

## Controlled acidity-mediated short-chain olefins synthesis over Mn-Zn-Zr/Zn-SAPO-34 catalyst via CO<sub>2</sub> hydrogenation

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## Experimental

### Synthesis of SAPO-34 and modified SAPO-34 Zeolites through the hydrothermal method

The SAPO 34 molecular sieves zeolite was prepared by the conventional hydrothermal method. The material was made from a combination gel with the following molar composition 1 Al<sub>2</sub>O<sub>3</sub>: 1.06 P<sub>2</sub>O<sub>5</sub>: 1.08 SiO<sub>2</sub>: 2.09 Morpholine: 66 H<sub>2</sub>O. Firstly, an aqueous solution of phosphoric acid was made and then pseudo-boehmite was added slowly into the solution. This mixture was stirred for 8 h to completely dissolve the components. Then aqueous solution of morpholine and fumed silica was dropwise added to that solution and stirred again for 12 h. After that, this solution was hydrothermally treated for 24 h at 200 °C. The dried precipitate was calcined at 550 °C for 6 h in the presence of air to obtain pure SAPO 34 Zeolite molecular sieves. The modified SAPO-34 i.e., Zn-SAPO-34 and Sn-SAPO-34 were prepared after loading 5 wt% of Zn and Sn metals over SAPO-34 molecular sieves

### Synthesis of binary Zn-Zr oxides and ternary Mn or In-Zn-Zr oxides catalysts by co-precipitation

The 15% ZnO-85% ZrO<sub>2</sub>, 15%In/12.75%ZnO/72.25%ZrO<sub>2</sub>, and 15%Mn/12.75%ZnO/72.25%ZrO<sub>2</sub> catalysts were prepared by the co-precipitation method. The calculated amount of salts In (NO<sub>3</sub>)<sub>3</sub>·xH<sub>2</sub>O, Mn (NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O, Zn (NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, and ZrO(NO<sub>3</sub>)<sub>2</sub>·xH<sub>2</sub>O were dissolved in DI water to make a 50 ml solution of 1M total metal ion concentration and stirred at 80 °C for 2 h. After that 1.5M Na<sub>2</sub>CO<sub>3</sub> solution and metal ion solution were dropwise added to 50 ml of DI water at 80 °C to maintain a pH of 8.0 under continuous stirring and then left for 2 h. Then, the obtained mixture was cooled at room temperature, followed by filtration, washing, and drying at 100 °C overnight. Finally, the powder was calcined in a muffle furnace at 500 °C for 5 h

### Catalyst characterizations

X-ray diffraction (XRD) patterns were recorded using a PROTO AXRD<sup>®</sup> Benchtop Powder Diffractometer. Transmission electron microscopy (TEM) and high-resolution TEM (HR-TEM) images were captured using a JEOL JEM-2100 instrument. Scanning electron microscopy (SEM) images were acquired with a Quanta 200 F from M/s FEI. X-ray photoelectron spectroscopy (XPS) was conducted on a Thermo Scientific NEXSA XPS spectrometer. N<sub>2</sub> adsorption-desorption isotherms at 93 K were measured using a Micromeritics ASAP 2020 Surface Area & Porosity Analyzer, applying the BET equation. The <sup>29</sup>Si and <sup>27</sup>Al NMR of the catalyst was carried out in the Avance III 500 MHz, Bruker Germany instrument. Before the analysis, samples were first ground using mortar and pestle which were then inserted into the rotor using the spatula. The NH<sub>3</sub> Temperature-Programmed Desorption (NH<sub>3</sub> TPD) experiments were carried out using the Micromeritics<sup>®</sup> Autochem II 2920 instrument. In-situ Diffuse Reflectance Infrared Fourier Transform (DRIFT) spectra were acquired to study the reaction intermediates and products, using a Bruker Tensor 37 instrument with a cryogenic indium antimonide (InSb) detector.

### Methanol to olefins activity of zeolites

Firstly, the activity of SAPO-34 and modified SAPO-34 (5%Zn- SAPO-34 or 5%Sn-SAPO-34) molecular sieves zeolites for methanol to olefins (MTO) reactions were conducted on a continuous flow quartz tube reactor between 300-380 °C temperature at atmospheric pressure. Before the reaction, 0.5g of zeolite catalysts was loaded and pre-treated in the presence of a 20 ml flow of N<sub>2</sub> at 550 °C for 2h. Then the reactor was cooled down to 320 °C to start the MTO reaction. A weight

hour space velocity (WHSV) of  $9.5\text{g}\cdot\text{g}_{\text{cat}}^{-1}\cdot\text{h}^{-1}$  of methanol was fed into the reactor using an HPLC pump which was first evaporated at  $120\text{ }^{\circ}\text{C}$  and then diluted with the  $20\text{ ml}$  flow  $\text{N}_2$ . After  $60\text{ min}$  of reaction at  $300\text{ }^{\circ}\text{C}$ , the reactants and products were analyzed using an online Agilent 7890B GC system. The temperature was further increased to  $340$ ,  $360$ , and  $380\text{ }^{\circ}\text{C}$  to check the activity of the MTO reaction at these temperatures. The selectivity of products was calculated using the formula given in Chapter 2 and methanol conversion was calculated using the following formula,

