**Electronic Supplementary Information**

# Selective synthesis of furfuryl acetate over solid acid catalysts and active site exploration using Density Functional Theory

B. J. Vaishnavi [a,b], S. Sujith [a], K. M. Rajashekhar Vaibhava [c], P. Jyothi Bhat [a], Rajappan Vetrivel [c] and Ganapati V. Shanbhag [a,c*]

[a] Materials Science and Catalysis Division, Poornaprajna Institute of Scientific Research, Bidalur, Devanahalli, Bengaluru, 562164, India

[b] Graduate Studies, Manipal Academy of Higher Education (MAHE), Manipal, 576104, Karnataka, India

[c] Center for Quantum and Computational Studies, Poornaprajna Institute of Scientific Research, Bidalur, Devanahalli, Bengaluru, 562164, India

## Experimental details

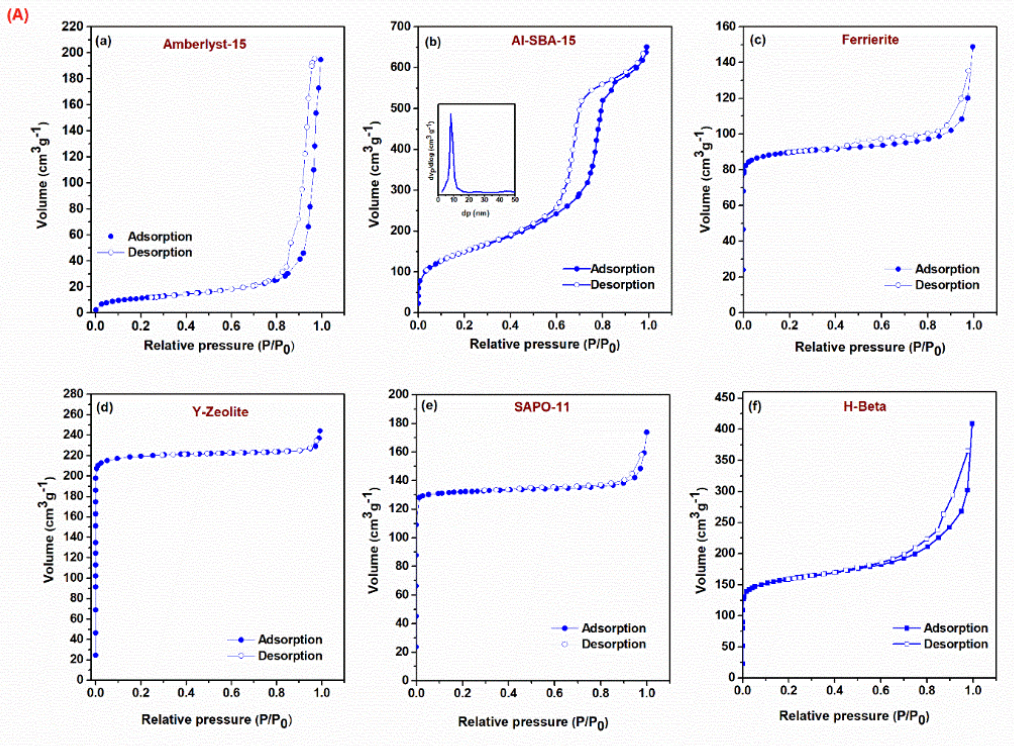
### Catalyst synthesis

SAPO-11 was synthesized as per the reported synthesis procedure [1]. Typically, 15 g of pseudo-boehmite and 25.3 g of orthophosphoric acid were stirred with 95 mL of distilled water to which 22.3 g of triethylamine and 1.6 g of ludox AS-40 were added. The mixture was stirred for 4 h at room temperature and then was transferred to a teflon-lined stainless-steel autoclave and heated in an oven at 200 °C for 24 h. The material was filtered, washed, dried, and calcined (600 °C for 6 h) to yield SAPO-11.

