

1 Supporting Information

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3 **Synergistically Stabilized SAPO-37-Tetragonal Zirconia**
4 **Composites: A Promising Catalyst for Ethyl Levulinate Synthesis**

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15 **Experimental**

16 **Materials and Synthesis protocol**

17 The chemicals used were: ortho-phosphoric acid (H_3PO_4 85%) purchased from Merck, pseudo
18 boehmite (Al_2O_3 75% grade PSB-M) from BeeChems, fumed silica (Aerosil 200) from Aldrich,
19 tetra propyl ammonium hydroxide (TPAOH (40% aqueous solution), tetra methyl ammonium
20 hydroxide (TMAOH, 25% aqueous solution) from TriTech, Isopropanol and zirconium
21 isopropoxide –isopropanol complex from Aldrich.

22 The SAPO-37 samples were prepared following a previously reported procedure. The initial
23 molar gel composition was $(\text{TPA})_2\text{O} : 0.025(\text{TMA})_2\text{O} : \text{Al}_2\text{O}_3 : \text{P}_2\text{O}_5 : 0.43\text{SiO}_2 : 50.0\text{H}_2\text{O}$. A
24 homogeneous solution of pseudoboehmite and dilute orthophosphoric acid was prepared
25 (Solution A). Solution B was prepared by mixing fumed silica with a mixture of TPAOH and
26 TMAOH under continuous stirring. Solution B was then added to Solution A with vigorous
27 stirring to form the final gel, which was transferred into a stainless-steel autoclave with Teflon

1 liners and heated at 200 °C for 20 hours. The final product was separated by centrifugation,
2 washed, and dried at 60 °C.

3 To incorporate zirconia onto SAPO-37, a solution of zirconium isopropoxide in hot isopropyl
4 alcohol (IPA) was prepared, followed by incipient wet impregnation (resulting in SAPO-37 Z
5 as). Approximately 7 wt% of zirconium was loaded, and the sample was subsequently reduced at
6 550 °C using a temperature-programmed method. The final sample was labeled SAPO-
7 37ZR. The SAPO-37 reduced without zirconia is labeled as SAPO-37R. The thermal stability of
8 the catalyst was studied by reducing it at a higher temperature of 650 °C.

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10 **Characterization Methods**

11 Fourier transform infrared (FTIR) spectra of the zirconium-embedded SAPO-37 samples were
12 recorded using a Jasco FT-IR spectrometer in ATR mode, scanning in the mid-IR region (4000–
13 400 cm⁻¹). Powder X-ray diffraction (XRD) analysis was carried out using a PANalytical X'Pert³
14 powder X-ray diffractometer with Cu K α radiation ($\lambda = 1.5405 \text{ \AA}$). The samples were scanned
15 over a 2θ range of 5°–80°. The presence of oxygen vacancies was studied using electron spin
16 resonance spectroscopy (ESR) recorded on a JES-FA200 ESR Spectrometer with X and Q bands
17 (JEOL, Japan) at a standard frequency of 8.75–9.65 GHz. Temperature-programmed oxidation
18 was carried out using a BELCAT-M instrument (Japan). Surface elemental analysis was
19 performed using X-ray photoelectron spectroscopy (XPS) on a photoelectron spectrometer
20 (Pervac, Poland) equipped with a VG Scienta R3000HP analyzer and an MX650
21 monochromator. The XPS spectra were deconvoluted using the Shirley method for baseline
22 correction. The organic content of the zirconium-embedded SAPO-37 was analyzed by
23 thermogravimetric analysis (TGA) using a PerkinElmer STA 6000 simultaneous thermal
24 analyzer. TGA was performed in a nitrogen atmosphere over a temperature range of 35–900 °C
25 with a heating rate of 10 °C/min. The morphologies of the synthesized materials were examined
26 using field emission scanning electron microscopy (FESEM, Jeol IT 800) operated at 10.00 kV.
27 Transmission electron microscopy (TEM) images were obtained using a JEOL JEM 2100
28 microscope. Solid-state NMR spectra were recorded on a Bruker Avance III HD at 9.4 T with
29 zirconia rotors spinning at 7 kHz. The acidic properties of the catalysts were analyzed by NH₃-
30 temperature programmed desorption (NH₃-TPD) using a BELCAT-M instrument (Japan).

1 Samples were preheated at 400 °C for 30 minutes in a quartz reactor, followed by ammonia
2 adsorption at 50 °C for 30 minutes. Physisorbed ammonia was removed by desorption at 50 °C,
3 and measurements were recorded from 50 °C to 600 °C at a heating rate of 10 °C/min.

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5 **Catalytic studies**

6 The synthesized t-ZrO₂-embedded SAPO-37 samples were investigated for their catalytic
7 activity in the synthesis of ethyl levulinate from furfuryl alcohol (FA). In a typical reaction, 0.05
8 g of the catalyst was mixed with 2 mmol of FA and 5 ml of ethanol in a 100 ml stainless steel
9 autoclave. The reaction parameters were optimized by varying the temperature (120–190 °C), the
10 reactant concentration (2 mmol–8 mmol), and the alcohol chain length. After the reaction, the
11 catalyst was separated from the products by centrifugation. The products were analyzed using
12 gas chromatography (Mayura Analytical, model 1100) equipped with an HP-5 capillary column
13 (30 m length × 0.25 mm inner diameter, 0.25 μm film thickness) and a flame ionization detector.
14 The products were confirmed by comparison with authentic samples. The temperature program
15 involved heating from 70 °C to 240 °C at a rate of 10 °C/min.

