Supporting information

Single-pot template-free synthesis of glycerol-derived C-Si-Zr mesoporous composite catalyst for fuel additives production

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1. Catalysts preparation

1.1 Synthesis of -SO_3H/C-Si and -SO_3H/C-Zr catalyst

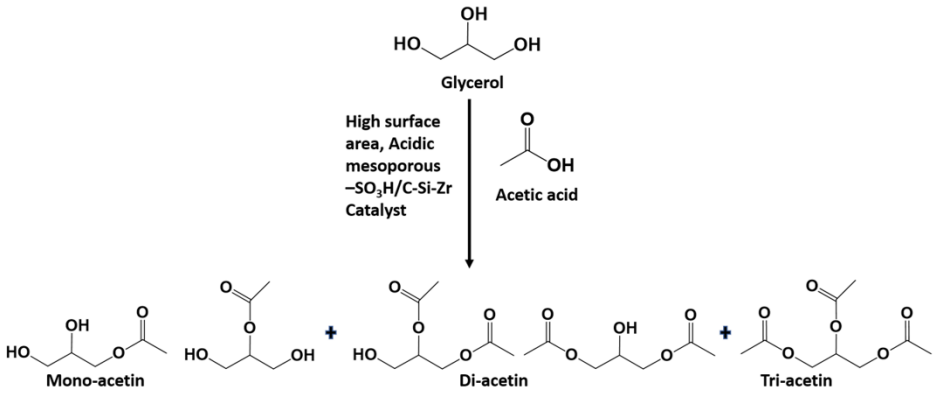
The synthesis procedure of -SO_3H/C-Si catalyst is almost similar to the preparation method of -SO_3H/C catalyst. Here, we only added the TEOS (98% pure, Merk) to the initial glycerol right at the beginning of sulfonation and carbonization step resulted in the involvement of silica in the chemical interaction with the carbon. Similarly, addition of Zirconia (IV) oxynitrate ($ZrO(NO_3)_2.xH_2O$) (99.5% pure, LOBAChemie Pvt. Ltd.) to the initial glycerol followed by simultaneous carbonization and sulfonation, such that chemical interaction occurred between zirconia and carbon.

1.2 Synthesis of -SO_3H/C-Si-Zr catalyst

The overall synthesis procedure consists of three main simple steps; (1) dissolving of zirconia (IV) oxynitrate in water; (2) mixing of glycerol with TEOS; and (3) mixing of the solutions (1) and (2), followed by simultaneous carbonization and sulfonation. For step (1), 20 g of $ZrO(NO_3)_2.xH_2O$ was dissolved into 20 ml of water and the solution was heated at 70-80 ^oC to make the clear solution. For step (2), 60 g of TEOS was mixing slowly into 20 g of glycerol with continuous stirring at the room temperature. Next, in step (3), solution (1) was added slowly into the solution (2) with continuous stirring at room temperature. Further, we followed the synthesis approaches, similar to the simultaneous carbonization and sulfonation step to facilitate the molecular level interaction of these elements with carbon.

2. Catalysts testing

2.1 Glycerol acetylation



Scheme S1. Glycerol acetylation reaction over -SO_3H/C-Si-Zr composite catalyst.

In a typical glycerol acetylation reaction, A batch reactor equipped with magnetic stirrer and condenser which charged with feed molar ratio (glycerol: acetic acid) 1:9 and 100 mg of the catalyst. The reactor was heated to desired reaction temperature (100 to 180 ^{o}C) for 5 h under continues stirring of mixture at 320 RPM and reflux condition. At the end of the reaction, the mixture was cooled up to room temperature. The reaction product and catalyst were separated by filtration and the catalyst was washed with distilled water and calcined at 300 ^{o}C for regeneration of catalyst for further uses. The reaction product was analysed by using Agilent GC (7890B) equipped with the HP-1 column (30m X 0.25mm) and Agilent MS (5977A) detector.