Al-SBA-15 was synthesized as per the reported procedure [2]. In a typical synthesis, 4 g of amphiphilic triblock co-polymer poly–(ethylene glycol)–block poly–(propylene glycol)–block poly–(ethylene glycol) and 120 g of 2M HCl were homogenized in 30 g of distilled water. To this solution, 8 g of tetraethyl orthosilicate was added dropwise and stirred for 24 h at 40 °C. The gel formed was transferred to teflon lined stainless steel autoclave and placed in a preheated oven (100 °C) for 48 h. The material was filtered, washed with distilled water, dried, and calcined at 550 °C

for 24 h to yield SBA-15. SBA-15 (2 g) was subjected to post-synthetic modification by isomorphically substituting Si with Al (0.88 g of anhydrous $AlCl_3$). The precursors were suspended in ethanol and aged for 10 h at 80 °C and further filtered, washed with ethanol, and dried at RT. The final material was calcined at 550 °C for 5 h to yield Al-SBA-15.

## Catalyst Characterization



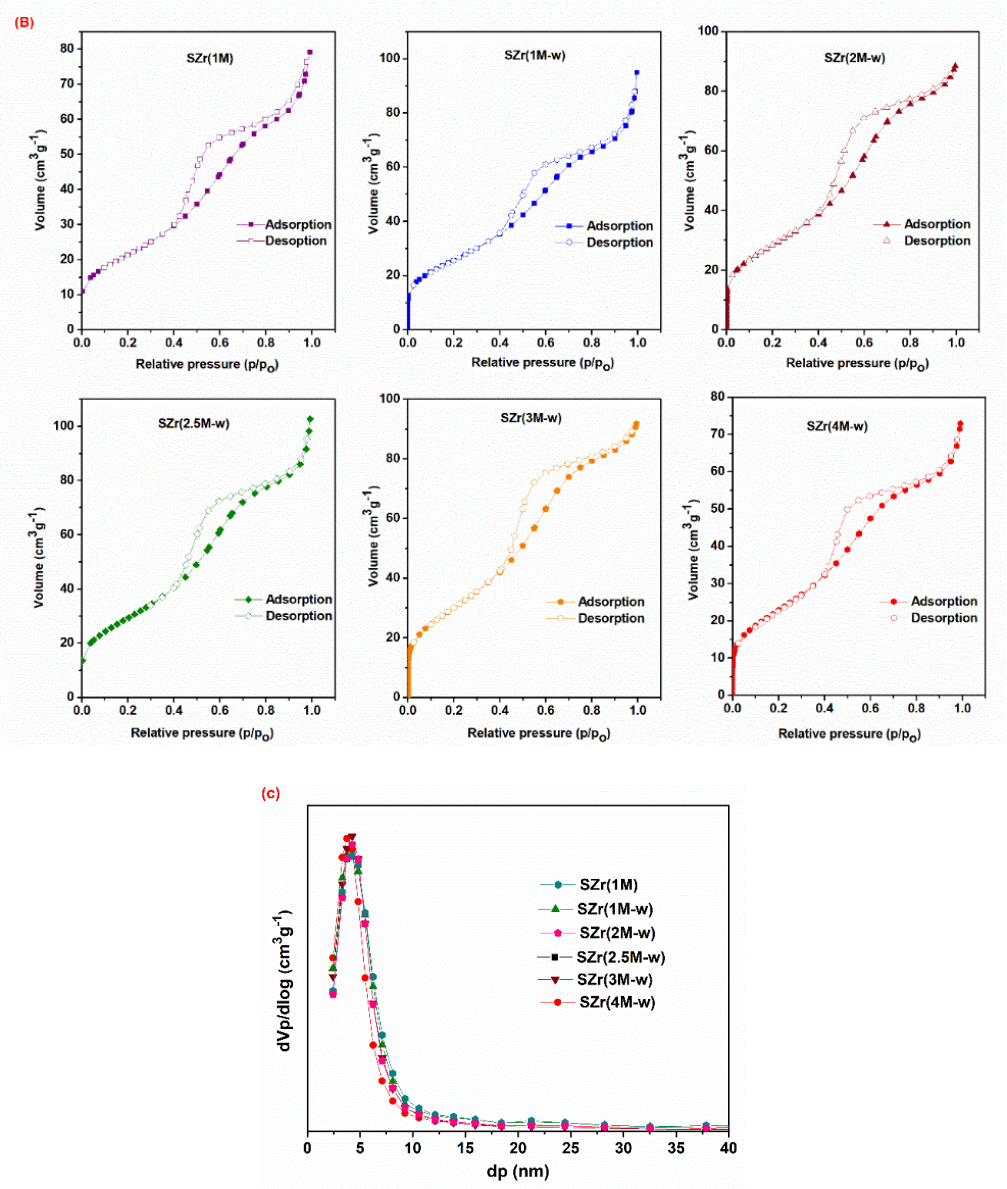



**Figure S1**. **(A)** $N_2$ sorption isotherms of all the screened catalysts- **(a)** amberlyst-15, **(b)** Al-SBA-15, **(c)** ferrierite, **(d)** Y-Zeolite, **(e)** SAPO-11, **(f)** H-Beta **(B)** $N_2$ sorption isotherms of sulfated zirconia catalysts with varied sulfation **(C)** Mean pore diameter of sulfated zirconia catalysts with varied sulfation

