Supplementary Information (SI) for Chemical Communications.

Controlled acidity-mediated short-chain olefins synthesis over Mn-Zn-Zr/Zn-SAPO-34 catalyst via CO_2 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_2O_3: 1.06 P_2O_5: 1.08 SiO_2: 2.09 Morpholine: 66 H_2O. 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_2, 15%In/12.75%ZnO/72.25%ZrO_2, and 15%Mn/12.75%ZnO/72.25%ZrO_2 catalysts were prepared by the co-precipitation method. The calculated amount of salts In $(NO_3)_3{\cdot}xH_2O$, Mn $(NO_3)_2{\cdot}4H_2O$, Zn $(NO_3)_2{\cdot}6H_2O$, and $ZrO(NO_3)_2{\cdot}xH_2O$ 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 Na2CO3 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® 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_2 adsorption-desorption isotherms at 93 K were measured using a Micromeritics ASAP 2020 Surface Area & Porosity Analyzer, applying the BET equation. The ^{29}Si and ^{27}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_3 Temperature-Programmed Desorption (NH_3 TPD) experiments were carried out using the Micrometrics® 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_2 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 $9.5 g \cdot g_{cat}^{-1} \cdot h^{-1}$ of methanol was fed into the reactor using an HPLC pump which was first evaporated at 120 °C and then diluted with the 20 ml flow N_2. After 60 min of reaction at 300 °C, the reactants and products were analyzed using an online Agilent 7890B GC system. The temperature was further increased to 340, 360, and 380 °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,

$$Methanol\ conversion\ (\%) = \frac{[mole\ of\ methanol]in - [mole\ of\ methanol]out}{[mole\ of\ methanol]in} * 100 \qquad (1)$$

$$Selectivity\ of\ a\ product(\%) = \frac{[mol\ of\ that\ product\ formed\ ]}{[Total\ mol\ of\ products\ formed]} * 100 \qquad (2)$$

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_2 hydrogenation to short-chain olefins

The CO_2 hydrogenation to short-chain olefins activity of the $ZnO\text{-}ZrO_2$-based oxides and 5%Zn-SAPO-34 was tested in high pressure fixed-bed continuous flow stainless steel reactor. First, $ZnO\text{-}ZrO_2$-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_2 balanced N_2 at 400 °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 °C temperature, and 20 bar pressure with a total GHSV of 5600 ml g_{cat}^{-1} h^{-1} having H_2: CO_2: N_2 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_2: CO: N_2 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_2 conversion, CO conversion, and product selectivity were calculated using the following formulas,

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

$$C_n\ Selectivity\ (\%) = \frac{mole\ of\ CO_2\ converted\ to\ C_n}{Total\ mole\ of\ Products\ Formed} * 100 \qquad (4)$$

