Supplementary information

For

A facile approach for the synthesis of solketal, a fuel additive from biowaste glycerol using transition metal-based solid acid catalyst

Sunita Maurya [a], Yogesh Chandra Sharma [a] *

[a] Department of Chemistry, Indian Institute of Technology, IIT-BHU, Varanasi-221005.

E-mail: ysharma.apc@itbhu.ac.in

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1. Carbon XPS spectra of SZZ catalyst

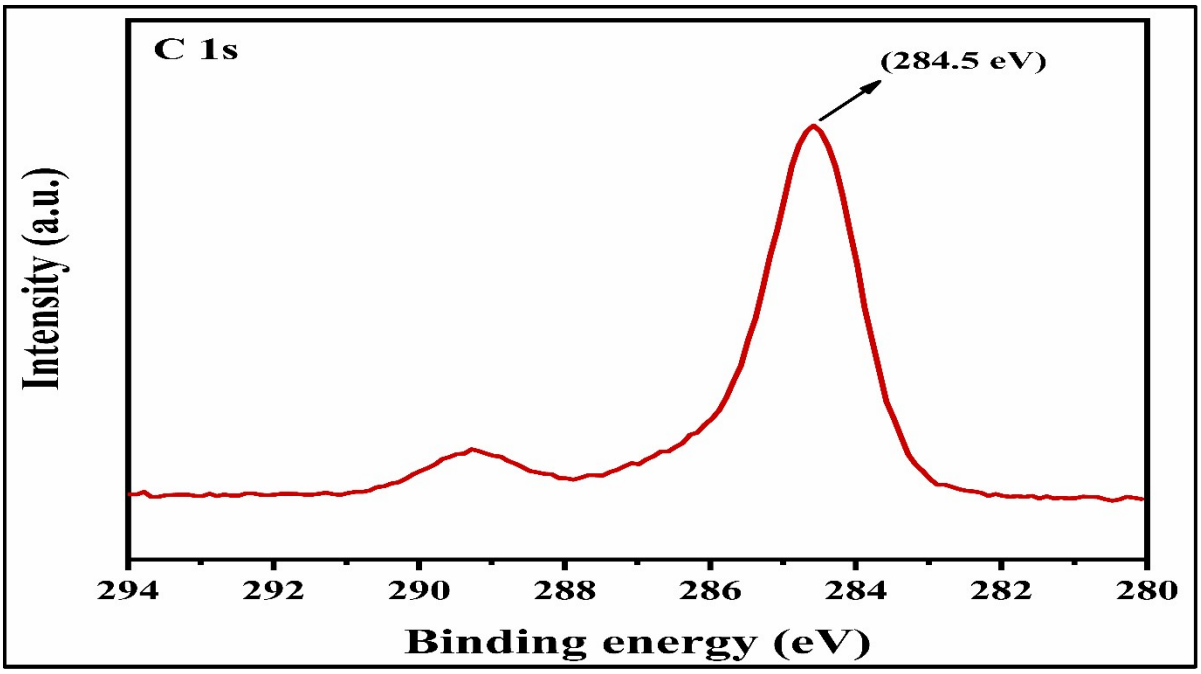

Fig. S1. C 1s spectra of SZZ catalyst

2. GC-MS spectra of synthesized product

The synthesized product's conversion, yield, and selectivity were confirmed using Agilent Technologies 7890B GC coupled with an MS of 19091P-MS4 system associated with an HP-5 capillary column with flame ionization detector (FID). Initially, the oven temperature was set to 80 ^{o}C, then ramped up at a rate of 20 ^{o}C/min to 220 ^{o}C. The injector and detector temperatures were optimized and maintained at 250 ^{o}C and 300 ^{o}C, respectively. 1,4-dioxane served as an internal standard in solketal synthesis for GC analysis.