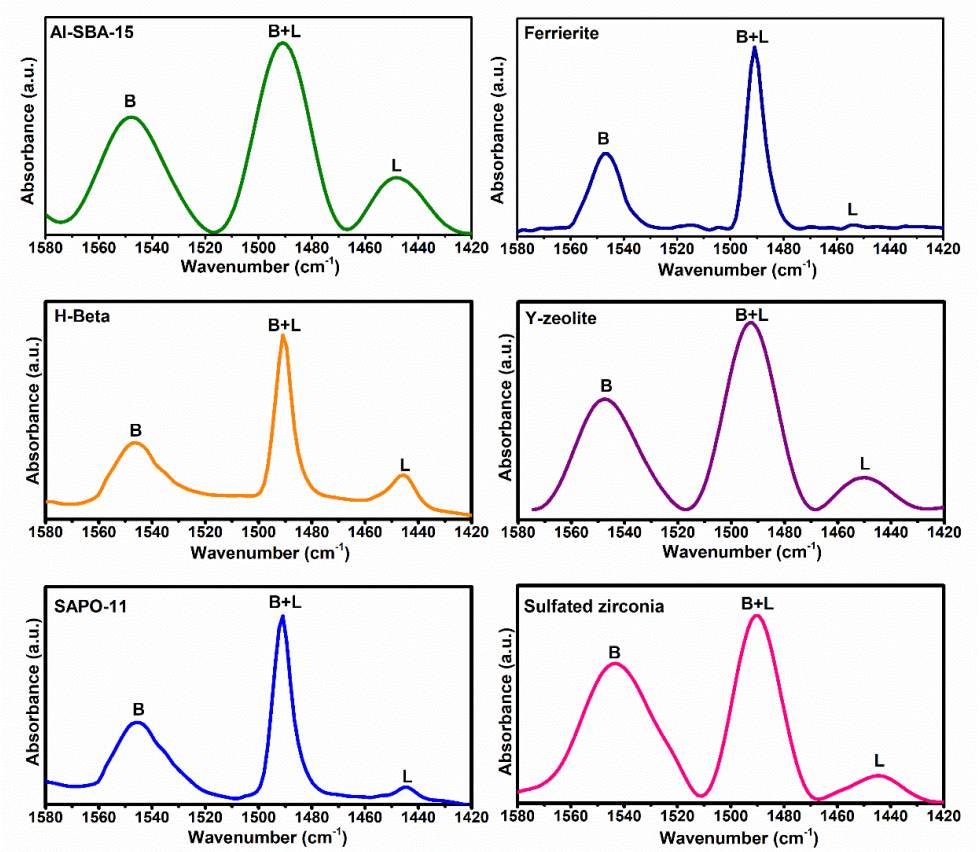



**Figure S2**. Pyridine-FTIR spectra of screened catalysts

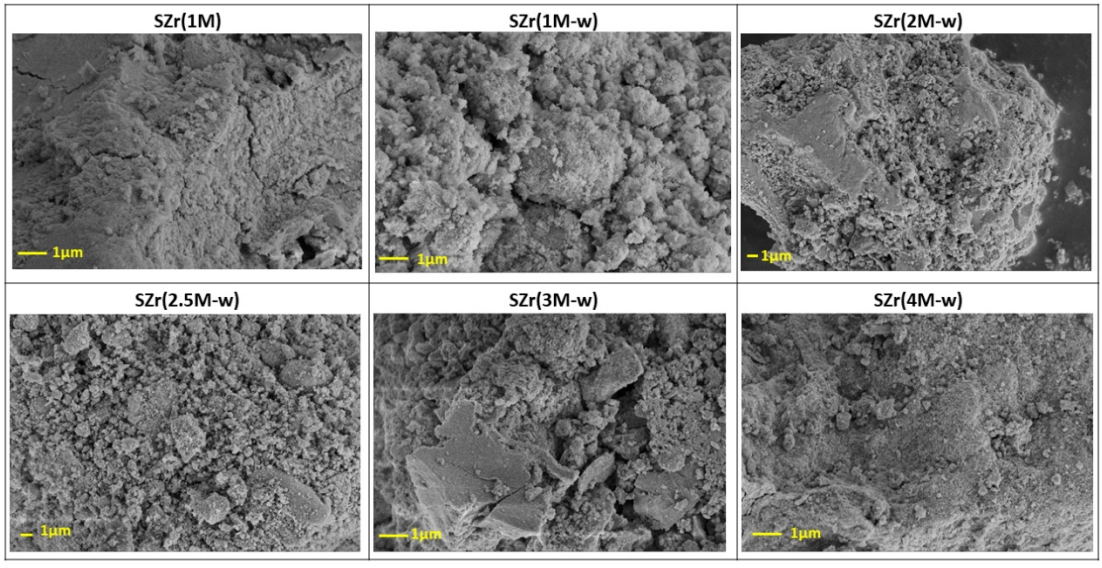



**Figure S3**. SEM micrographs of sulfated zirconia catalysts with different sulfation.

**Catalytic activity study**

**Table S1. Components in GC analysis and their retention time**

| Entry | Retention time | Component |
|---|---|---|
| 1 | 4.4 | Acetic acid |
| 2 | 6.7-6.8 | Furfuryl acetate |
| 3 | 7.5 | 2,2'-difurfurylmethane |
| 4 | 8.4 | Furfuryl alcohol |
| 5 | 11.5 | Difurfuryl ether |