16 The reusability of the catalyst was tested by separating it from the reaction mixture, followed by
17 drying at 70 °C. The regeneration of the catalyst was carried out by reducing the used catalyst at
18 550 °C for 3 hours.

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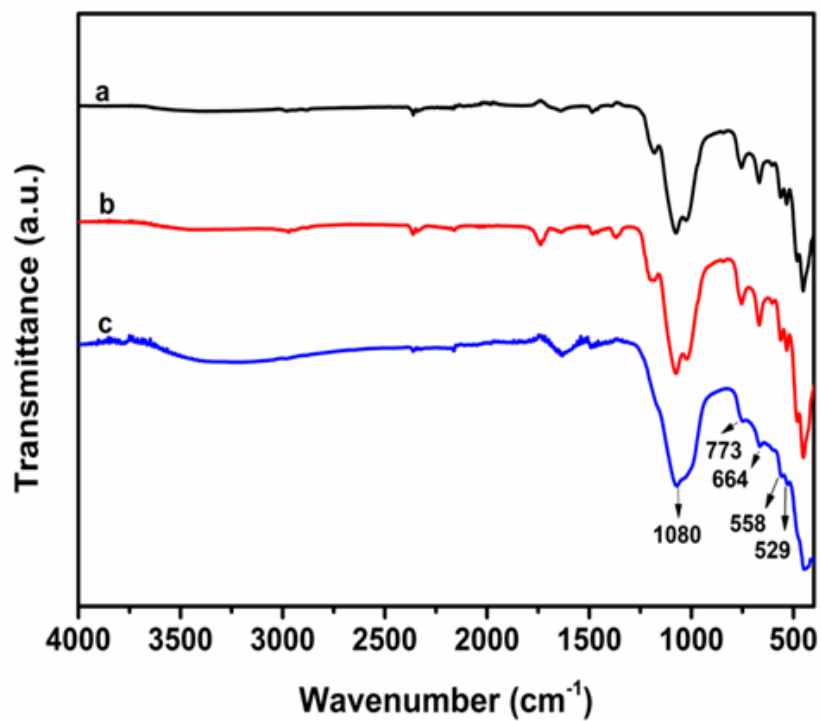


Fig. S1 FTIR spectra of a) SAPO-37as, b) SAP-37Z, and c) SAP-37ZR.

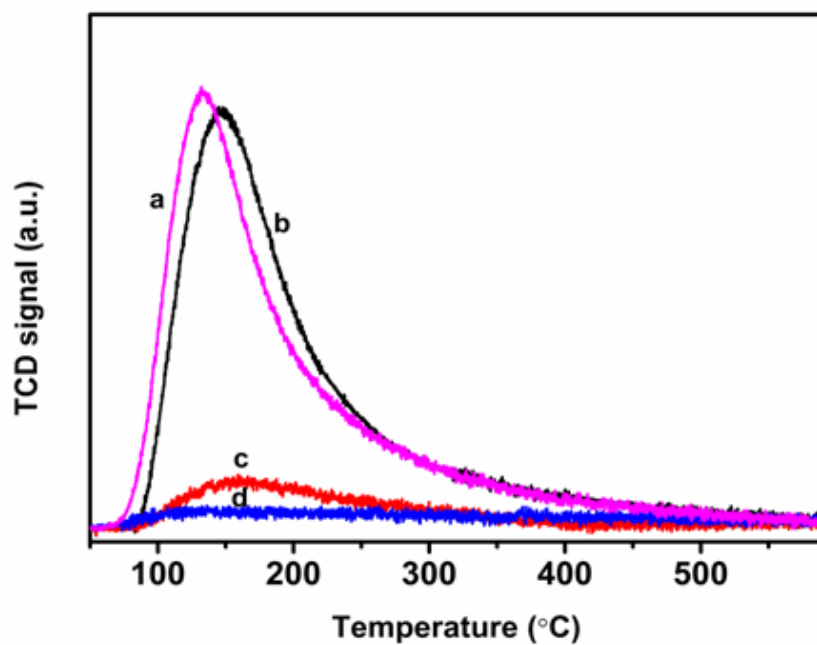


Fig. S2 Temperature programmed oxidation profile of a) SAP-37 R, b) SAP-37ZR, c) *t*-ZrO₂, and d) monoclinic-ZrO₂.