$$\begin{aligned} \text{Methanol conversion (\%)} \\ = \frac{[\text{mole of methanol}]_{\text{in}} - [\text{mole of methanol}]_{\text{out}}}{[\text{mole of methanol}]_{\text{in}}} * 100 \end{aligned} \quad (1)$$

$$\text{Selectivity of a product (\%)} = \frac{[\text{mol of that product formed}]}{[\text{Total mol of products formed}]}$$

$$* 100 \quad (2)$$

The activity of the different zeolite catalysts for the methanol-to-olefins reaction is presented in Figure S5. The methanol conversion increased for all the zeolites with an increase in temperature. For SAPO-34 zeolite, methanol conversion was 35, 65, 85, and 98% with short-chain olefins selectivity of 86.6, 85.8, 85.3 and 85.2% at  $320$ ,  $340$ ,  $360$ , and  $380\text{ }^{\circ}\text{C}$ , respectively. The  $\text{CH}_4$  selectivity remains less than 2% at all screened temperatures. For the modified (Zn or Sn)-SAPO-34, methanol conversion decreased compared to the SAPO-34 at all screened temperatures. Methanol conversion for Zn-SAPO-34 was 30, 58, 78, and 95%, with short-chain olefin selectivity of 86.5, 85.3, 84.5, and 84%, whereas for Sn-SAPO-34, methanol conversion was 28, 60, 80, and 92%, with short-chain olefin selectivity of 80.9, 80.4, 80.7, and 81.1% at  $320$ ,  $340$ ,  $360$ , and  $380\text{ }^{\circ}\text{C}$ , respectively. The major effect after the Zn and Sn introduction over SAPO-34 can be observed in the  $\text{C}_2\text{-C}_3$  olefins selectivity. Despite the decrease in methanol conversion, Zn and Sn-SAPO-34 show an increase in the selectivity of the  $\text{C}_2\text{-C}_3$  olefins compared to the SAPO-34. At  $340\text{ }^{\circ}\text{C}$ ,  $\text{C}_2\text{-C}_3$  olefins selectivity for SAPO-34, Zn-SAPO-34 and Sn-SAPO-34 was 60.2%, 67% and 62.6%, respectively. Since the Zn-SAPO-34 catalyst exhibits the maximum  $\text{C}_2\text{-C}_3$  olefins, it was employed in the subsequent reaction with the ZnO-ZrO<sub>2</sub> based-oxides catalysts.

### **The Activity of binary Zn-Zr oxides and ternary Mn or In-Zn-Zr oxides catalysts and 5%Zn-SAPO-34 bifunctional catalysts for CO<sub>2</sub> hydrogenation to short-chain olefins**

The CO<sub>2</sub> hydrogenation to short-chain olefins activity of the ZnO-ZrO<sub>2</sub>-based oxides and 5%Zn-SAPO-34 was tested in high pressure fixed-bed continuous flow stainless steel reactor. First, ZnO-ZrO<sub>2</sub>-based oxides (50 wt%) and 5% Zn-SAPO-34 zeolite (50 wt%) were mortar mixed and then pelletized (50-60 mesh). A total of 1 g of pelletized catalyst was loaded inside the reactor and then pre-treated with 20% H<sub>2</sub> balanced N<sub>2</sub> at  $400\text{ }^{\circ}\text{C}$  for 5 h to reduce the reducible species in the catalysts. A similar process was carried out for the other oxides and zeolites integration manners. The activity was performed at  $340\text{ }^{\circ}\text{C}$  temperature, and 20 bar pressure with a total GHSV of  $5600\text{ ml g}_{\text{cat}}^{-1}\text{ h}^{-1}$  having H<sub>2</sub>: CO<sub>2</sub>: N<sub>2</sub> in a 3:1:1 volume ratio. Similarly, the syn gas to short-chain olefins activity of Mn-Zn-Zr/Zn-SAPO-34 catalyst was evaluated at the same reaction conditions with H<sub>2</sub>:

CO: N<sub>2</sub> in a 2:1:1 volume ratio. The reactants and products were quantified using an online Agilent 7890B GC system after 24 h of reaction. The CO<sub>2</sub> conversion, CO conversion, and product selectivity were calculated using the following formulas,

$$CO_2 \text{ conversion (\%)} = \frac{[mol \text{ of } CO_2]_{in} - [mol \text{ of } CO_2]_{out}}{[mol \text{ of } CO_2]_{in}} * 100 \quad (3)$$

$$C_n \text{ Selectivity (\%)} = \frac{\text{mole of } CO_2 \text{ converted to } C_n}{\text{Total mole of Products Formed}}$$

\* 100 (4)