| 6 | 14.6-14.7 | 5-(furan-2-ylmethyl)furan-2-yl-acetate |
| 7 | 15.7 | Difurfuryl furan |

GC program: Oven: 80 °C (1 min), @ 20 °C/min to 120 °C (1min), @ 10 °C/min to 165 °C (1min), @20 °C/min to 200 °C (1min), 15 °C/min to 245 °C (15min)

**Representative chromatograms**

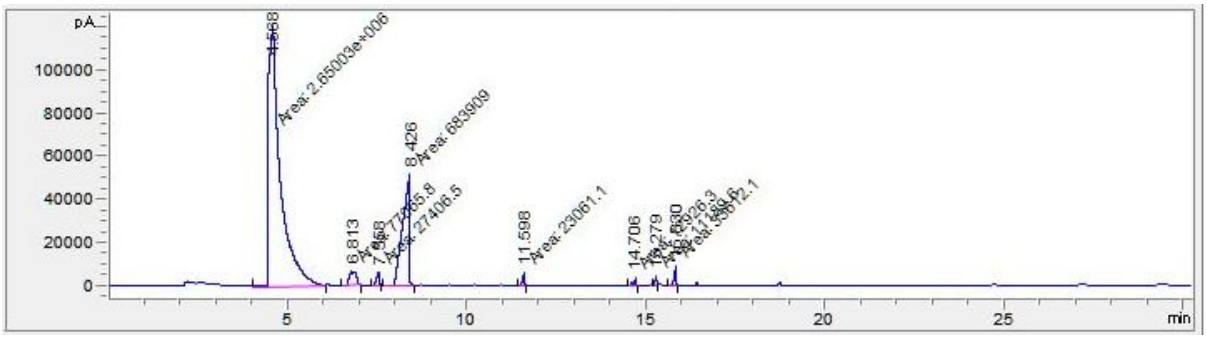



**Figure S4.** Effect of temperature. Reaction conditions: Catalyst- SZr(2.5M-w), catalyst concentration- 1.5wt%, reactants mole ratio- 1:10 (FA: acetic acid), reaction time- 15mins, temperature- 110 °C