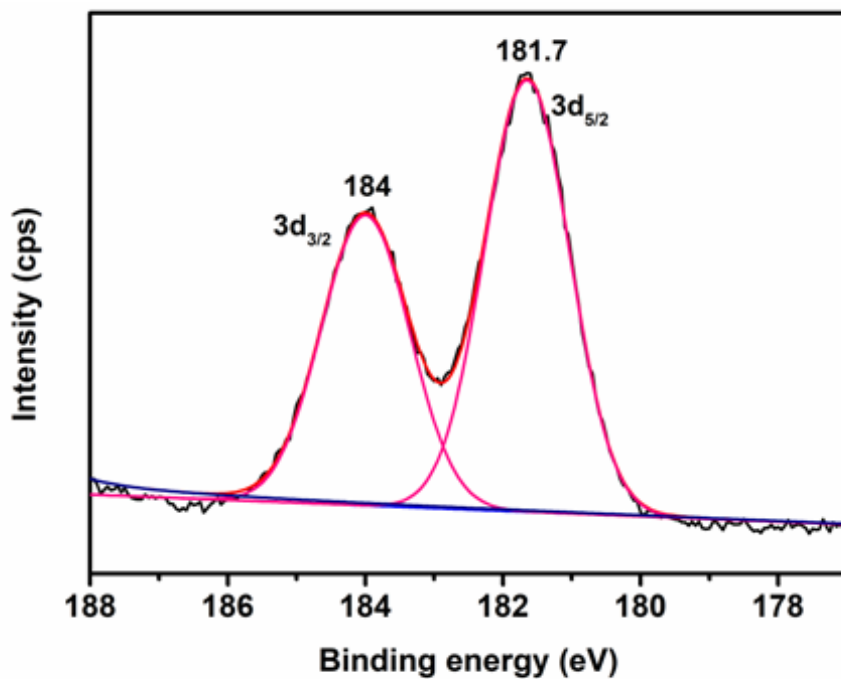


Fig. S3 Zr-3d XPS profile of SAP-37ZR samples.

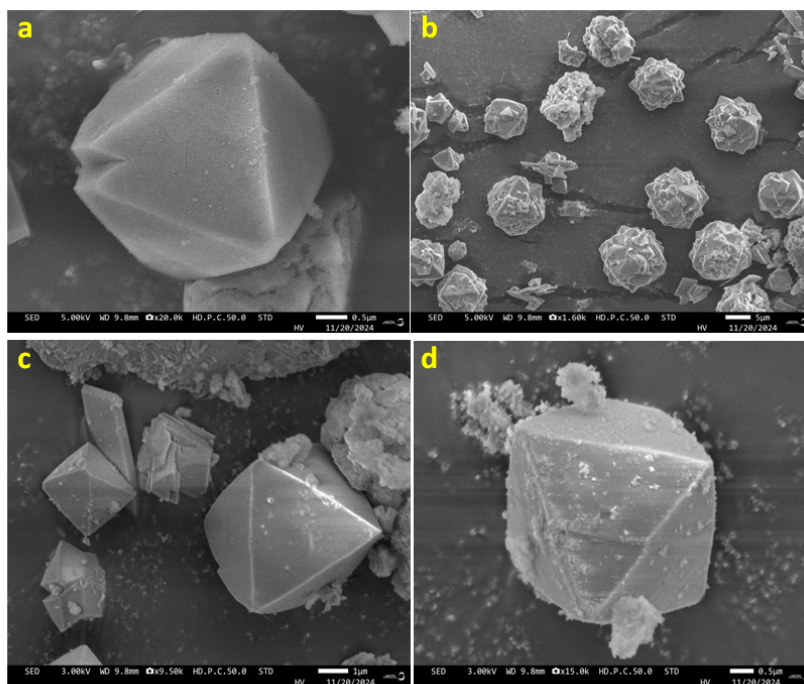
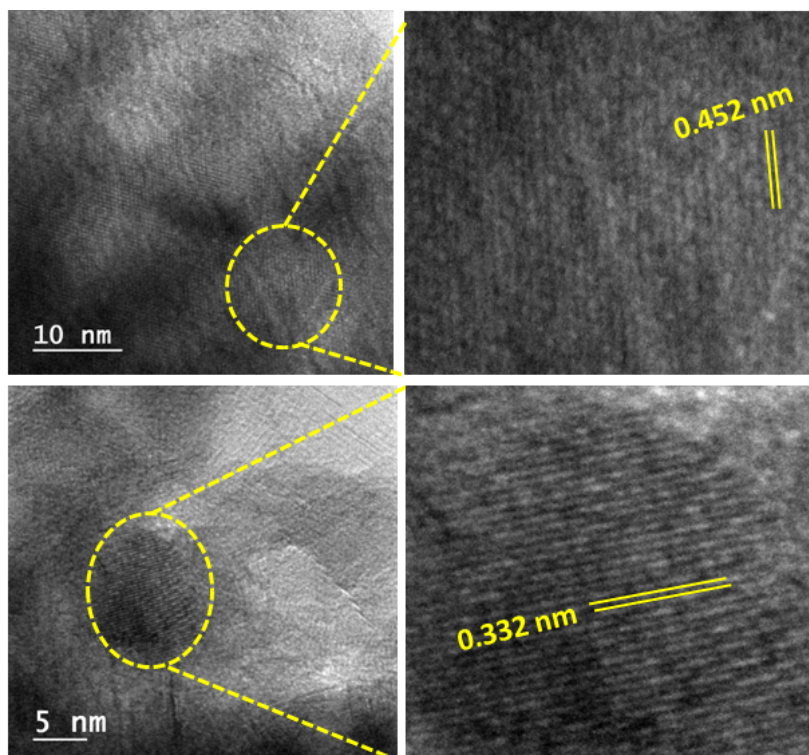