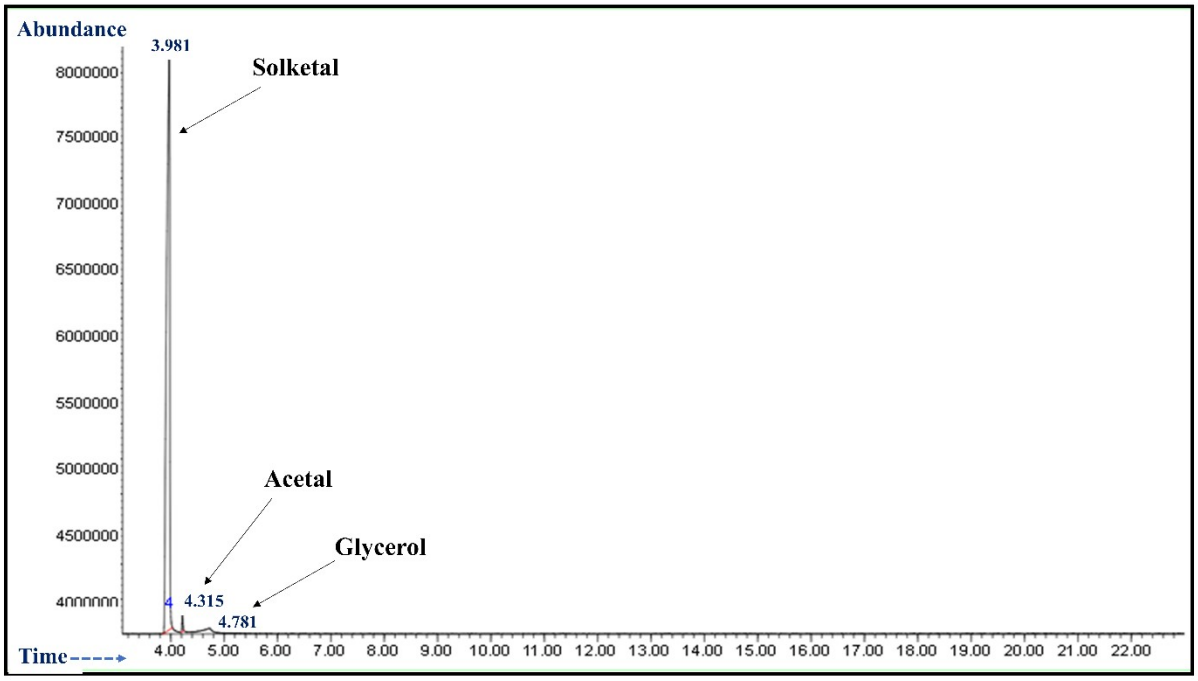

Fig. S2. GCMS spectra of synthesized product

3. ^{1}H and ^{13}C NMR spectra of solketal

The NMR spectroscopy characterized the acetalization product of glycerol. The chemical identity of the synthesized product was validated through NMR analysis, and the obtained characteristic peaks were compared to the corresponding peak with the reactant and product. **Fig. S3 (a)** displays the ^{1}H and **Fig. S3 (b)** ^{13}C NMR spectra of the solketal. In ^{1}H NMR spectra (**Fig. S3 (a)**, two singlet characteristic peaks of six methyl hydrogen were observed at chemical shift values of 1.26 and 1.30 ppm, while a broad singlet peak at 2.0 ppm is attributed to the hydroxyl (-OH) moiety. The multiple peaks of the chemical shift value of 3.36 to 4.80 ppm represent the -CH and -CH_2 groups' integration of the five-membered solketal ring**. Fig. S3 (b)** represents the ^{13}C NMR spectra. The characteristics peak was noticed at 25.77 and 27.11 ppm, which were attributed to the -CH_3 carbon within the cyclic product. The chemical shift value obtained at 76.52 and 76.78 ppm assigned for the -CH_2-CH-CH_2- carbon, while two additional peaks were noted at 66.58 ppm and 62.67 ppm assigned to the two -CH_2 carbon of the cyclic ring. The highly deshielded peak that emerged at 108.56 ppm indicates the ketal carbon that corroborates the formation of solketal as a product. Additionally, extra multiplet peaks that appeared at 39.65 ppm are associated with the DMSO-d6 solvent.[53] The ^{1}H and ^{13}C NMR of synthesized solketal were acquired using a BRUKER BioSpin 500, Advance III HD 500 MHz spectrometer.