3. Supporting results

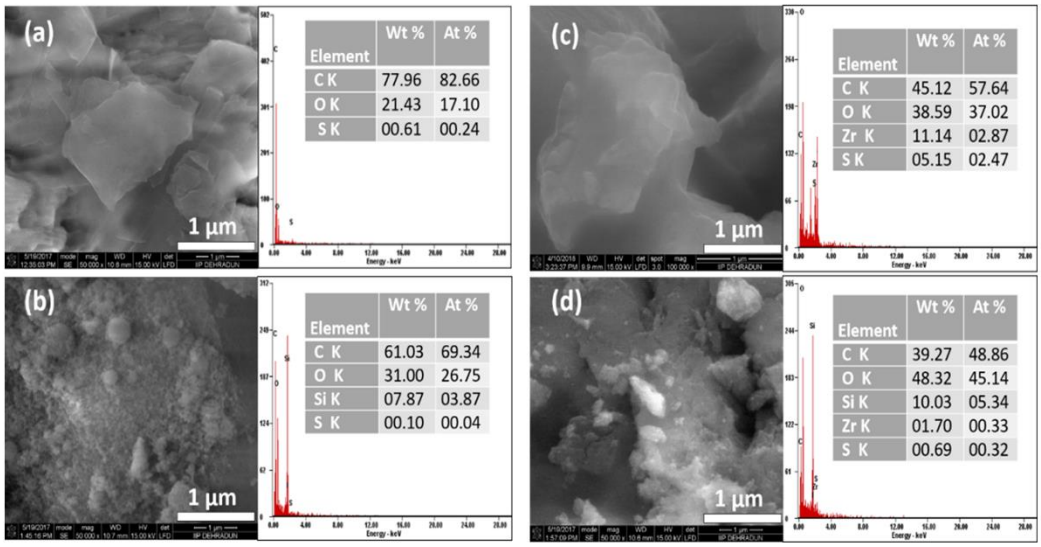


Fig. S1 SEM images & EDX of samples: (a) -SO_3H/C, (b) -SO_3H/C-Si, (c) -SO_3H/C-Zr and (d) -SO_3H/C-Si-Zr

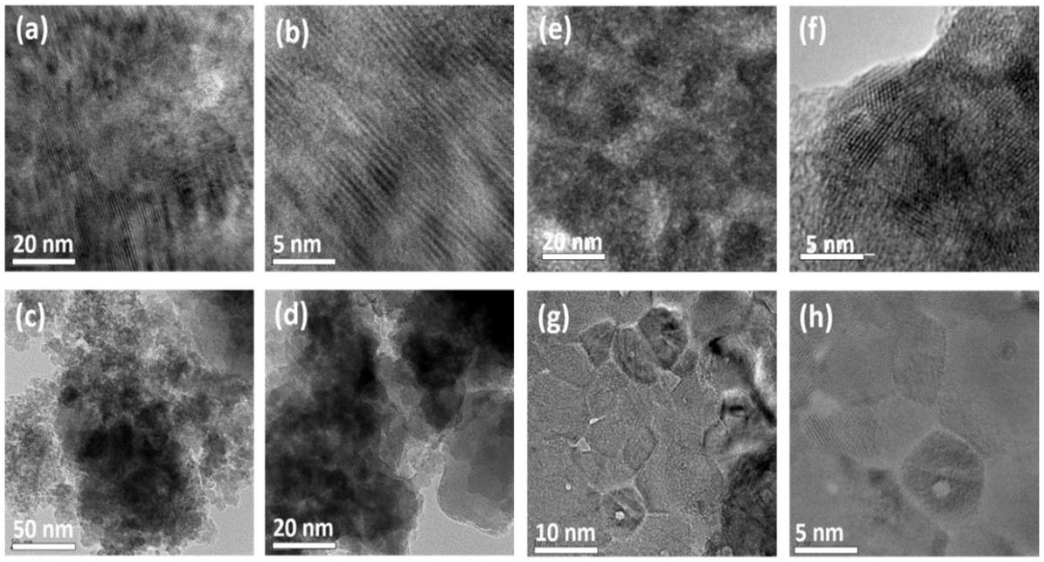


Fig. S2 TEM images of samples: (a) (b) -SO_3H/C, (c) (d) -SO_3H/C-Si, (e) (f) -SO_3H/C-Zr and (g) (h) -SO_3H/C-Si-Zr