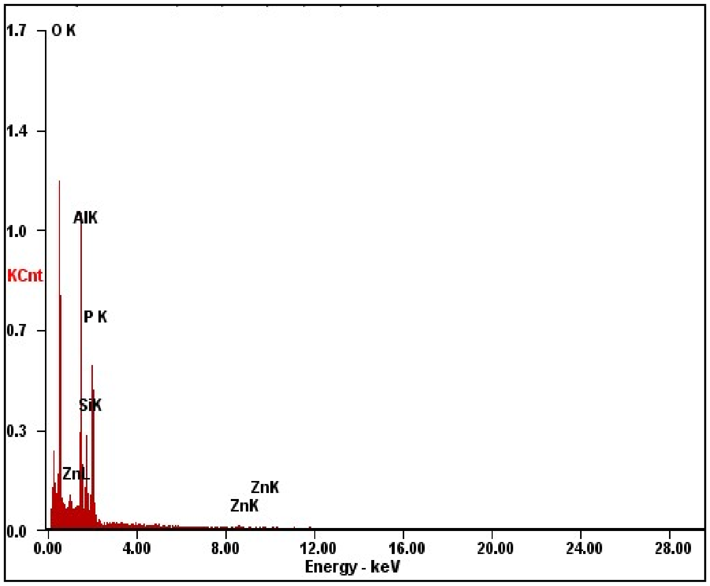
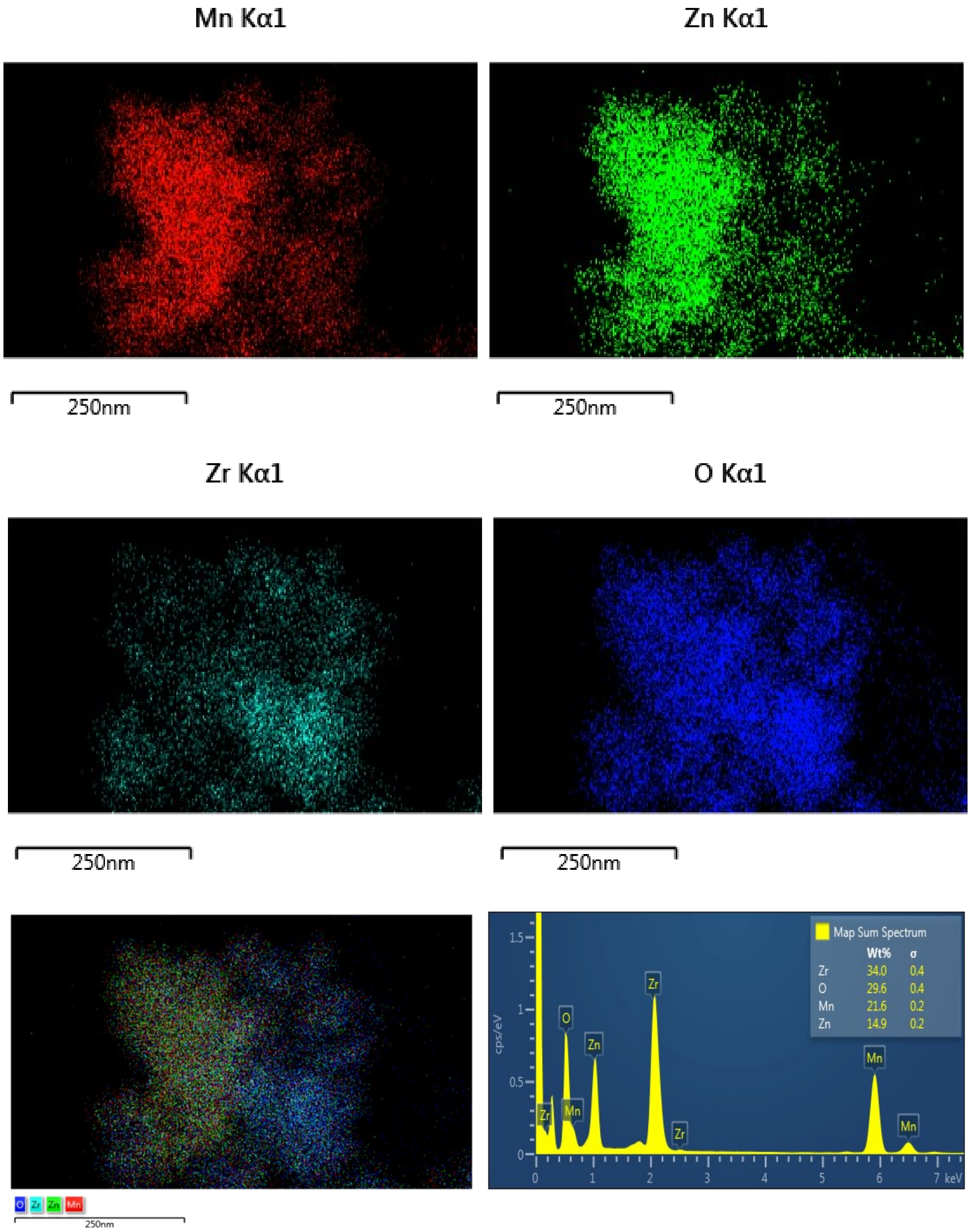