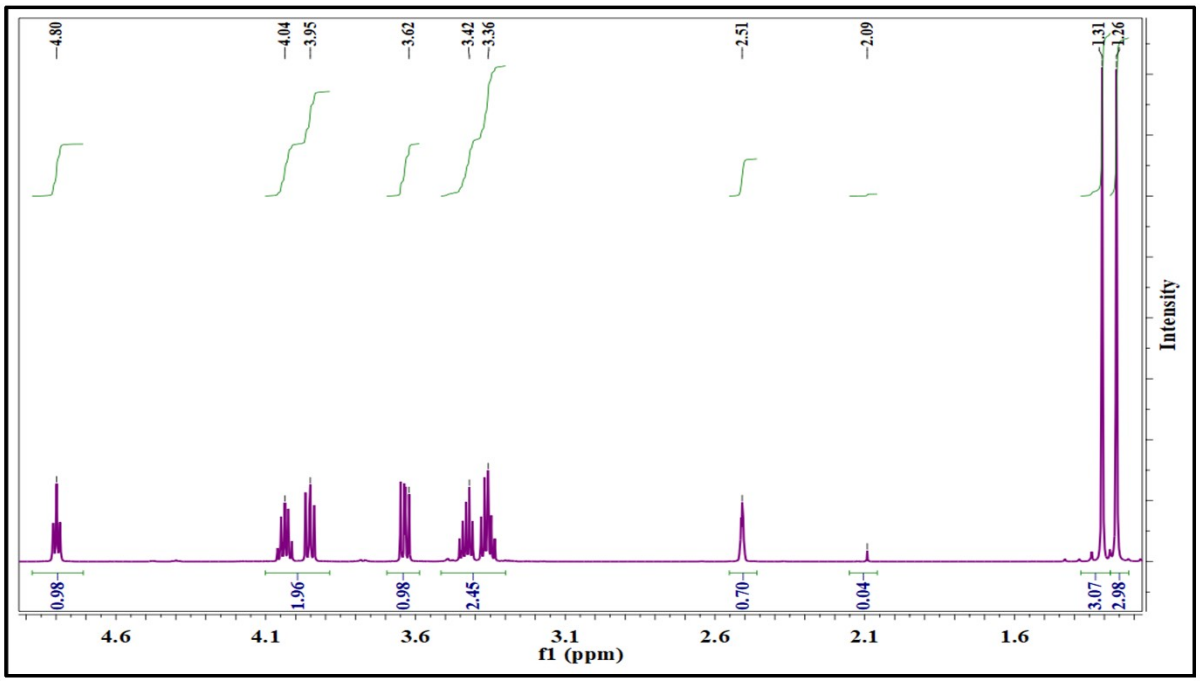

Fig. S3 (a). ^{1}H-NMR spectra of the synthesized product

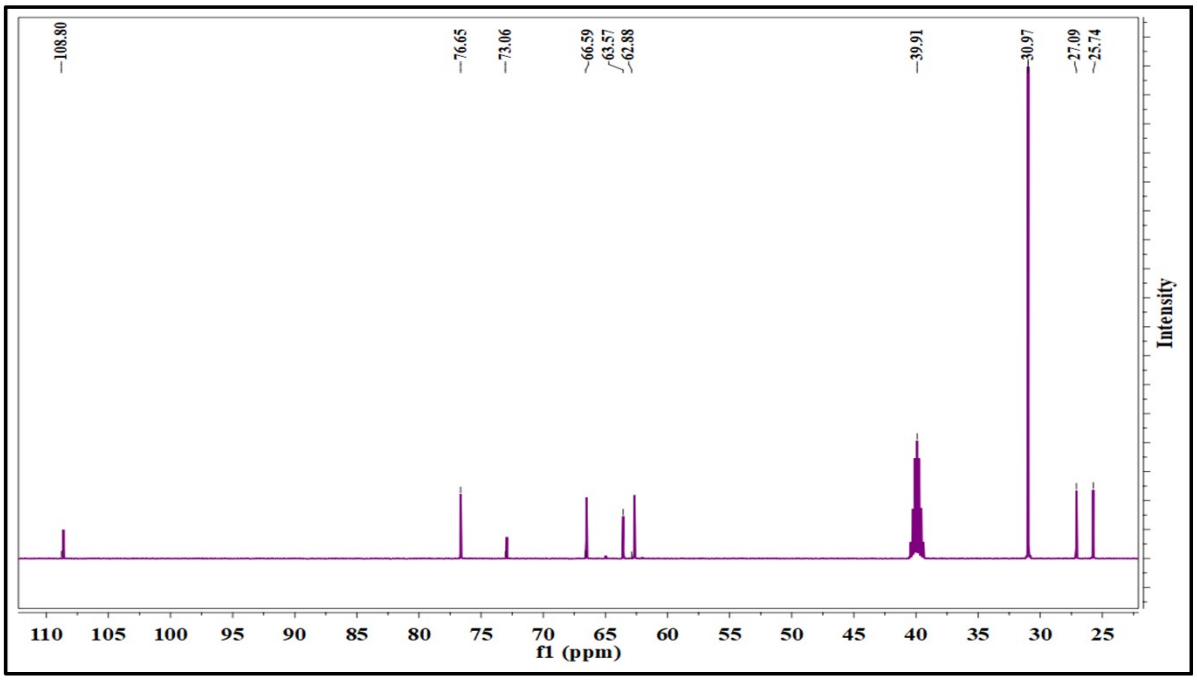

Fig. S3 (b). ^{13} C-NMR spectra of the synthesized product

4. FT-IR spectra of glycerol and synthesized product