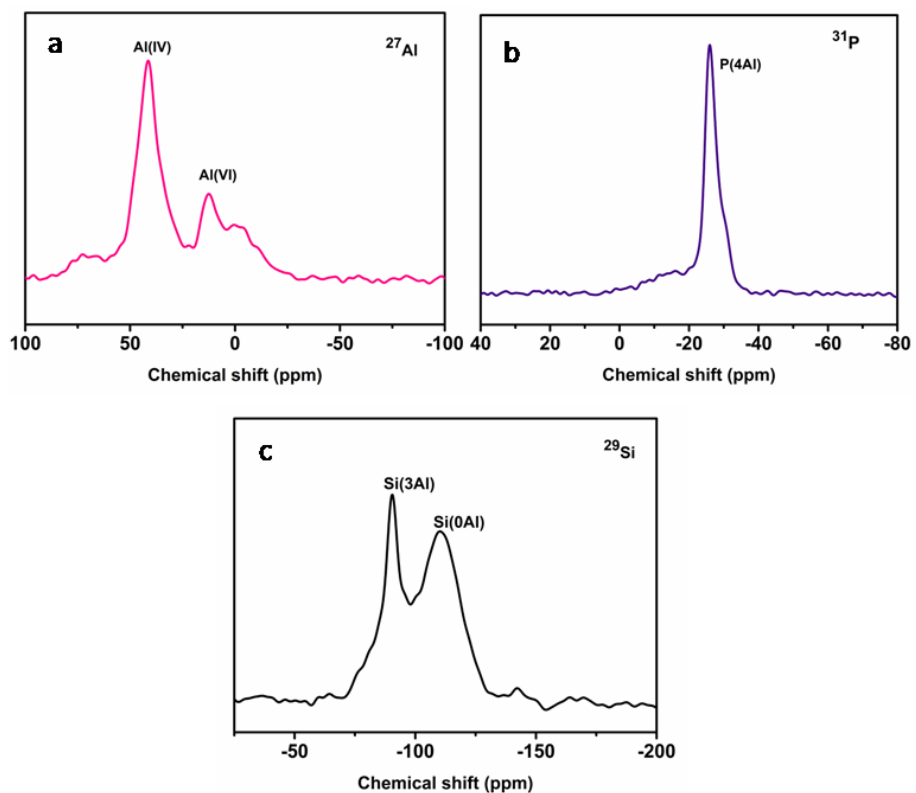
Fig. S4 SEM images of (a), (b) SAPO-37-as sample, and (c), (d) SAP-37R sample.

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10 Fig. S5 TEM analysis of SAP-37ZR, 0.452 nm-(333) and 0.332 nm-(642) plane of SAPO-37.

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18 Fig. S6 MAS NMR spectra of SAP-37ZR a) ^{27}Al , b) ^{31}P and c) ^{29}Si nuclei.

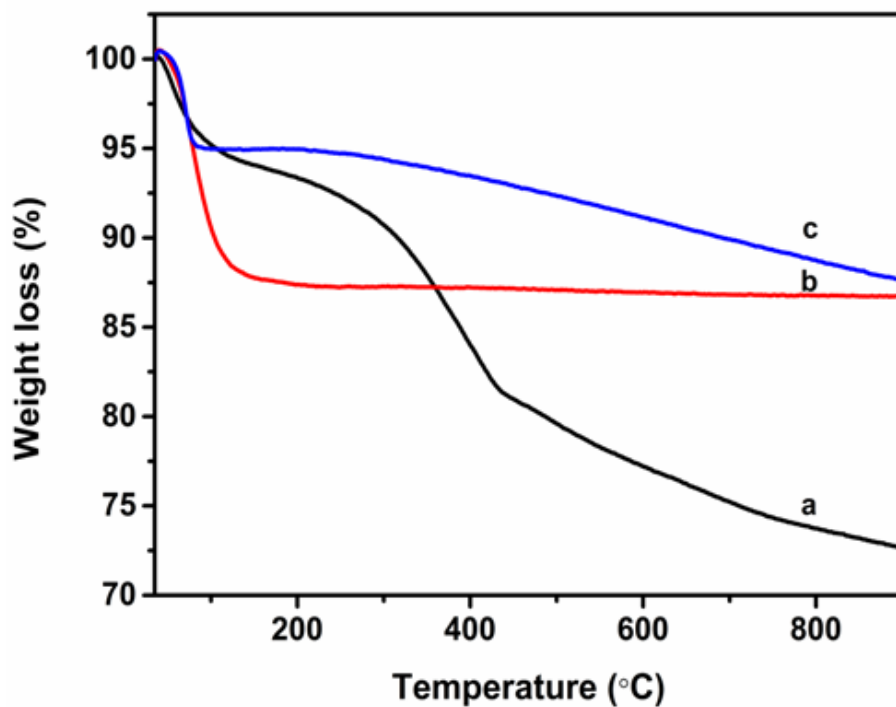


Fig. S7 Thermogravimetric analysis of a) SAP-37Z, b) SAP-37ZR, and c) used SAP-37ZR.