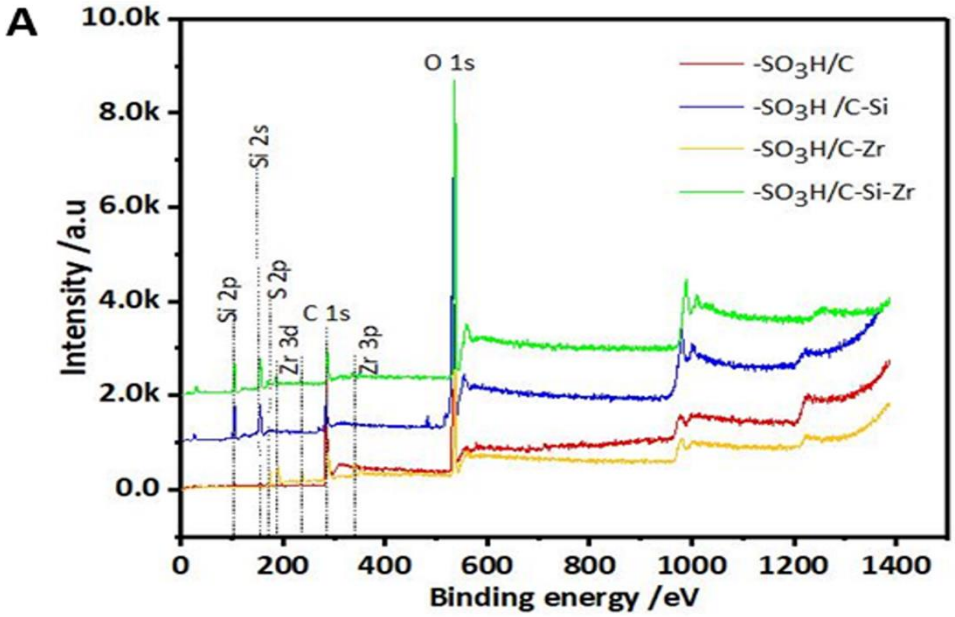


Fig. S3A XPS survey spectra of (a) -SO_3H/C, (b) -SO_3H/C-Si, (c) -SO_3H/C-Zr and (d) -SO_3H/C-Si-Zr

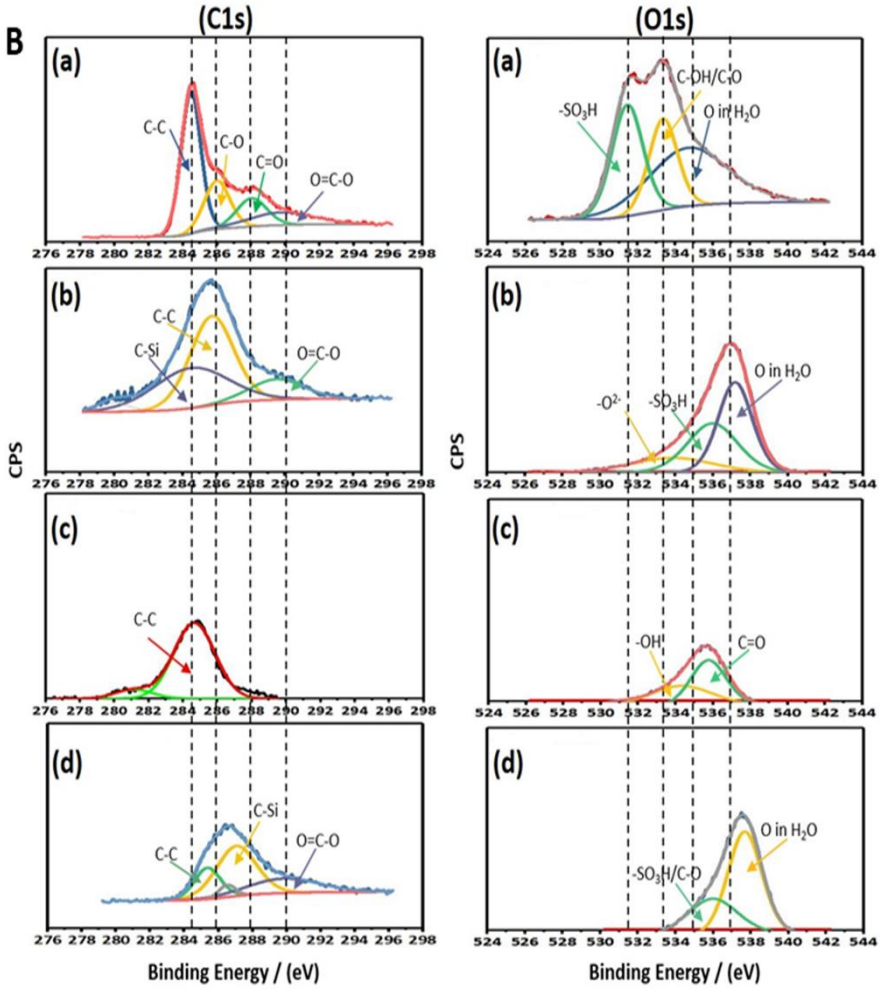


Fig. S3B XPS C1s and O1s spectra of samples: a) -SO_3H/C, (b) -SO_3H/C-Si, (c) -SO_3H/C-Zr and (d) -SO_3H/C-Si-Zr