Figure S1. EDX analysis of the Zn-SAPO-34 catalyst



	Wt%	σ
Zr	34.0	0.4
O	29.6	0.4
Mn	21.6	0.2
Zn	14.9	0.2

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

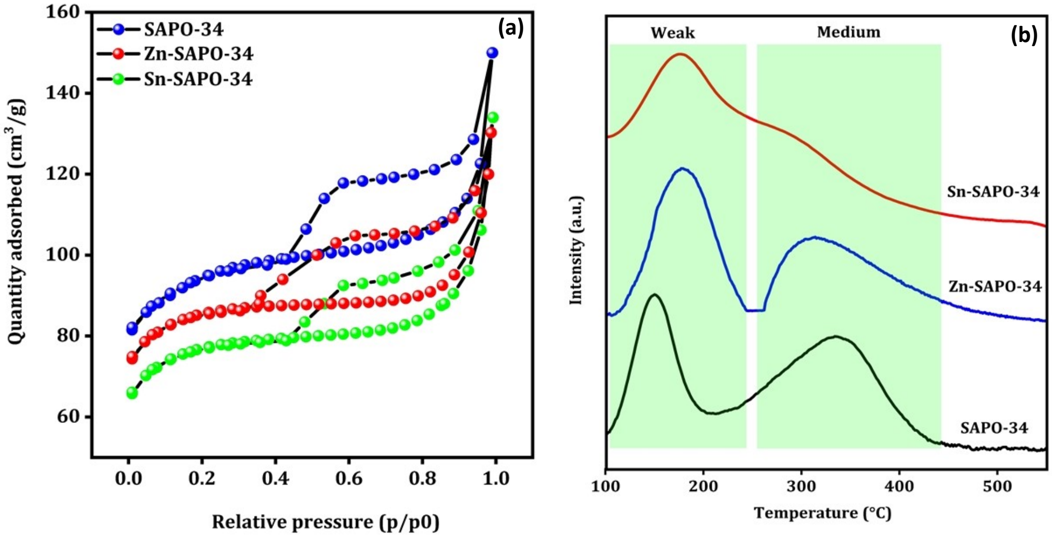


Figure S3. N_2 adsorption-desorption isotherms (a) and NH_3 TPD (b) analysis of SAPO-34 and modified SAPO-34 zeolites