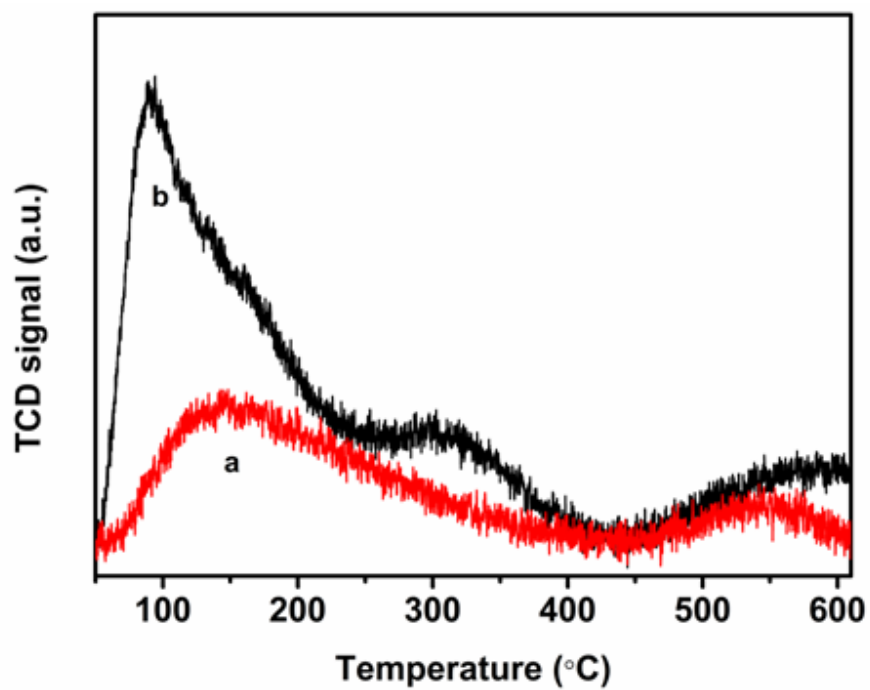


Fig. S8 Ammonia-temperature programmed desorption profile of a) SAP-37R and b) SAP-37ZR.

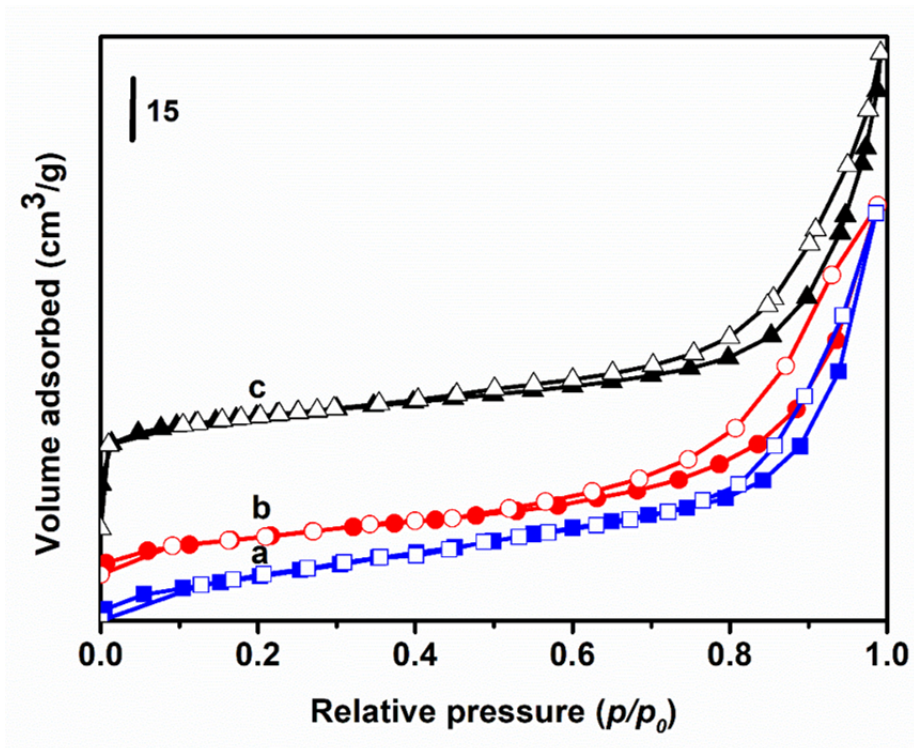


Fig. S9 Nitrogen sorption studies of a)SAPO-37 as, b) used SAP-37ZR, and c) SAP-37 ZR .

