temperature = 30 °C, Time= 120 min, Catalyst weight = 1 wt%.

Fig. S2. FTIR spectra of fresh and recycled catalyst

Table S1. Comparison of CsPWA with the reported catalysts for the esterification of glycerol with acetic acid

Scheme S1. Formation of intermediate acylium ion



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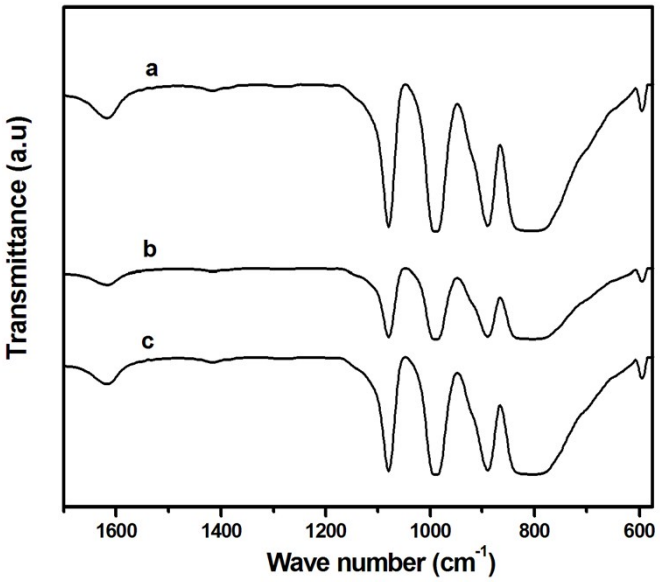

Fig. S2. FTIR spectra of CsPWA: (a) Fresh catalyst (b) after acetylation reaction, (c) after esterification reaction

Table S1. Comparison of CsPWA with the reported catalysts for the esterification of glycerol with acetic acid

Catalyst	Temp (°C)	Mole ratio	Glycerol conversion (mol%)	Acetins Selectivity (mol%)			Reference
				Mono	Di	Tri	
Niobium phosphate	120	1:4	100	38	49	7	10
MoO_3/TiO_2–ZrO_2	120	1:6	100	52	41	7	19
WO_3/TiO_2–ZrO_2	120	1:6	99	53	40	7	19
TiO_2–ZrO_2	120	1:6	91	55	39	6	20
PWA/Silica	120	1:16	82	30	64	5	21
TPA/Cs-ZrO_2	120	1:5	95	45	50	5	22
PWA/Activated carbon	120	1:16	86	25	63	11	23
TPA/Nb_2O_5	120	1:5	98	25	55	20	24
HSiW/ZrO_2	120	1:10	100	7	61	32	25
HPW/ZrO_2	120	1:10	99	7	63	30	25
HPMo/ZrO_2	120	1:10	98	12	62	26	25
AgPW	120	1:10	96	49	46	5	26
CsPWA	85	1:8	98.1	20	53	27	This work

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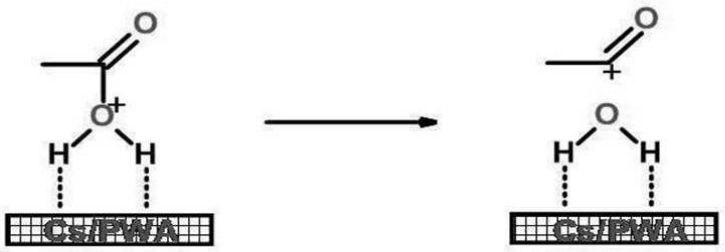
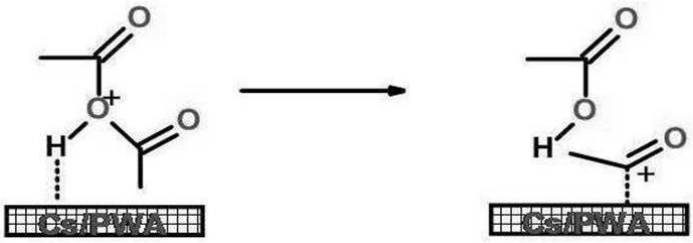


a) Protonated acetic acid on catalyst surface and its dehydration to the acylium ion



b) Protonated acetic anhydride on catalyst surface and its transformation to the acylium ion

The high selectivity towards triacetin using acetic anhydride as acetylating agent compared to acetic acid can be explained on the basis of formation of intermediate acylium ion. Before the formation of acyl cation, the interaction of CsPWA catalyst surface with protonated acetic acid and acetic anhydride takes place. In case of acetic acid, the two hydrogen atoms are interacting with CsPWA structure through hydrogen bonds and the formation of acylium ion is difficult as it is away from the catalyst surface and not well stabilized. However, with acetic anhydride the formation of acylium ion is more assisted on the catalyst surface favoring its formation through covalent bond interaction.