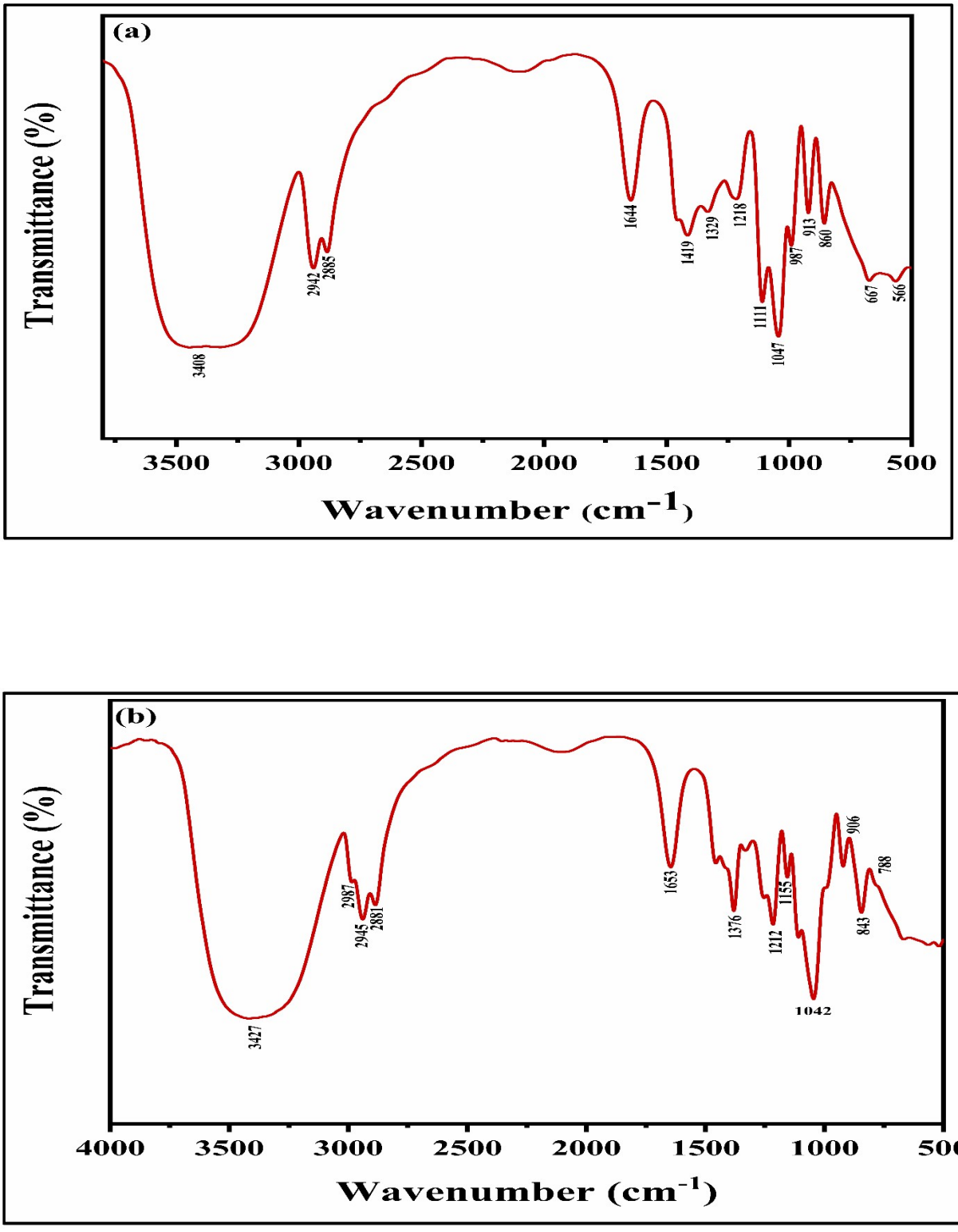

Fig. S4. (a) FT-IR spectra of glycerol, (b) FT-IR spectra of synthesized product

5. Reusability of SZZ catalyst

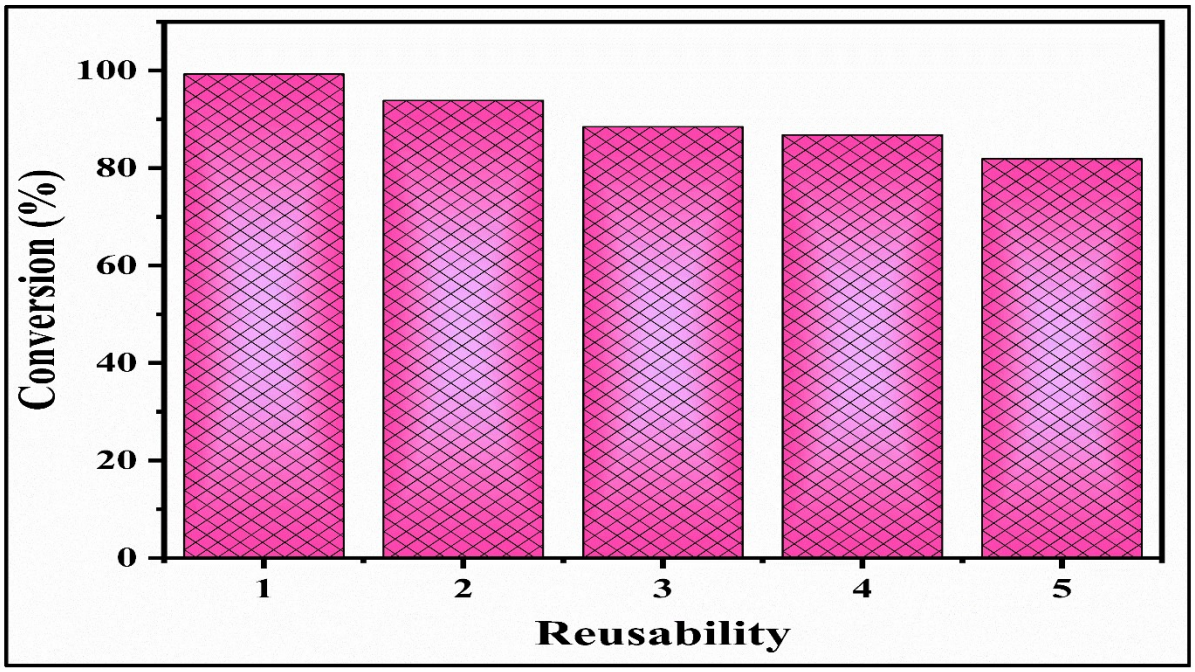

Fig. S5. Reusability of synthesized SZZ catalyst in solketal synthesis