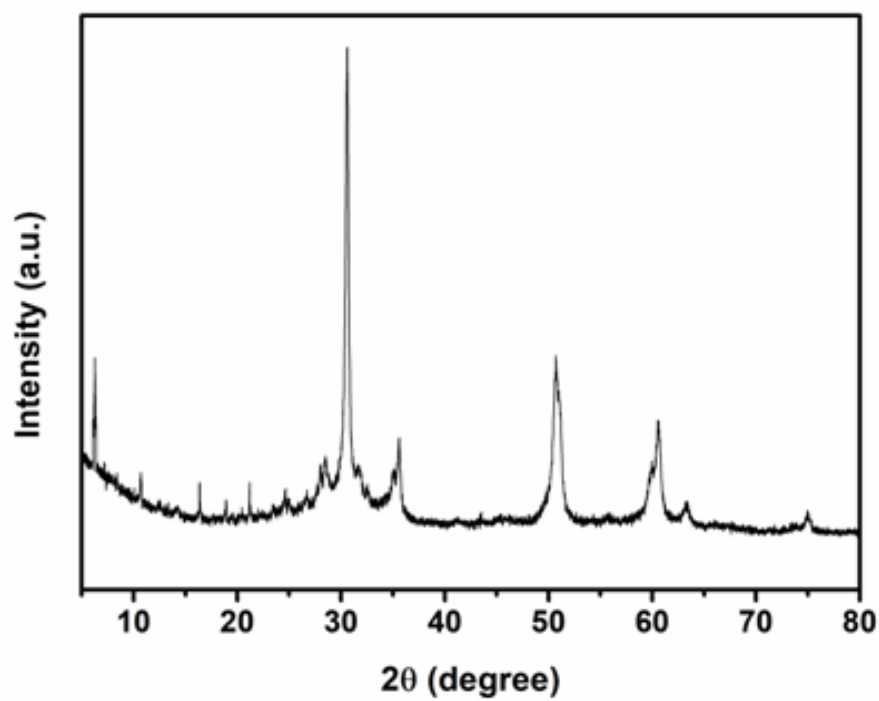
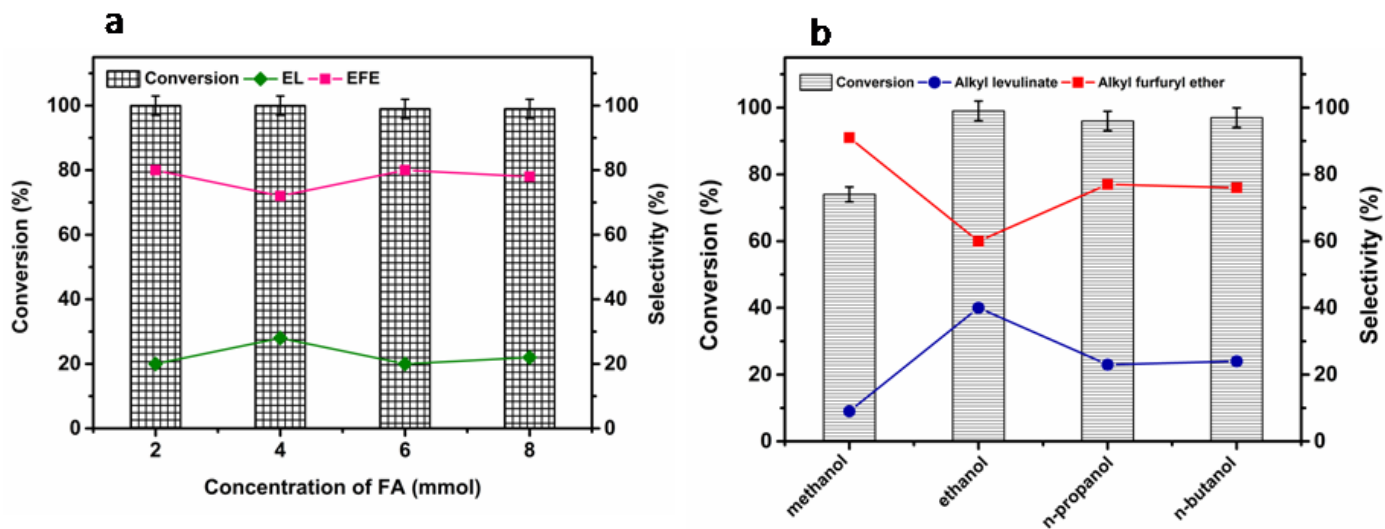


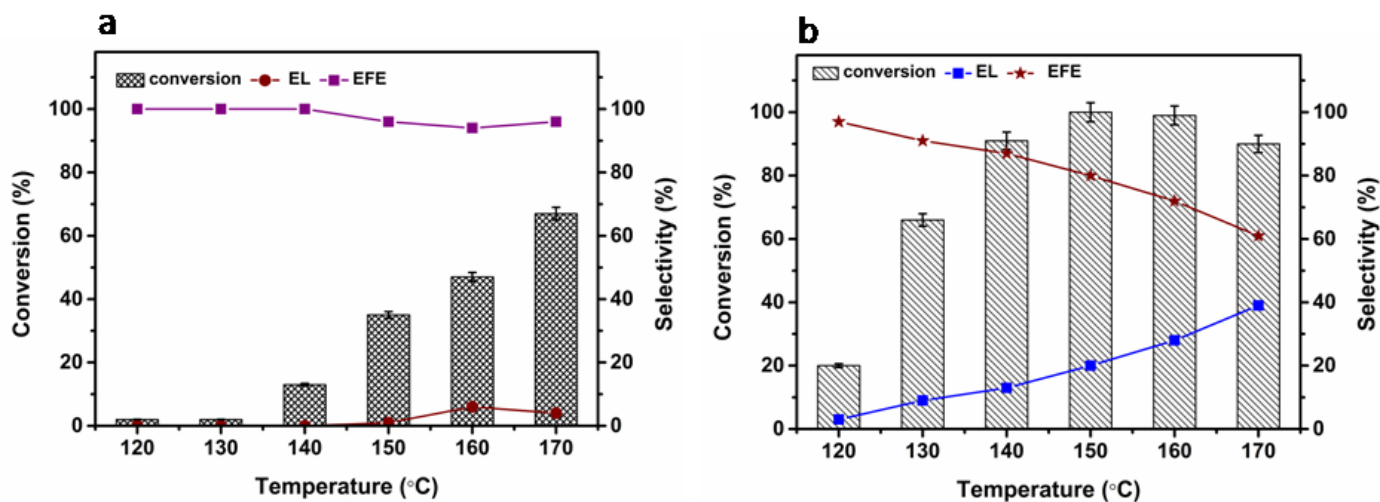
Fig. S10 : Powder XRD pattern of SAP-37ZR reduced at 650 °C.