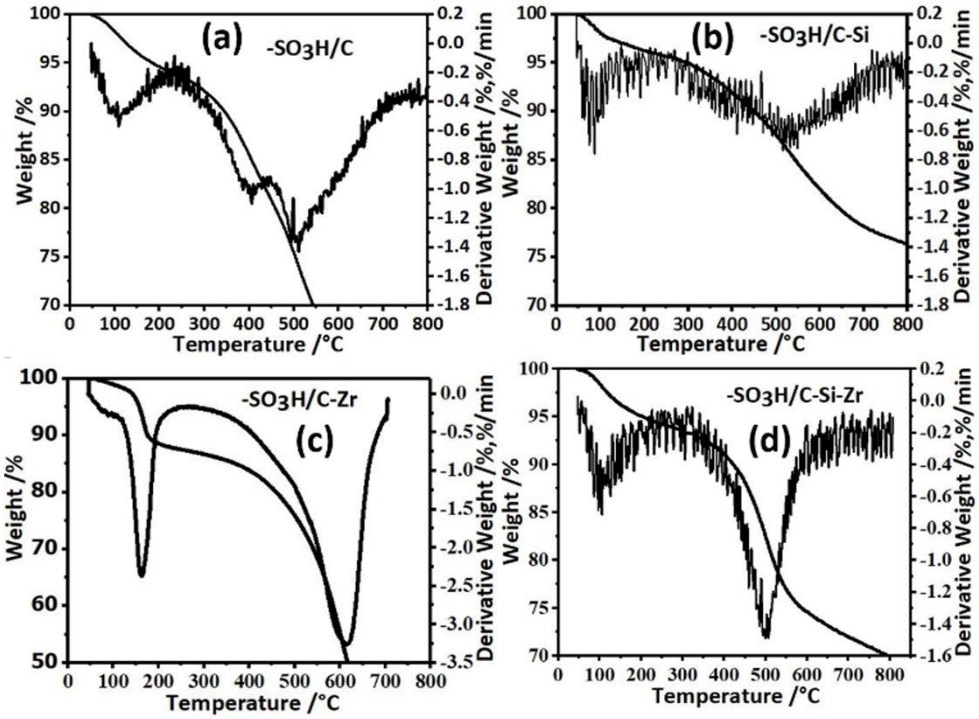


Fig. S4 DT-TGA thermogram of the samples: (a) -SO_3H/C, (b) -SO_3H/C-Si, (c) -SO_3H/C-Zr and (d) -SO_3H/C-Si-Zr

4. Supporting Tables

Table S1 Performance comparison of the present catalysts with reported for glycerol acetylation reaction.

S. No.	Catalyst	Temp (^{O}C)	RT (h)	Conv. (%)	Selectivity (%)			Ref.
					MA.	DA.	TA.	
1	-SO_3H/C-Si-Zr*	150	5	96.7	2.3	-	97.7	
2	TPA3/MCM-41	100	6	87	25	60	15	1
3	TPA_3/ZrO_2	80	8	80	60	36	4	
4	Amberlyst-15	80	8	100	21.1	63.8	15.1	2
7	$PrSO_3H$-SBA-15	80	8	100	15.8	64.6	19.6	
17	Amberlyst-36	105	10	95.6	70.3	4.5	–	3
19	Dowex-2	105	10	95.2	80.8	5.1	–	
22	Amberlyst-15(dried)	110	5	97.1	7.8	47.7	44.5	4
25	SBAH-15(15)	110	3	100	14	67	19	5
27	PW2_AC	120	3	86	25	63	11	6
28	AC-SA5	120	3	91	38	28	34	7
29	PMo3_NaUSY	110	3	68	37	59	2	8
30	Amberlyst-15	110	0.5	97	31	54	13	9
34	Ar-SBA-15	125	4	96	15	47	38	10
35	F-SBA-15	125	4	90	14	50	36	
36	Pr-SBA-15	125	4	80	17	44	39	

*Present studies catalyst; Temp (temperature); RT (reaction temperature); Conv.(conversion); MA. (Mono-acetin); DA. (Di-acetin); TA. (Tri-acetin); (Ref.(reference)

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