6. Catalyst leaching test (Hot filtration method)

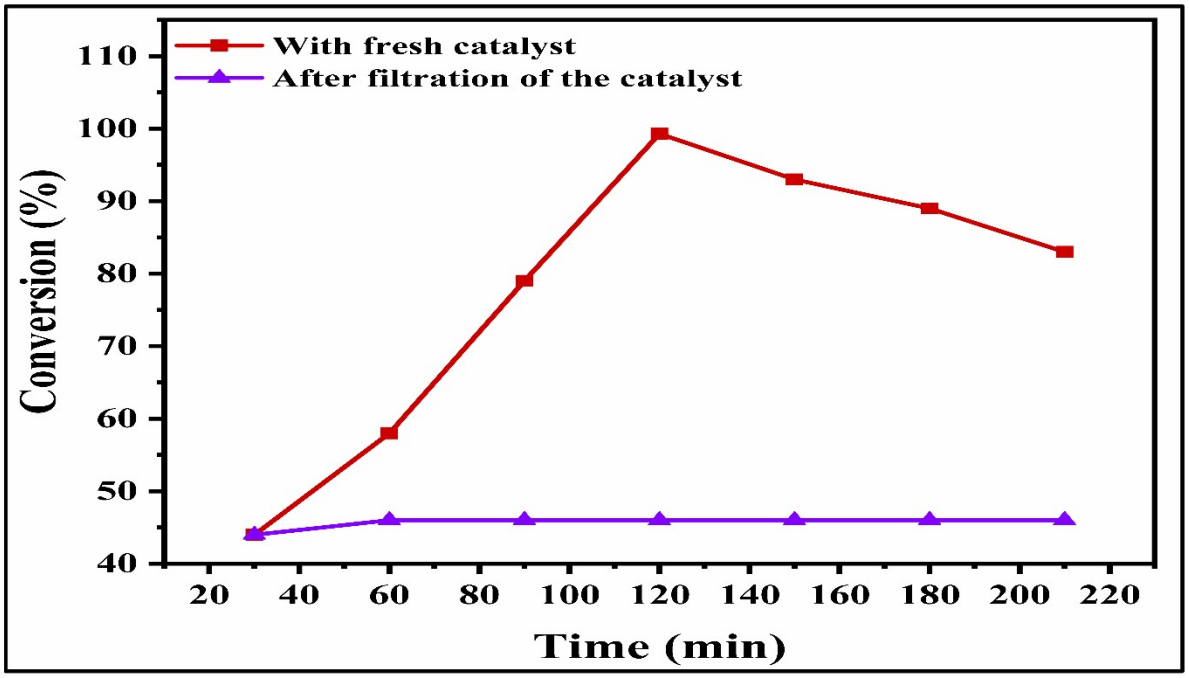

Fig. S6. Heterogeneity of SZZ catalyst

7. XRD graph of reused SZZ catalyst

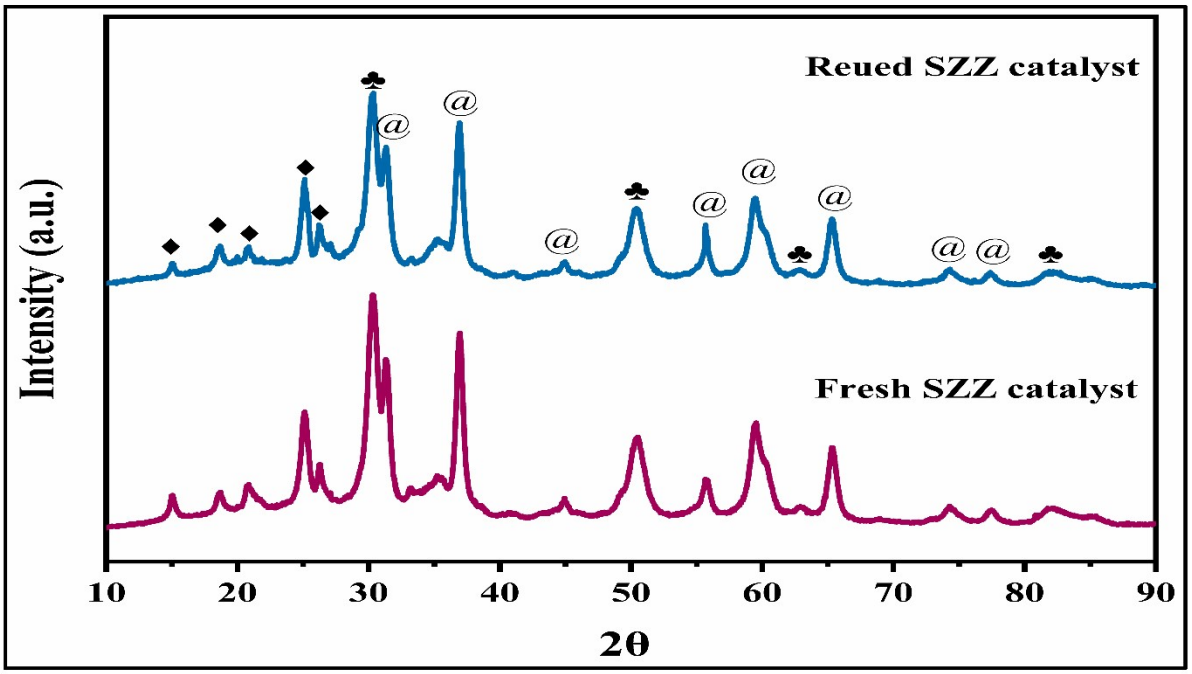

Fig. S7. XRD image of reused SZZ catalyst