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2 Fig. S11 Optimization of reaction parameters on furfuryl alcohol (FA) transformation using
 3 SAPO-37ZR catalyst at (a) reactant concentration, and (b) different alcohols.

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6 Fig. S12 Catalytic activity of furfuryl alcohol transformation (a) without catalyst, and (b) with
 7 SAPO-37ZR catalyst at different reaction temperatures.

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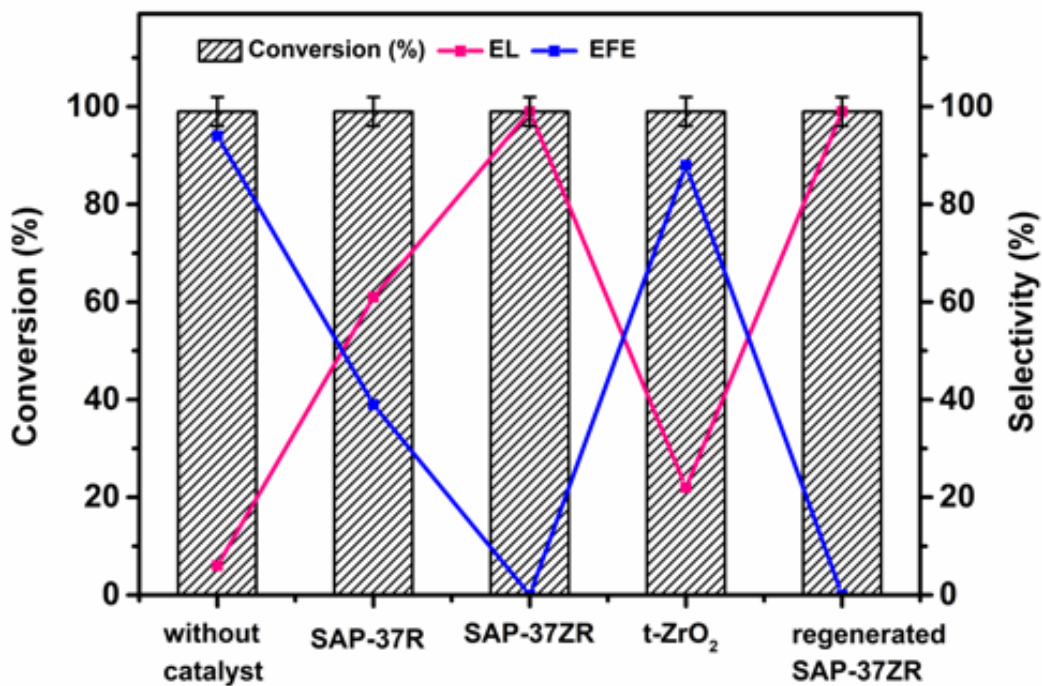


Fig. S13 Product distribution with different catalysts at 190 °C.