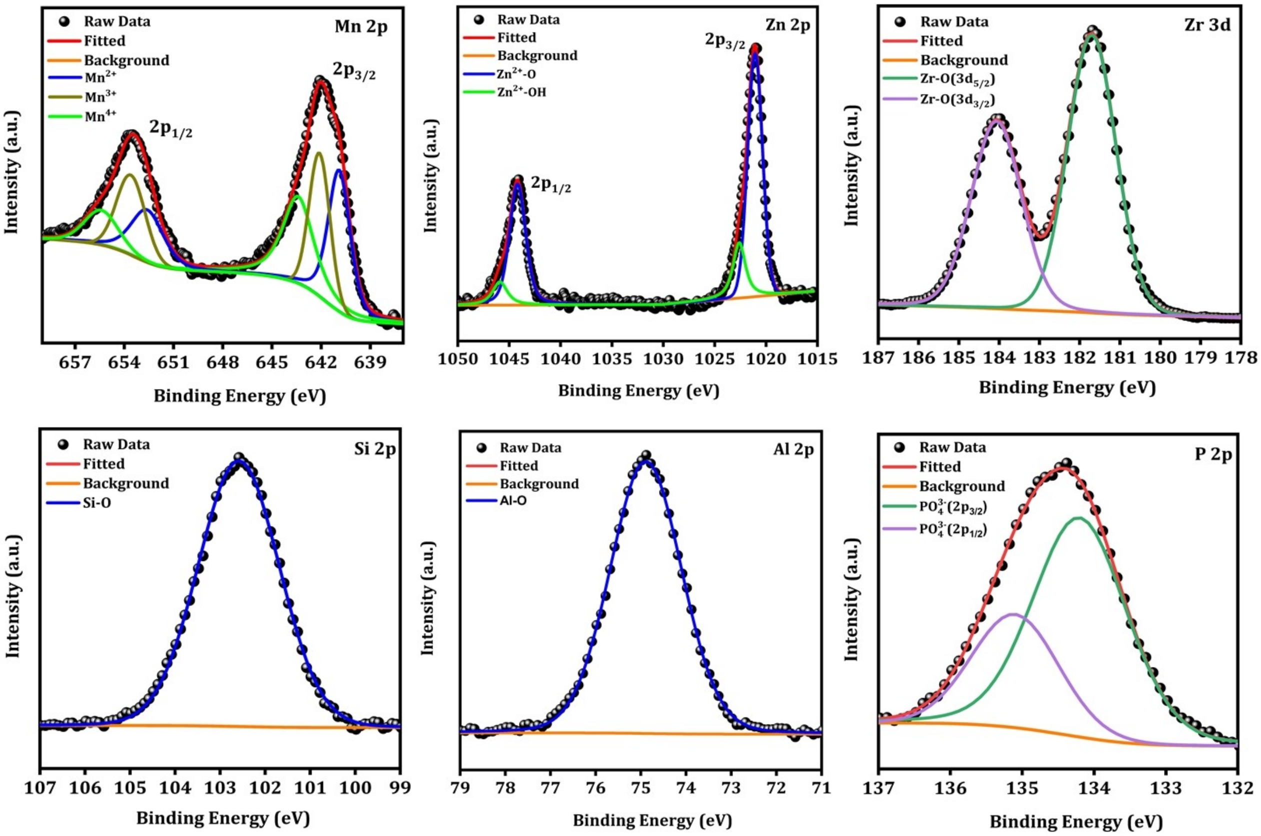


Figure S4. XPS analysis results of Mn-Zn-Zr/Zn-SAPO-34 catalyst

The deconvoluted peaks for the Mn $2p_{3/2}$, which are located at 641.0, 642.1, and 643.5 eV, represent the Mn^{2+}, Mn^{3+}, and Mn^{4+} electronic states of Mn bonded to the oxygen atom, respectively. The Zn 2p region exhibited two strong peaks at 1021.10 eV (Zn $2p_{3/2}$) and 1044.10 eV (Zn $2p_{1/2}$), which can be ascribed to Zn^{2+} ions in ZnO species. The Zr 3d region exhibited binding energy peaks at 181.7 eV ($3d_{5/2}$) and 184.0 eV ($3d_{3/2}$) with strong spin-orbit coupling for the Zr^{4+} oxidation state in the ZrO_2 phase. In Si 2p XPS, a single peak at 102.6 eV can be attributed to the Si^{4+} oxidation state in the Si-O bonds. Similarly, the Al 2p XPS analysis also exhibited a binding energy peak at 74.9 eV, which was assigned to the Al^{3+} oxidation state in Al-O bonds. In P 2p XPS, two deconvoluted peaks correspond to the P-O bonds.