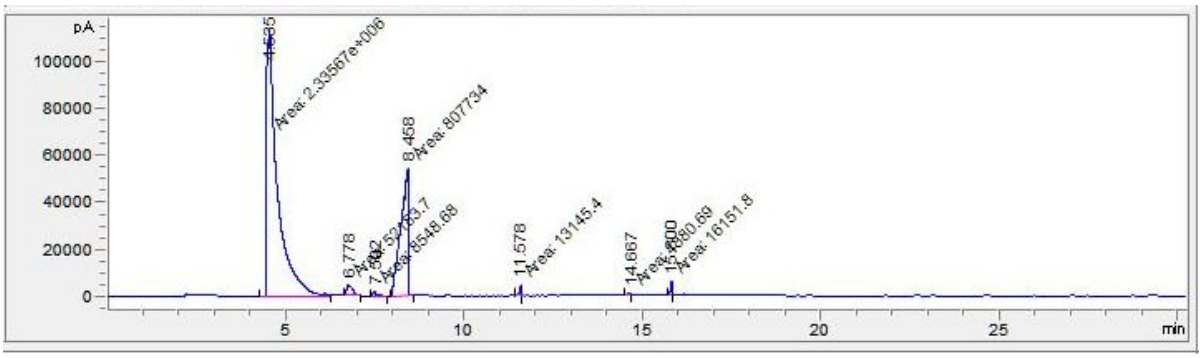



**Figure S5**. Effect of catalyst loading. Reaction conditions: Catalyst- SZr(2.5M-w), temperature- 100 °C, reactants mole ratio- 1:10 (FA: acetic acid), reaction time- 15mins, Catalyst concentration- 0.37wt%

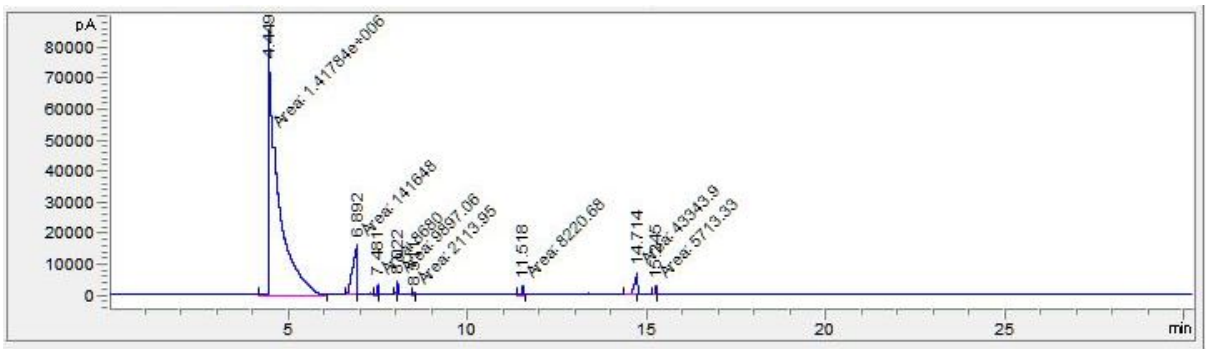



**Figure S6.** Catalyst screening. Reaction conditions: Catalyst- amberlyst-15, temperature- 100 °C, reactants mole ratio- 1:10 (FA: acetic acid), Catalyst concentration- 1.5wt%, reaction time- 6h

**Table S2. Performance of different screened catalysts for FA esterification reaction with acetic acid**

| Catalyst | FA conversion (%) | FAc Selectivity (%) | Others selectivity (%) | | | | | Carbon Balance (%) | FAc yield (%) |
|---|---|---|---|---|---|---|---|---|---|
| | | | SP1 | SP2 | SP3 | SP4 | Others | | |
| Blank reaction | 9.0 | 36.1 | 12.0 | 19.3 | 9.5 | 23.1 | 0.0 | 99 | 3.2 |
| Y-Zeolite (SAR5.1) | 12.9 | 30.7 | 8.6 | 39.6 | 13.5 | 7.6 | 0.0 | 98 | 4.0 |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| H-Beta (SAR25) | 14.4 | 31.3 | 3.9 | 20.4 | 14.3 | 21.8 | 8.3 | 98 | 4.5 |
| SAPO-11 | 16.9 | 29.9 | 3.4 | 17.8 | 8.6 | 31.4 | 8.8 | 98 | 5.1 |
| Al-SBA-15 (SAR35) | 17.0 | 36.8 | 19.9 | 15.0 | 22.0 | 6.2 | 0.0 | 98 | 6.3 |
| Ferrierite (SAR20) | 16.8 | 38.5 | 5.6 | 13.7 | 9.1 | 25.9 | 7.2 | 98 | 6.5 |
| Sulfated zirconia | 28.2 | 46.7 | 13.5 | 10.3 | 12.5 | 12.4 | 4.6 | 99 | 13.2 |
| Amberlyst-15 | 42.6 | 42.6 | 6.1 | 8.2 | 7.3 | 5.9 | 30.0 | 98 | 18.1 |