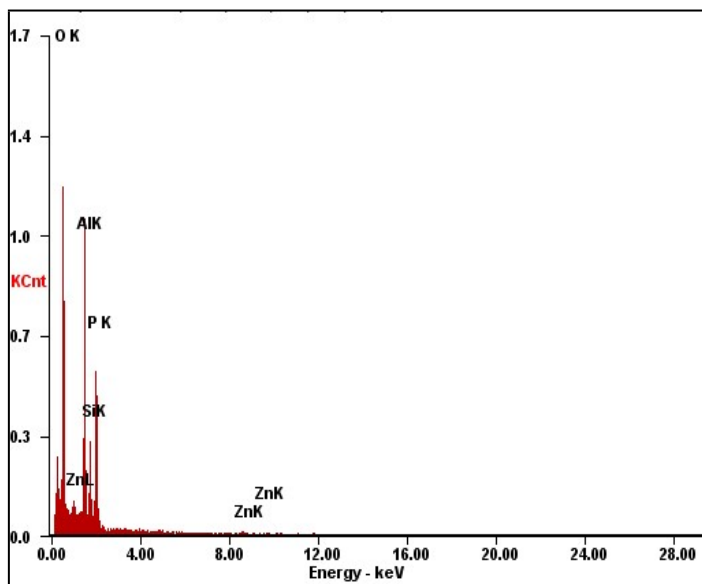


Figure S1. EDX analysis of the Zn-SAPO-34 catalyst

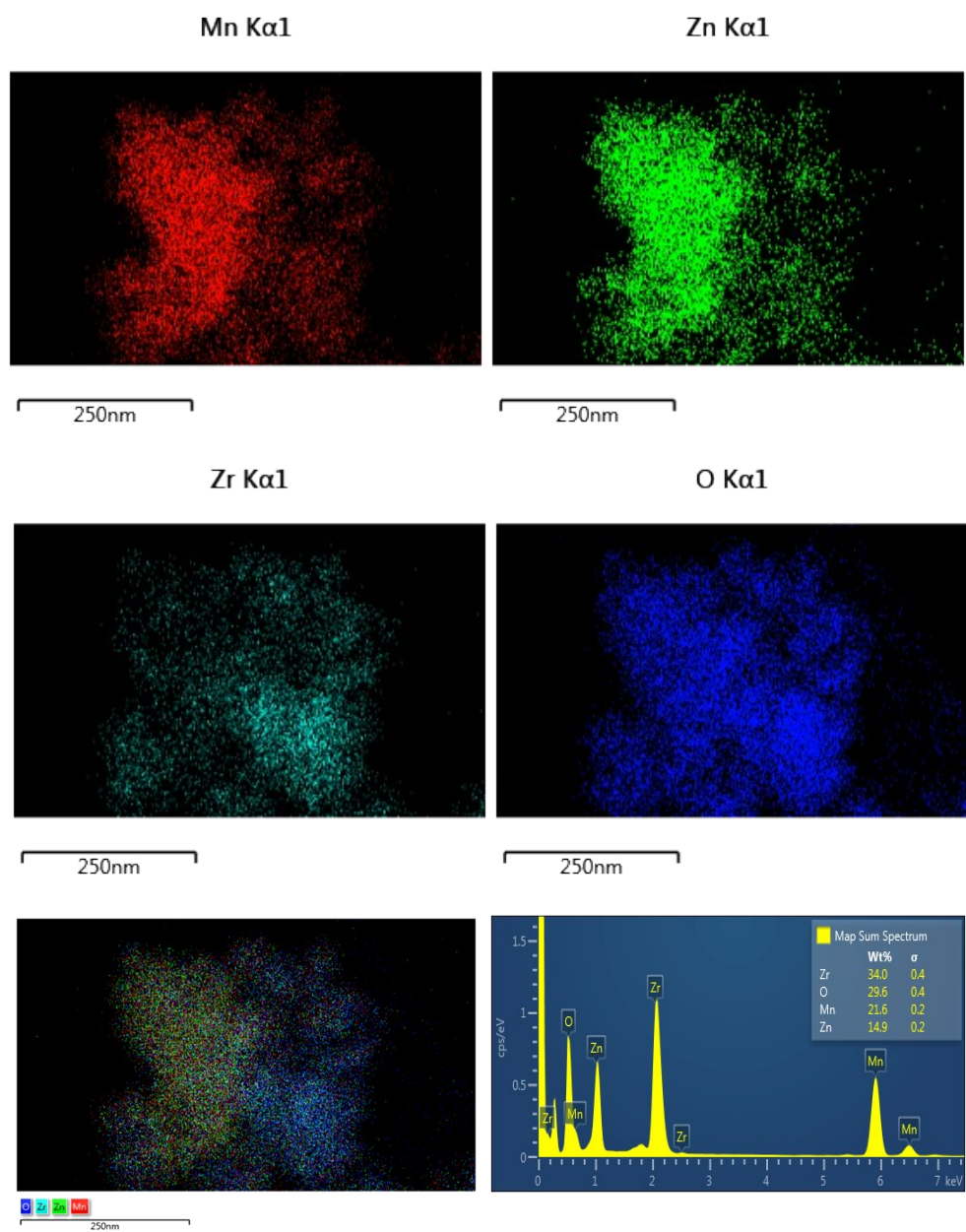
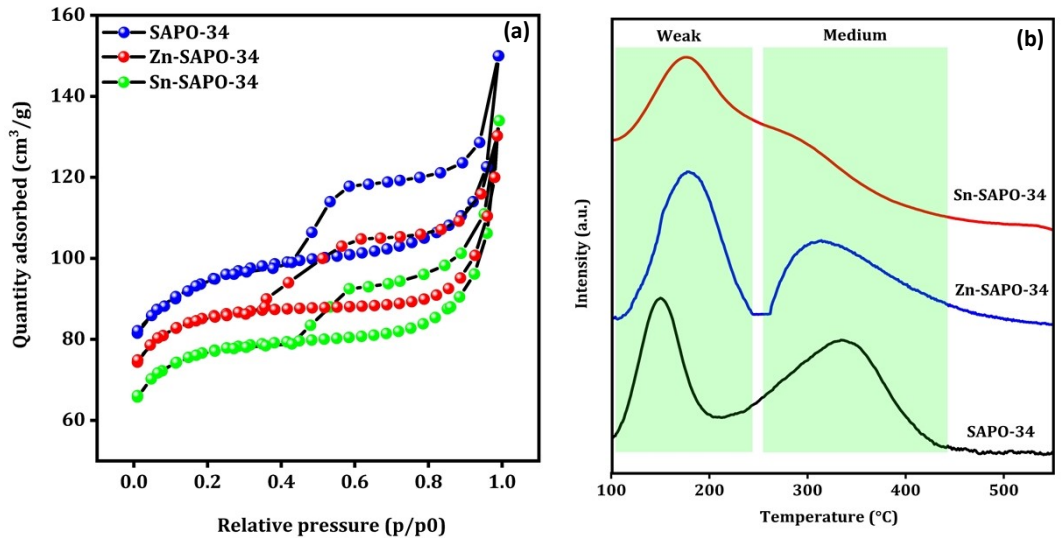