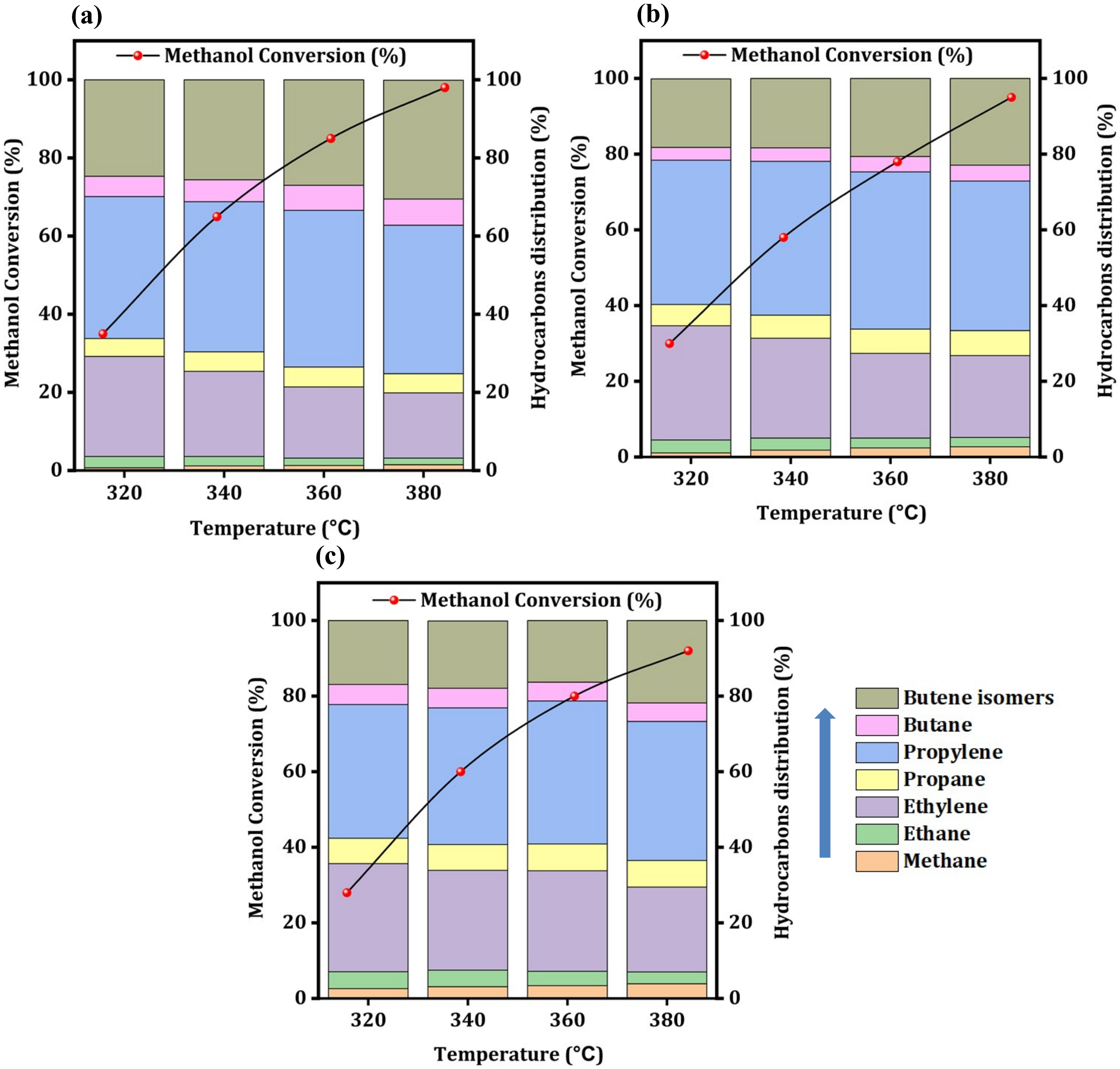


Figure S5. The activity of the SAPO-34 (a), Zn-SAPO-34 (b), and Sn-SAPO-34 (c) Zeolites for methanol to olefins (MTO) reaction

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 °C, respectively. The 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 °C, respectively. The major effect after the Zn and Sn introduction over SAPO-34 can be observed in the C_2-C_3 olefins selectivity. Despite the decrease in methanol conversion, Zn and Sn-SAPO-34 show an increase in the selectivity of the C_2-C_3 olefins compared to the SAPO-34. At 340 °C, C_2-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 C_2-C_3 olefins, it was employed in the subsequent reaction with the ZnO-ZrO_2 based-oxides catalysts.

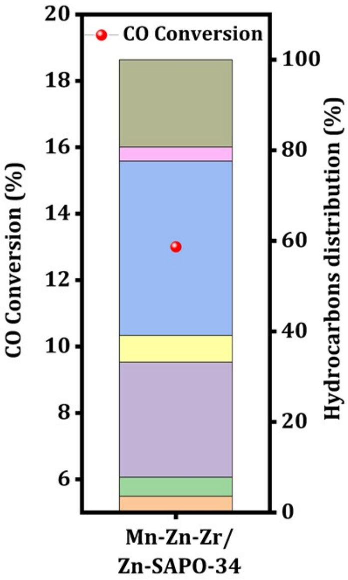


Figure S6. The activity of ZnO-ZrO_2 based oxides admixed with Zn-SAPO-34 catalyst for direct CO hydrogenation