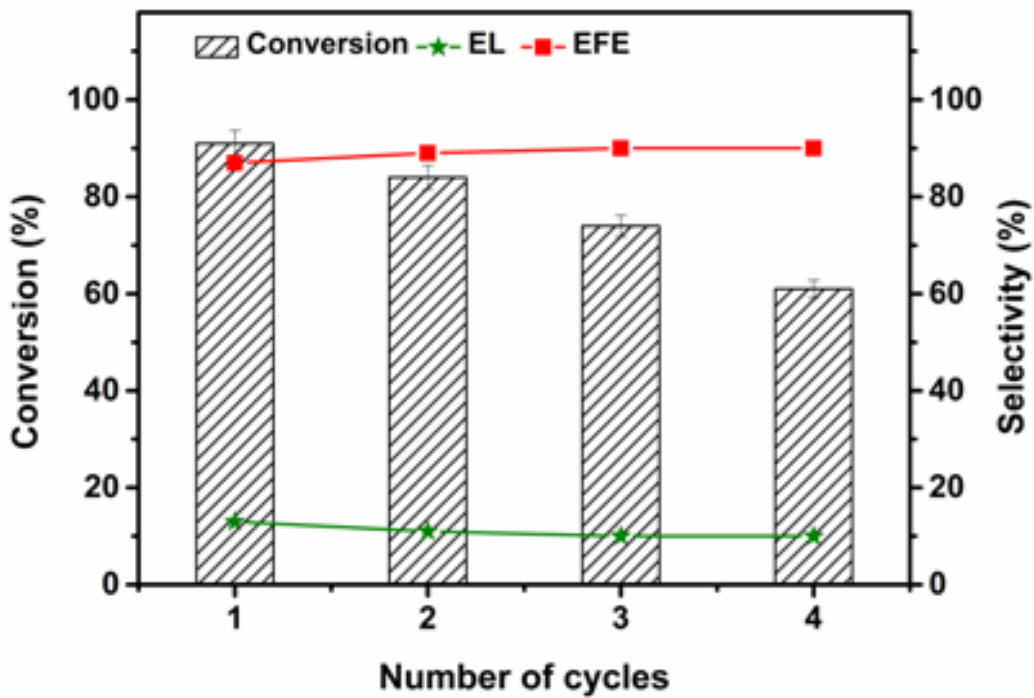


Fig. S14 Recyclability studies on SAPO-37ZR catalyst on FA conversion at 140 °C.

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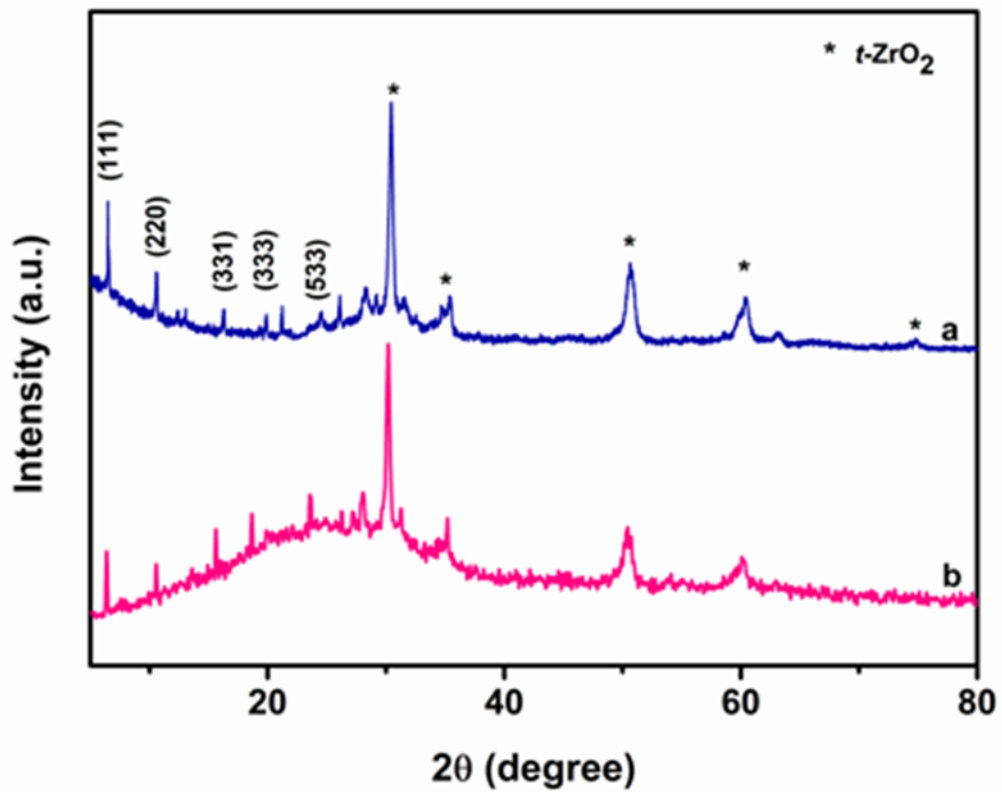


Fig. S15 Powder XRD of a) SAP-37ZR, and b) spent catalyst SAP-37ZR.

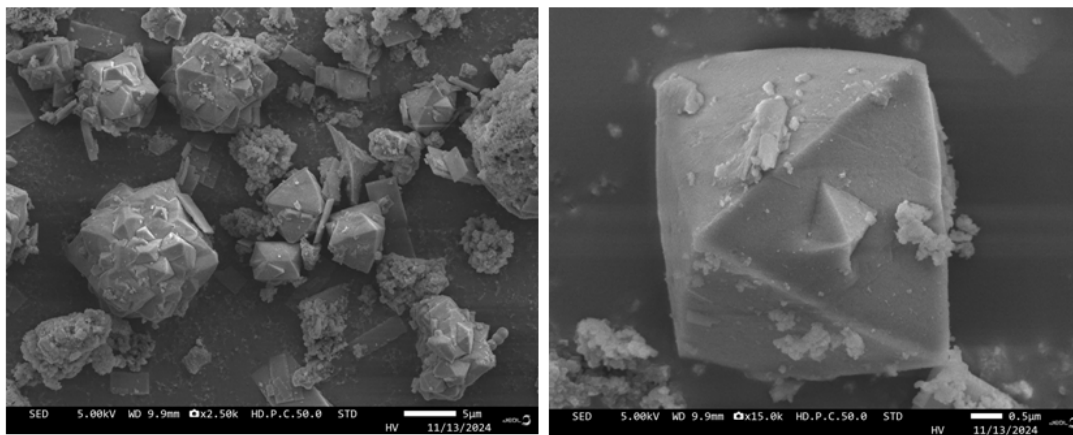


Fig. S16 Scanning Electron Micrograph of regenerated SAP-37ZR