Figure S2. TEM EDX elemental mapping of Mn-Zn-Zr oxides catalyst



**Figure S3.**  $N_2$  adsorption-desorption isotherms (a) and  $NH_3$  TPD (b) analysis of SAPO-34 and modified SAPO-34 zeolites

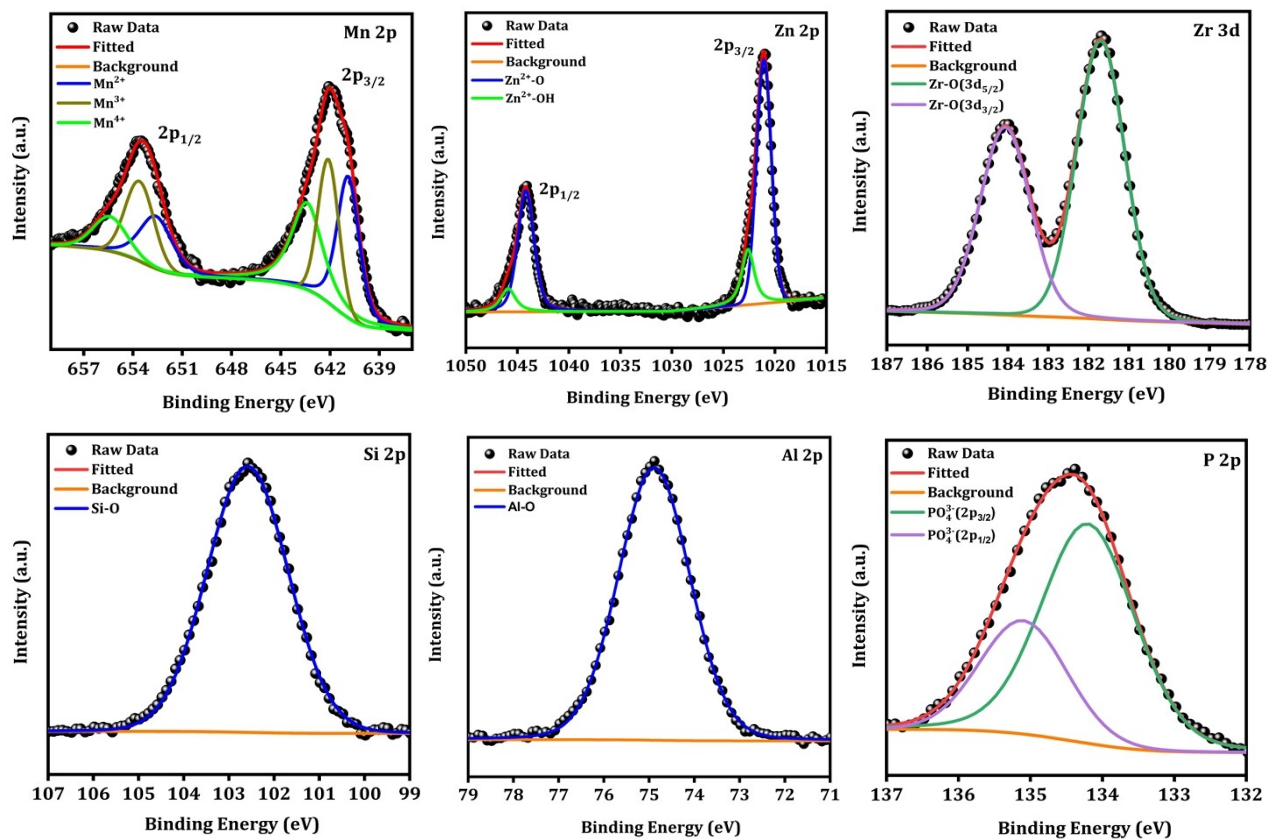