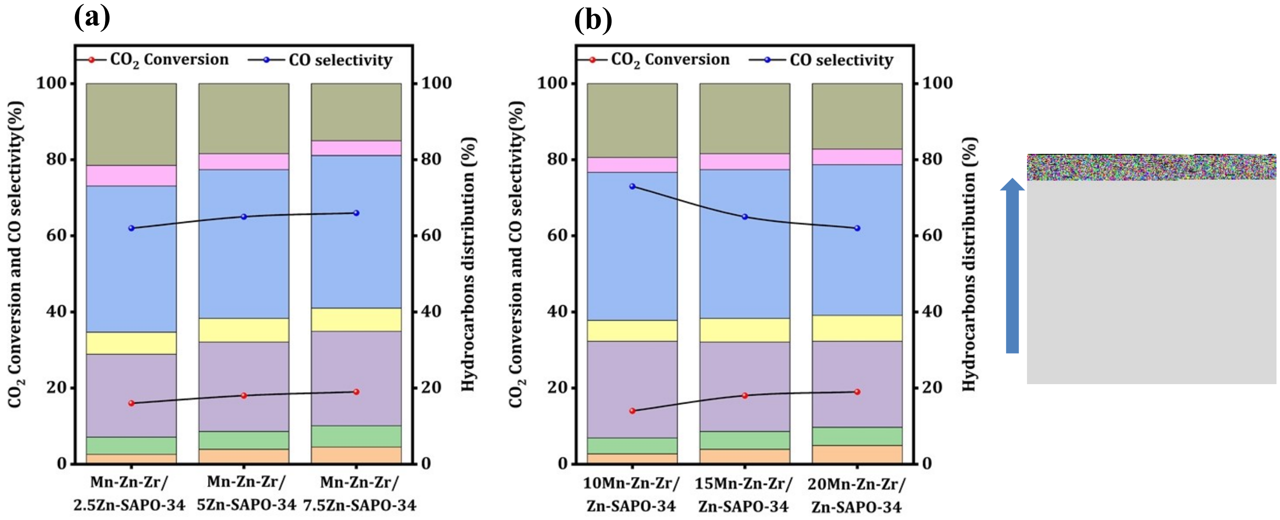


Figure S7. Effect Zn in Zn-SAPO-34 (a), and Mn in Mn-Zn-Zr oxides catalysts (b) in catalytic activity

Increasing the wt% of Zn from 2.5 to 7.5% reduced the selectivity of C_4 hydrocarbons while slightly increasing the selectivity of C_2, C_3, and CH_4 hydrocarbons. The CO_2 conversion and CO selectivity variations are interesting since they remain constant after changing the Zn amount. This demonstrates that the effect of Zn loading only affects the performance of SAPO-34 zeolite in the MTO reaction and does not affect the performance of Mn-Zn-Zr oxides in CO_2 hydrogenation. Similarly, as displayed in Figure S7b, the effect of Mn variation on hydrocarbon distribution is negligible. However, we noticed that by increasing the proportion of Mn in Mn-Zn-Zr oxides CO_2 conversion slightly increased with Mn loading from 10 to 20 wt%, with a decrease in CO selectivity.

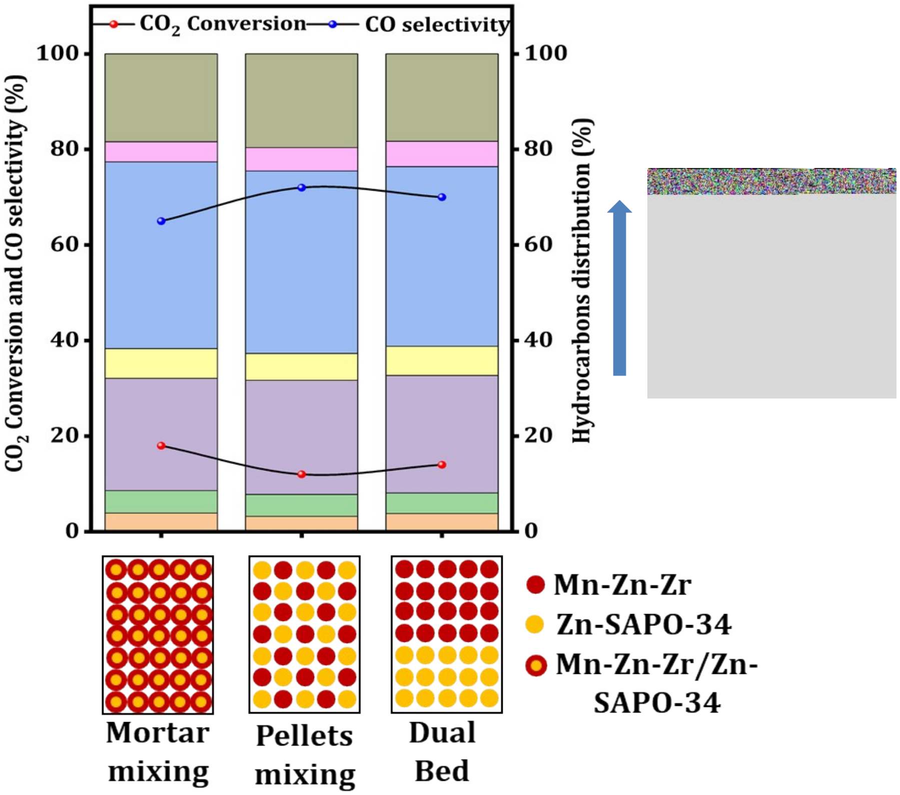


Figure S8. Effect of different integration manner of Mn-Zn-Zr/Zn-SAPO-34 catalyst on CO_2 hydrogenation to short-chain olefin**s**