8. FTIR spectra of reused SZZ catalyst

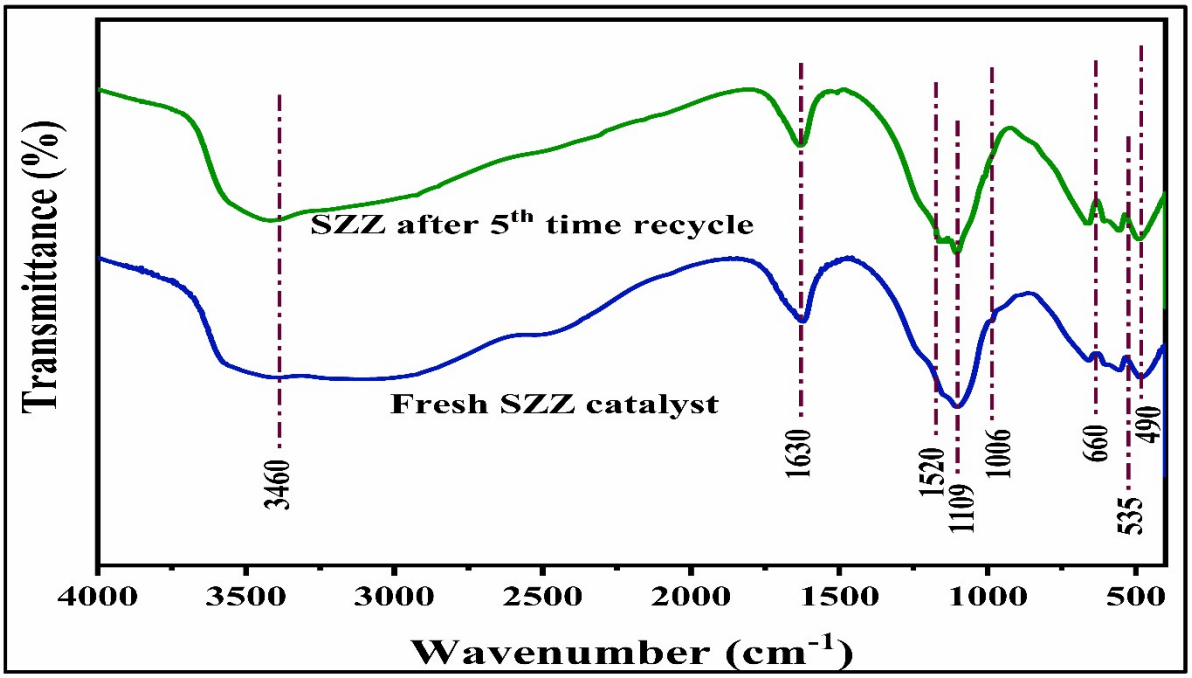

Fig. S8. FTIR spectra of reused catalyst

9. SEM image of reused SZZ catalyst

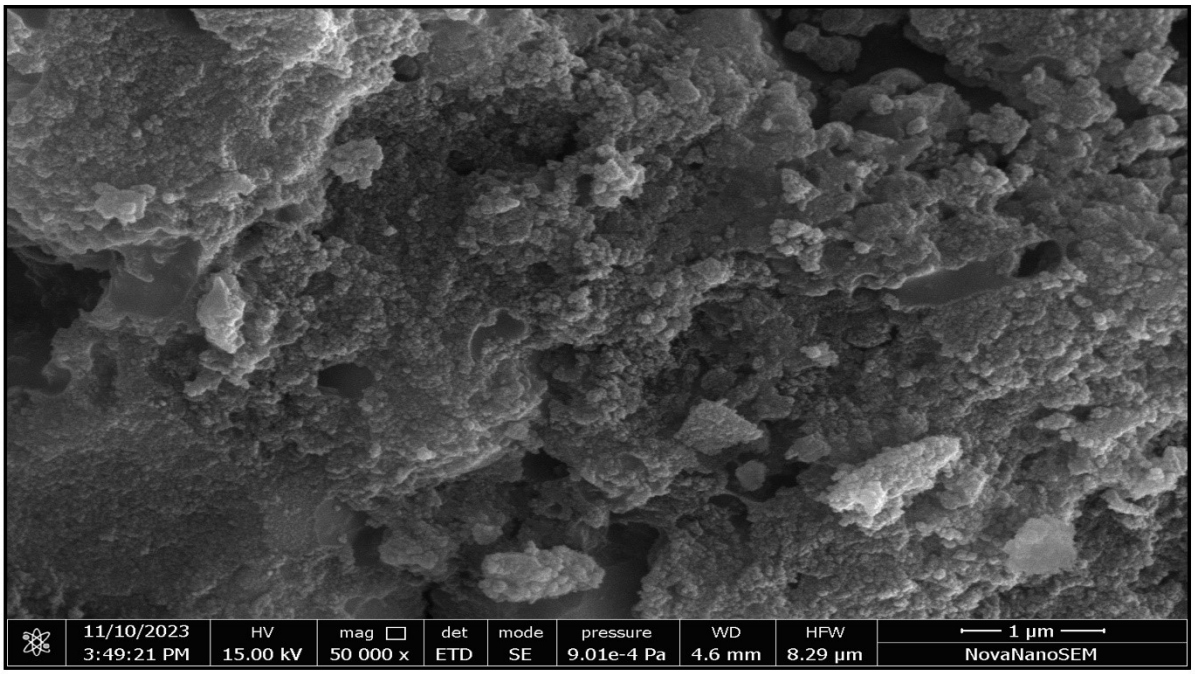

Fig. S9. SEM image of reused SZZ catalyst