Figure S4. XPS analysis results of Mn-Zn-Zr/Zn-SAPO-34 catalyst



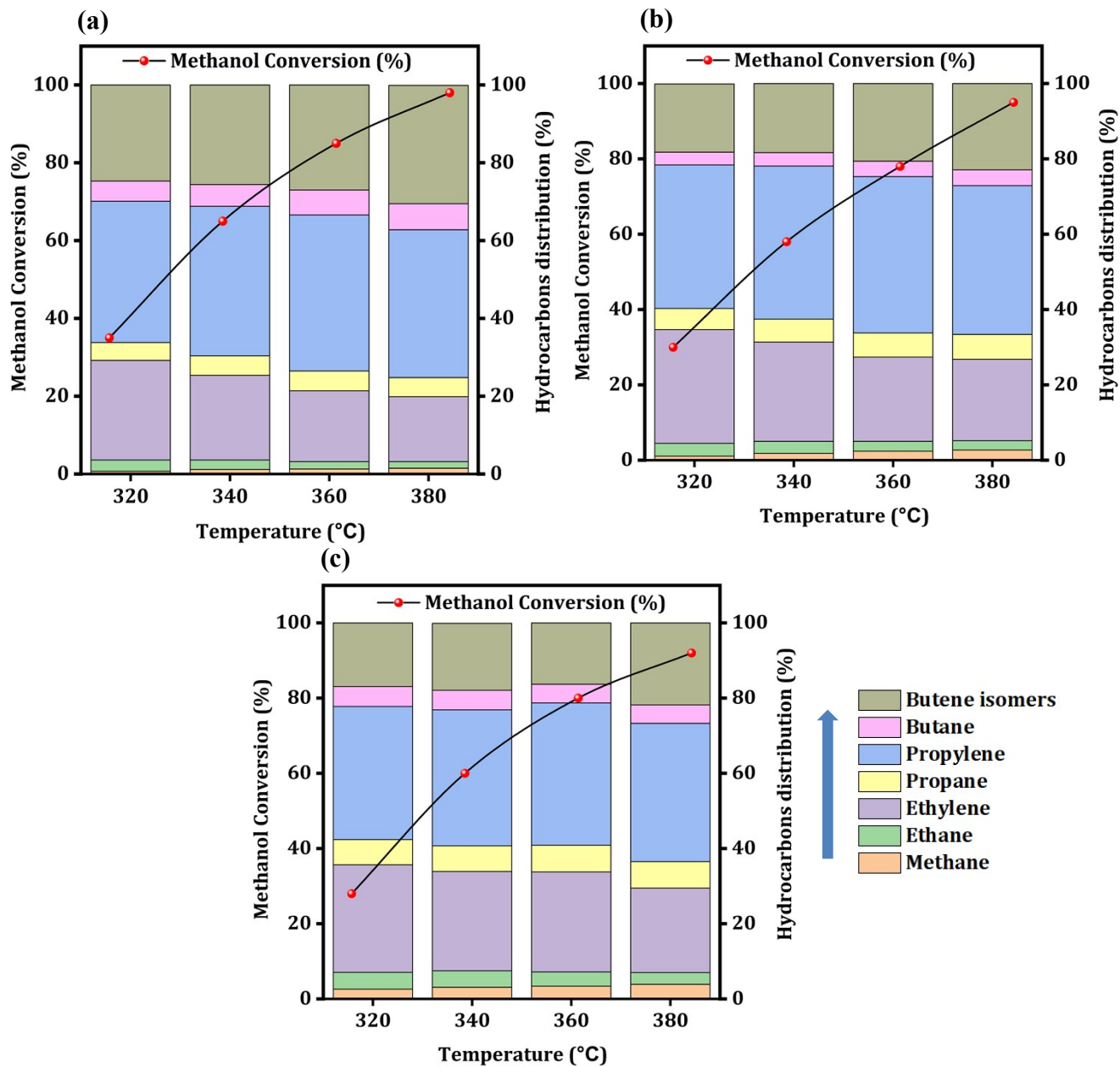
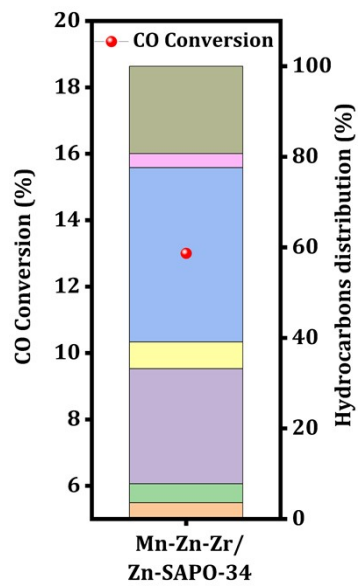
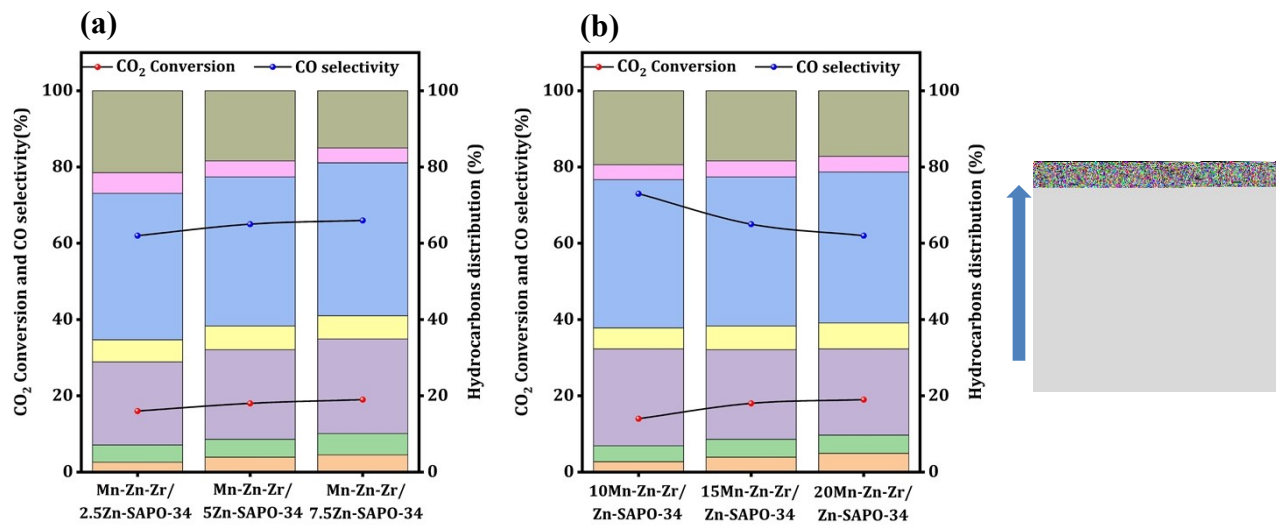