It was found that the activity of mortar mixing and then pelletized catalyst remained superior to the other integration method. When both components were pelletized separately and subsequently mixed, i.e., pellet mixing or placing oxides above the zeolite’s component, i.e., dual bed, the CO_2 conversion decreased and CO selectivity increased compared to mortar mixing. For pellet mixing and dual bed configuration, CO_2 conversion was 12 and 14% with 72 and 79% CO selectivity, respectively. It's noteworthy to observe that even after altering the active components' integration method, the selectivity of short-chain olefins remains rather constant. The short-chain olefins selectivity for pellet mixing and dual bed configuration was 81.7% and 80.5%, respectively.

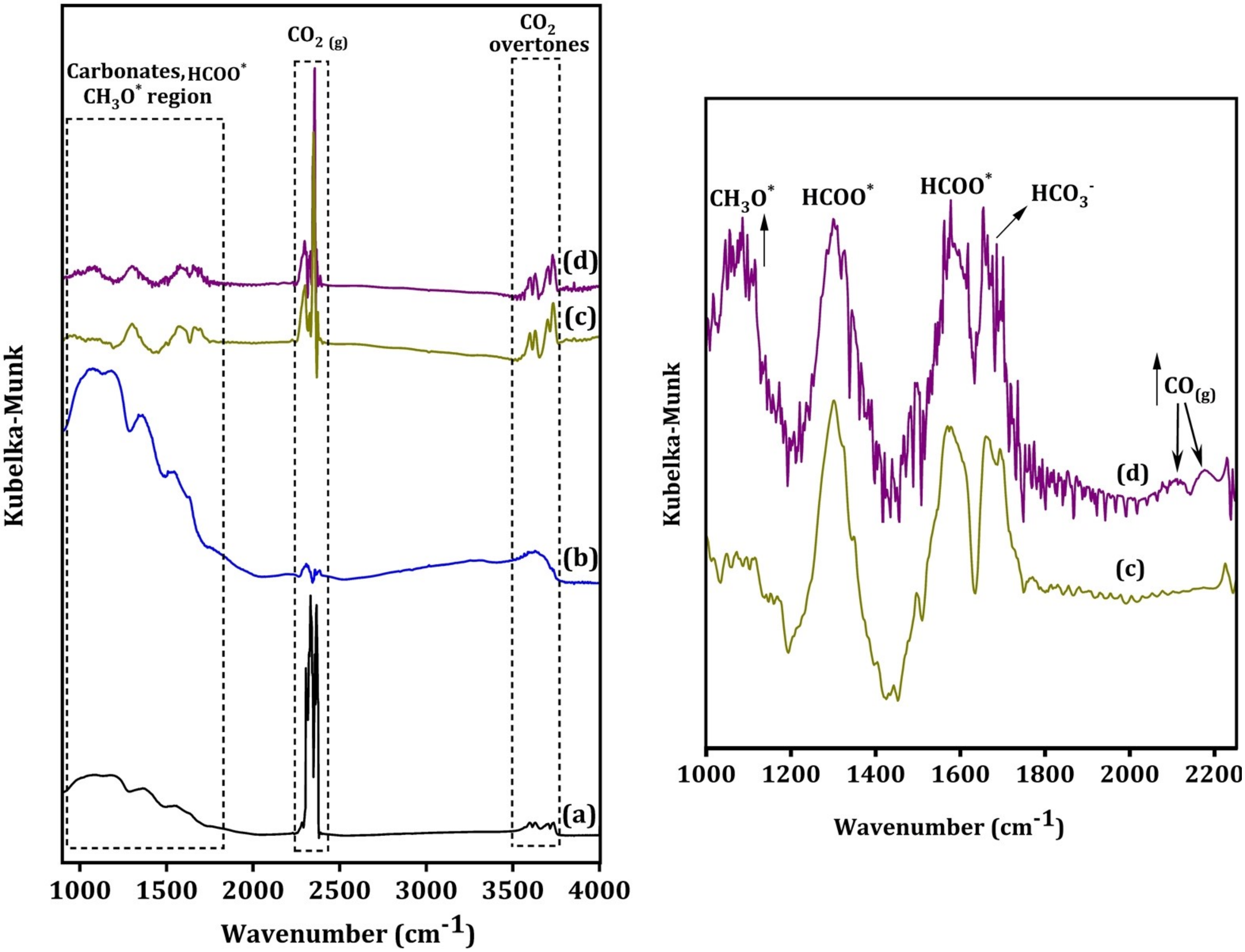


Figure S9. *in-situ* DRIFTS spectra over Mn-Zn-Zr/Zn-SAPO-34 catalyst at 340 °C, after CO_2 adsorption for 15 min (a) then He Purging (b), and after flow of H_2+CO_2 (3:1) for 10 min (c) and 20 min (d)