10. Influence of variable parameters on acetalization using SZT catalyst

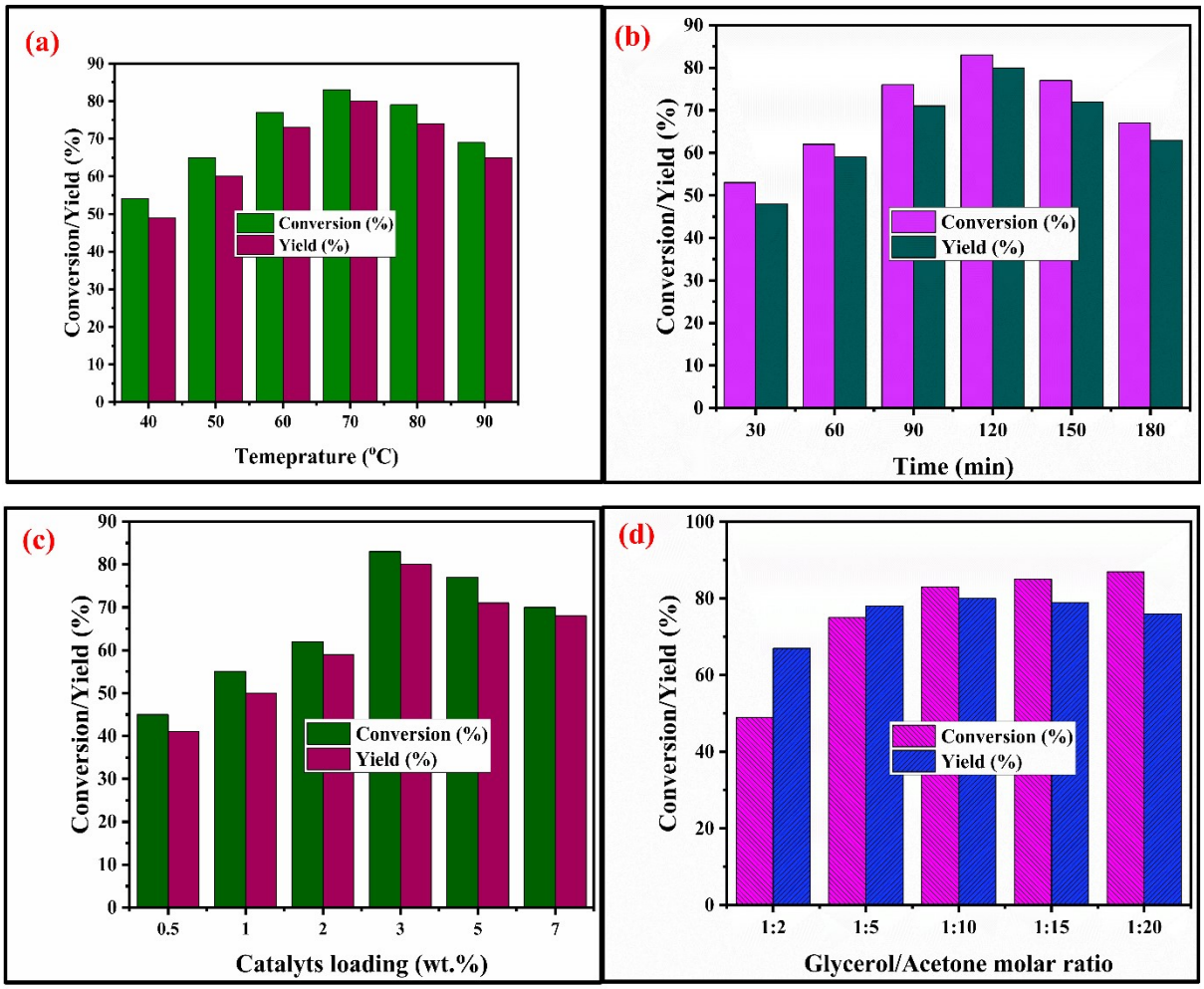

Fig. S10. Optimization of (a) reaction temperature (glycerol to acetone 1:10 molar ratio, catalyst wt. % = 3, time=120 min.) (b) reaction time (glycerol to acetone=1:10 molar ratio, catalyst wt. % = 3, reaction temperature = 70 °C). (c) catalyst weight percentage (glycerol to acetone 1:10 molar ratio, time=120 min. reaction temperature = 70 °C) (d) Glycerol to acetone molar ratio (reaction temperature = 70 °C, catalyst wt. % = 3, time=120 min.)