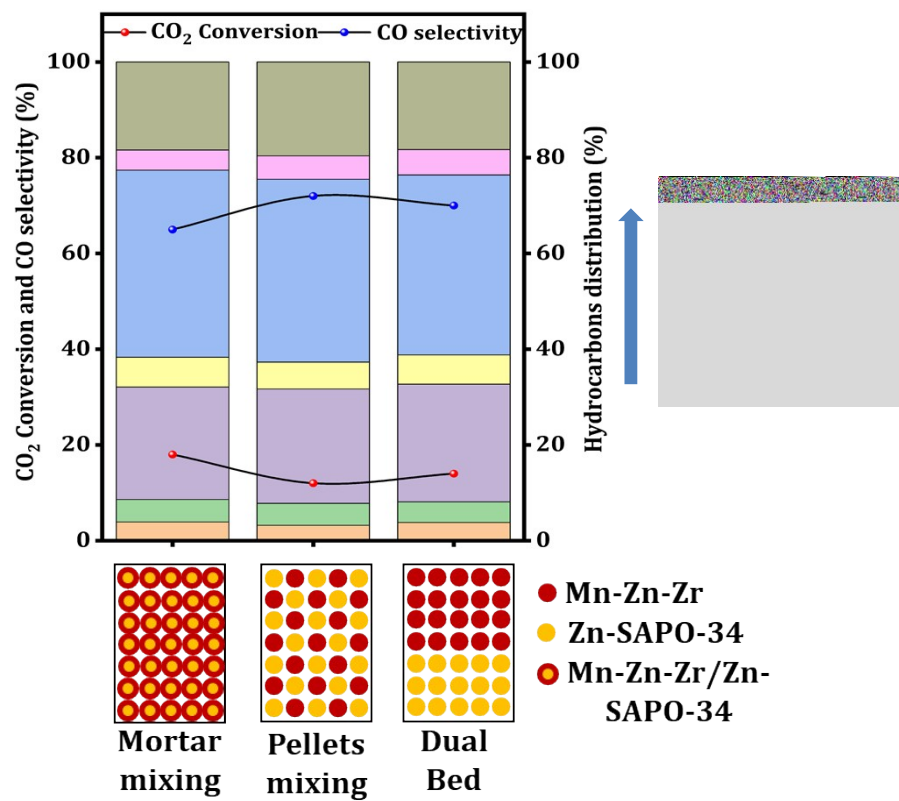
Figure S5. The activity of the SAPO-34 (a), Zn-SAPO-34 (b), and Sn-SAPO-34 (c) Zeolites for methanol to olefins (MTO) reaction