SP1- 2,2'-difurfurylmethane, SP2- difurfuryl ether, SP3- 5-(furan-2-ylmethyl)furan-2-yl-acetate, SP4- Difurfuryl furan

Catalyst screening. Reaction conditions: catalyst concentration - 1.5wt%, temperature- 70 °C, reaction time- 4 h, mole ratio- 1:10 (FA: acetic acid).

**Table S3 Acidity of the fresh and spent SZr(2.5M-w) catalyst for comparison**

| Catalyst | Acidity (mmol $g^{-1}$) from $NH_3$ TPD | | | |
|---|---|---|---|---|
| | Weak | Moderate | Strong | Total |
| SZr(2.5M-w) | 0.01 | 0.09 | 0.13 | 0.23 |
| SZr (2.5M-w)-Used | 0.01 | 0.06 | 0.13 | 0.20 |

**Plausible reaction mechanism**

**Table S4. Hammett acidity values of solid acid catalysts used in this study**

| S.No. | Catalysts | $T_m$ (K) from $NH_3$-TPD | $1/T_m$ | Ho |
|---|---|---|---|---|
| 1 | Sulfated Zirconia | - | - | –14.5 |
| 2 | $H_2SO_4$ | - | - | –11.9 |
| 3 | Y-Zeolite (SAR 5.1) | 488 | 0.002049 | –10.4 |
| 4 | Ferrierite (SAR20) | 441 | 0.002268 | –8.4 |

| | | | | |
|---|---|---|---|---|
| 5 | Al-SBA-15 (SAR35) | 440 | 0.002273 | –8.3 |
| 6 | H-Beta (SAR25) | 435 | 0.002299 | –8.1 |
| 7 | SAPO-11 | 388 | 0.002577 | –5.6 |
| 8 | Amberlyst-15 | - | - | –2.2 |

Note: Catalysts 1,2 and 8 are from references [3,4]. Catalysts 3-7, Hammett acidity values were determined using the formula $H_o = a+b\ (1/T_m)$ where a and b are empirical constants specific for aluminosilicate catalysts and $T_m$ is temperature peak maximum obtained from $NH_3$-TPD profile as given in references [5,6]

**Table S5. Three trials to find the repeatability of the experiments**

| Trial | FA Conversion (%) | FAc selectivity (%) | FAc Yield (%) |
|---|---|---|---|
| 1 | 83.3 | 85.1 | 70.9 |
| 2 | 83.0 | 85.8 | 71.2 |
| 3 | 83.8 | 85.0 | 71.2 |

Reaction conditions: Catalyst- SZr, catalyst concentration- 1.5wt%, temperature- 100 °C, reactants mole ratio- 1:10 (FA: acetic acid), reaction time- 6 h. The calculated % error for the data < ±1 %

**References**


1. P. Meriaudeau, V. Tuan, V. T. Nghiem, S. Lai, L. Hung and C. Naccache, *Journal of catalysis*, 1997, **169**, 55-66.
2. G. V. Shanbhag, S. Kumbar and S. Halligudi, *Journal of Molecular Catalysis A: Chemical*, 2008, **284**, 16-23.
3. H. Hattori and Y. Ono, Solid acid catalysis: from fundamentals to applications, CRC Press, 2015.
4. W. Wang, X. Ji, H. Ge, Z. Li, G. Tian, X. Shao and Q. Zhang, *RSC Adv*., 2017, 7, 16901-16907.
5. A. Corma*, Chem. Rev.* 1995, 95, 3, 559–614.
6. J. C. Yori, L. M. Krasnogor and A. A. Castro, *React Kinet Catal Lett,* 1986, 32, 27-32.