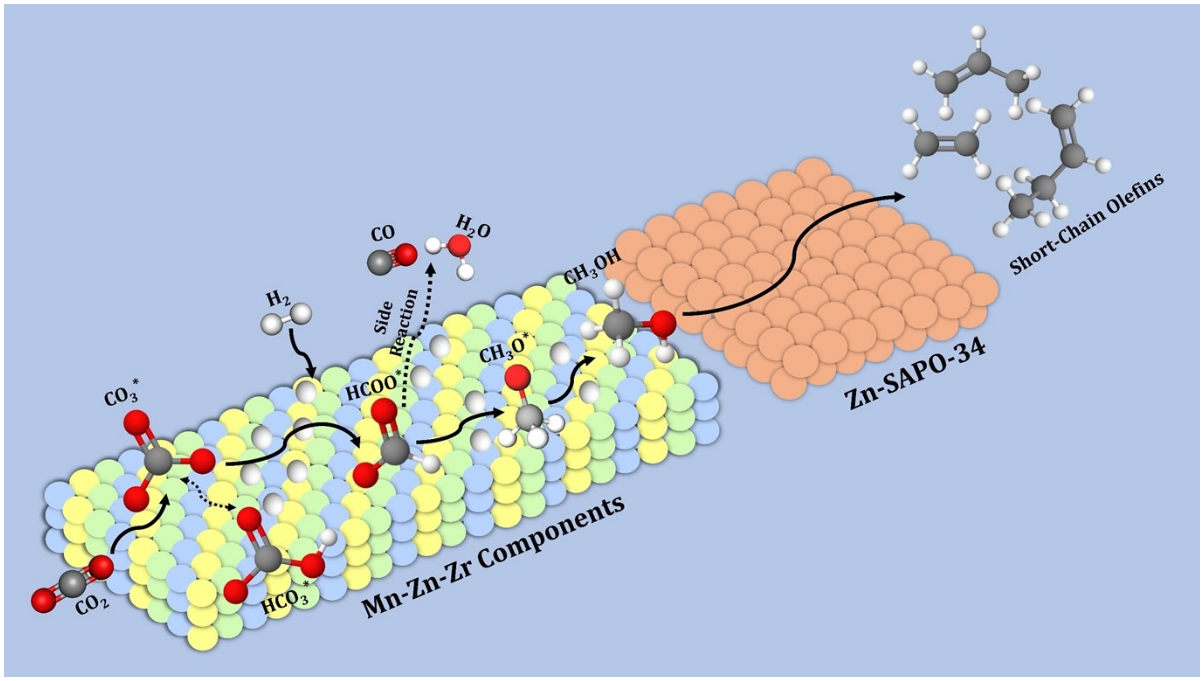


Figure S10. Proposed reaction pathway for methanol synthesis based on the *in-situ* DRIFTS analysis results obtained over Mn-Zn-Zr/Zn-SAPO-34 catalyst

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_{cat}^{-1} h^{-1}), H_2: CO_2 ratio	CO_2 conversion (%)	CO Selectivity (%)	Selectivity (%) in HCs		C_2-C_4 O/P ratio	Ref.
					CH_4	C_2-$C_4^=$		
1	$ZnAl_2O_4$/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_2O_3–$ZnZrO_x$/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_2O_3/SAPO-34	390, 40, 1800, 4	27.6	85	1.8	83.9	6.5	5
6	$ZnGa_2O_4$/SAPO-34	370, 30, 2700, 3	13	50	1.0	86	8.6	6
7	In_2O_3/ZrO_2 SAPO-34	400, 15, 15000, -	23	90	-	82	-	7
8	**Mn-Zn-Zr/Zn-SAPO-34**	**340, 20, 5600, 3**	**18**	**65**	**3.9**	**81**	**5.4**	**Our Work**

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