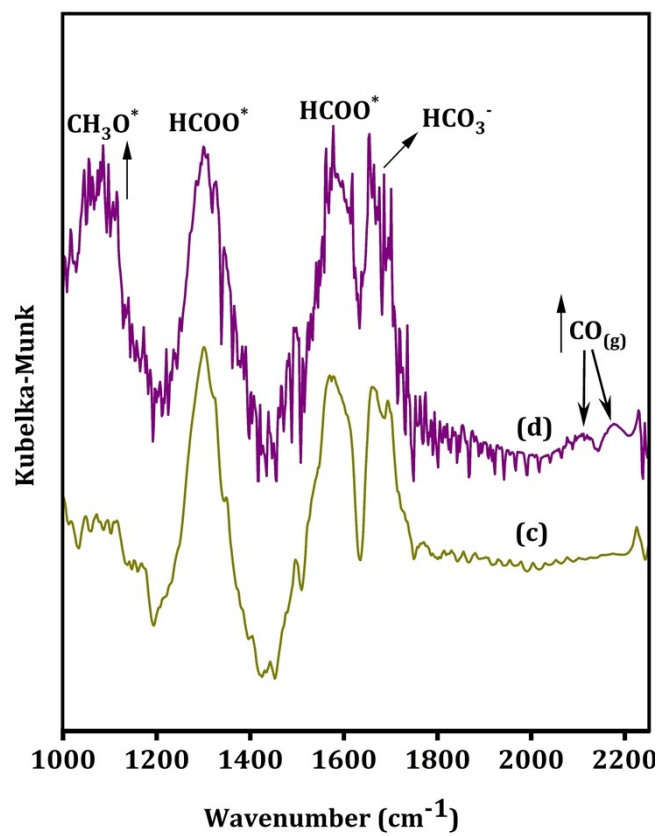
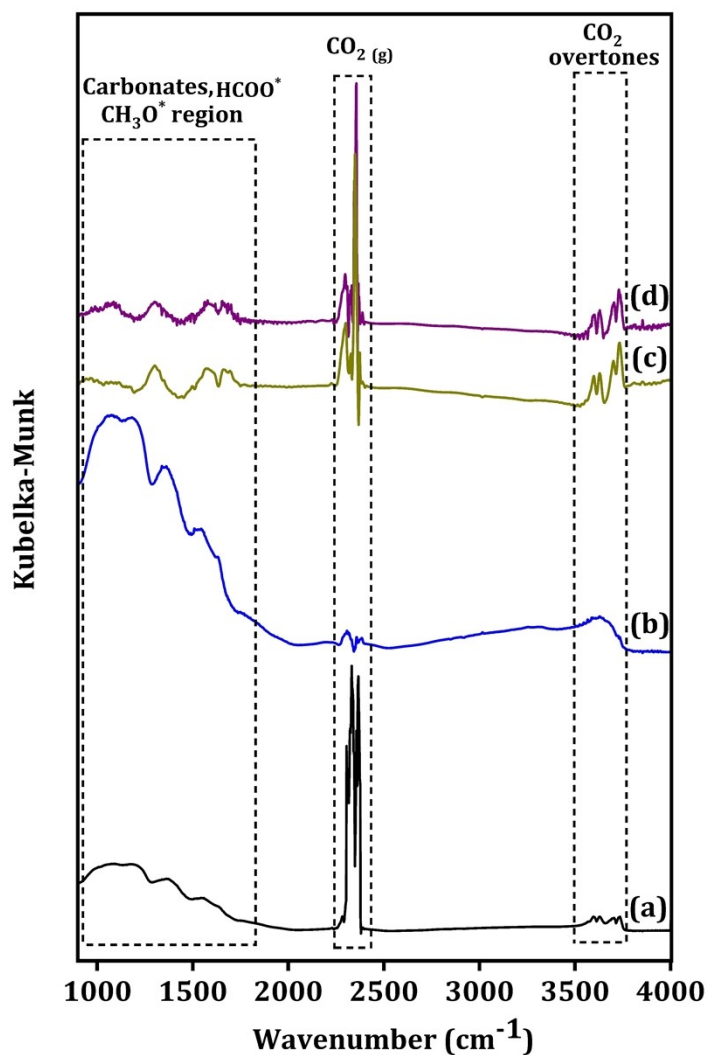
**Figure S6.** The activity of ZnO-ZrO<sub>2</sub> based oxides admixed with Zn-SAPO-34 catalyst for direct CO hydrogenation



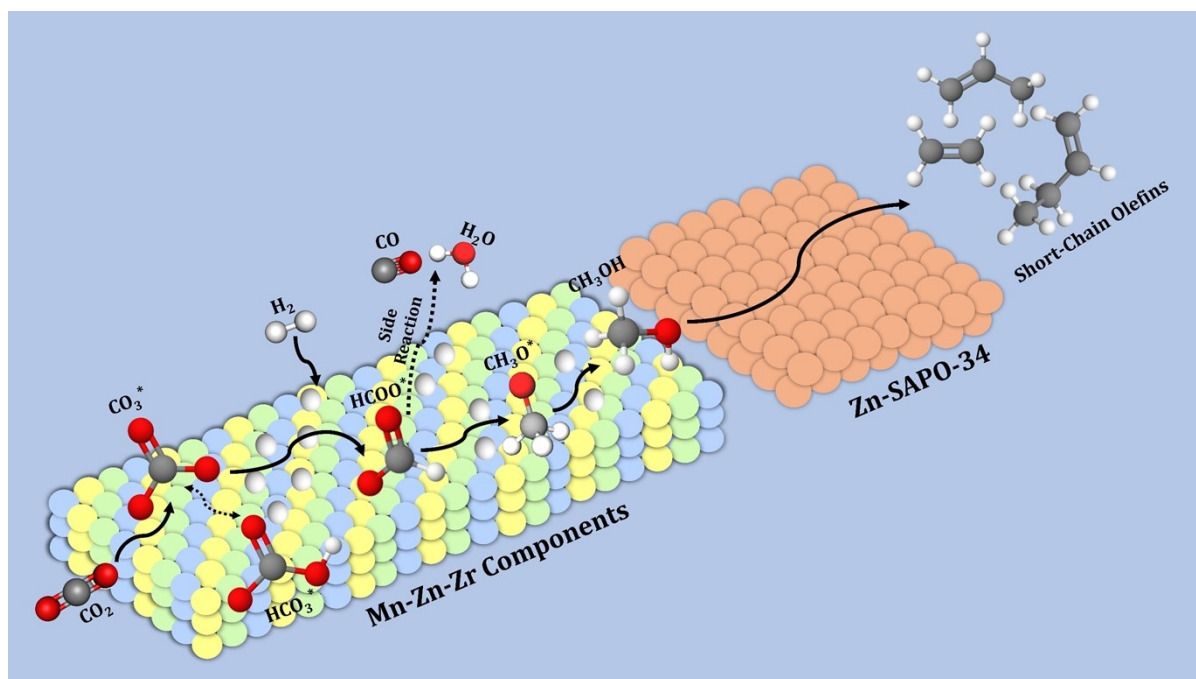
**Figure S7.** Effect Zn in Zn-SAPO-34 (a), and Mn in Mn-Zn-Zr oxides catalysts (b) in catalytic activity



**Figure S8.** Effect of different integration manner of Mn-Zn-Zr/Zn-SAPO-34 catalyst on CO<sub>2</sub> hydrogenation to short-chain olefins



**Figure S9.** *in-situ* DRIFTS spectra over Mn-Zn-Zr/Zn-SAPO-34 catalyst at 340 °C, after CO<sub>2</sub> adsorption for 15 min (a) then He Purging (b), and after flow of H<sub>2</sub>+CO<sub>2</sub> (3:1) for 10 min (c) and 20 min (d)



**Figure S10.** Proposed reaction pathway for methanol synthesis based on the *in-situ* DRIFTS analysis results obtained over Mn-Zn-Zr/Zn-SAPO-34 catalyst

**Table S1.** Comparison of our catalyst with some of the best reported previously published catalysts

S. No.	Catalysts	Reaction Conditions, T (°C), P (bar), GHSV (mL g <sub>cat</sub> <sup>-1</sup> h <sup>-1</sup> ), H <sub>2</sub> : CO <sub>2</sub> ratio	CO <sub>2</sub> conversion (%)	CO Selectivity (%)	Selectivity (%) in HCs		C <sub>2</sub> -C <sub>4</sub> O/P ratio	Ref.
					CH <sub>4</sub>	C <sub>2</sub> -C <sub>4</sub>		
1	ZnAl <sub>2</sub> O <sub>4</sub> /SAPO-34	370, 30, 5400, 3	15	49	0.7	87	8.7	1
2	CuCe/SAPO-34	397, 20, 5800, 3	13.5	57	-	61.8	-	2
3	In <sub>2</sub> O <sub>3</sub> -ZnZrO <sub>x</sub> /SAPO-34	380, 30, 9000, 3	17	55.8	1.6	85	7.7	3
4	CuZnZr@(Zn-)SAPO-34	400, 20, 3000, -	19.6	58	-	60.5	-	4
5	ZnO-Y <sub>2</sub> O <sub>3</sub> /SAPO-34	390, 40, 1800, 4	27.6	85	1.8	83.9	6.5	5
6	ZnGa <sub>2</sub> O <sub>4</sub> /SAPO-34	370, 30, 2700, 3	13	50	1.0	86	8.6	6
7	In <sub>2</sub> O <sub>3</sub> /ZrO <sub>2</sub> SAPO-34	400, 15, 15000, -	23	90	-	82	-	7
8	<b>Mn-Zn-Zr/Zn-SAPO-34</b>	<b>340, 20, 5600, 3</b>	<b>18</b>	<b>65</b>	<b>3.9</b>	<b>81</b>	<b>5.4</b>	<b>Our Work</b>

## References

- 1 X. Liu, M. Wang, H. Yin, J. Hu, K. Cheng, J. Kang, Q. Zhang and Y. Wang, *ACS Catal.*, 2020, **10**, 8303–8314.
- 2 M. Sedighi and M. Mohammadi, *Journal of CO2 Utilization*, 2020, **35**, 236–244.
- 3 S. Dang, S. Li, C. Yang, X. Chen, X. Li, L. Zhong, P. Gao and Y. Sun, *ChemSusChem*, 2019, **12**, 3582–3591.
- 4 J. Chen, X. Wang, D. Wu, J. Zhang, Q. Ma, X. Gao, X. Lai, H. Xia, S. Fan and T.-S. Zhao, *Fuel*, 2019, **239**, 44–52.
- 5 J. Li, T. Yu, D. Miao, X. Pan and X. Bao, *Catalysis Communications*, 2019, **129**, 105711.
- 6 X. Liu, M. Wang, C. Zhou, W. Zhou, K. Cheng, J. Kang, Q. Zhang, W. Deng and Y. Wang, *Chem. Commun.*, 2017, **54**, 140–143.
- 7 J. Gao, C. Jia and B. Liu, *Catal. Sci. Technol.*, 2017, **7**, 5602–5607.