

Supporting Information

Bifunctional Catalyst Ga₂O₃-*m*ZrO₂/SAPO-34 for CO₂ Hydrogenation: Ga₂O₃-*m*ZrO₂ Improving Light Olefins

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1. Materials and Methods

1.1. Materials

zirconium nitrate ($\text{Zr}(\text{NO}_3)_4 \cdot 5\text{H}_2\text{O}$, 99.99%) and Gallium nitrate (III) hydrate ($\text{Ga}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$, 99.9%) were purchased from Macklin. Glucose (99.5%) was purchased from Aladdin. Citric acid anhydrous and ethanol (EtOH , $\geq 99.7\%$) were purchased from Shanghai Titan Scientific Co., Ltd. Aqueous ammonia (NH_4OH , 25~28% in H_2O) was provided from Shanghai Boer Chemical Reagent Co., Ltd. Ammonium carbonate ($(\text{NH}_4)_2\text{CO}_3$, Analytical Reagent) was purchased from 9Ding Chemical. Tetraethylammonium hydroxide (TEAOH, 35wt% in water) and colloidal silica (SiO_2 , 30% in H_2O) were supplied from Alfa Aesar. Phosphoric acid (H_3PO_4 , $\geq 85.0\text{wt}\%$) was supplied from Shanghai Ling feng Chemical Reagent Co., Ltd. Aluminum isopropoxide (AIP, $> 99\text{wt}\%$) was purchased from Sinopharm Chemical Reagent Co., Ltd.

1.2. Experimental Methods

1.2.1. Synthesis of $m\text{ZrO}_2$, $t\text{ZrO}_2$, Ga_2O_3 , GaZrO_x (coprecipitation, sol-gel) and Ga_2O_3 - $m\text{ZrO}_2$ / $t\text{ZrO}_2$ with different loading ratios of Ga_2O_3 (x% G-mZ/tZ)

The $m\text{ZrO}_2$ was synthesized by precipitation method with slightly adjustment according to previous study.¹ $\text{Zr}(\text{NO}_3)_4 \cdot 5\text{H}_2\text{O}$ was dissolved in water, and the mixed solution of NH_4OH and ethanol ($V_{\text{NH}_4\text{OH}}:V_{\text{Ethanol}} = 1:3$) was added slowly and steadily until the pH reached 9.2. The

suspension was continuously vigorously stirred for 30 minutes at 80 °C. Then, the solid was separated by filtration, washed three times with deionized water, dried at 80 °C, and calcined at 500 °C for 3 hours in muffle furnace. The tZrO₂ was synthesized by precipitation method with slightly adjustment according to previous study.² Zr(NO₃)₄·5H₂O was dissolved in H₂O, and a certain concentration of (NH₄)₂CO₃ aqueous solution was added slowly and steadily until the pH maintained 7.0. The solution was then stirred at 70 °C for about 4 hours, aged at 70 °C for 12 hours, centrifuged, washed, and dried. Finally, the precipitation was calcined at 500 °C for 5 hours.

For the synthesis of Ga₂O₃, Ga(NO₃)₃·xH₂O was dissolved in deionized water. An (NH₄)₂CO₃ aqueous solution of a certain concentration was then added slowly and steadily at 30 °C while continuously measuring the pH. When a clear precipitate had formed and the pH approached 7.0, the addition rate was reduced but remained steady to stabilize the pH around 7.0. The mixture was stirred at 70 °C for 2 hours, subsequently centrifuged, dried, and calcined at 500 °C for 3 hours. GaZrO_x (co-precipitation) was synthesized similarly to Ga₂O₃, but included both Ga and Zr elements with a Ga₂O₃ to ZrO₂ mass ratio of 0.15, designated as GaZrO_x(C). GaZrO_x (sol-gel) has been slightly adjusted on the basis of previous studies.³ The compound was first synthesized by dissolving specific Ga and Zr ions in water (Ga₂O₃ to ZrO₂ mass ratio of 0.15) and stirring at room temperature for 2 hours. The chelating agent glucose (glucose to metal ion molar ratio of 3:1) was then added, and stirring continued for 1 hour to evenly mix the metal ions and glucose. The mixture was then stirred in an 80 °C oil bath until a gel formed, dried at 110 °C, and calcined at 300 °C for 1 hour, followed by 500 °C for 3 hours. The sample is labeled

as $\text{GaZrO}_x(\text{S})$.

$x\%$ G- $m\text{Z}$ ($x = 5, 10, 15, 20, 25$, $x = m(\text{Ga}_2\text{O}_3)/m(m\text{ZrO}_2)$) catalysts were prepared by citric acid complex method. Taking 5% G- $m\text{Z}$ as an example, 0.068 g $\text{Ga}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$ were dissolved in 25 mL H_2O , then 0.0615 g citric acid was slowly added to the above solution. After stirring for 1 h, 0.5 g carrier $m\text{ZrO}_2$ was added, and the mixture was ultrasonic treated for 2 h. Subsequently, the above solution was stirred at 80 °C until it became a gel. Then, the product was dried at 100 °C and calcined at 450 °C for 4 h. Similarly, catalysts with different loading ratios of Ga_2O_3 only need to change the mass of $\text{Ga}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$ in the precursor solution and the corresponding citric acid mass. 15% G- $t\text{Z}$ was synthesized by the same method, except that the $m\text{ZrO}_2$ carrier was replaced by $t\text{ZrO}_2$.

1.2.2. Synthesis of SAPO-34

The SAPO-34 molecular sieve was prepared by hydrothermal method with the following molar compositions: 1.0 Al_2O_3 : 1.0 P_2O_5 : 0.15 SiO_2 : 2.0 TEAOH : 50 H_2O . Briefly, AIP, TEAOH and deionized water were mixed together and stirred at room temperature for 30 minutes until a uniform suspension was formed. Then H_3PO_4 and colloidal silica are slowly added to the above solution and vigorously stirred for 4 h to form colloidal sol. After that, the obtained colloidal sol was sealed into a 30 ml Teflon-lined autoclave and crystallized at 200 °C for 20 h. The solid was centrifuged, washed three times with deionized water, dried at 373 K, and calcined at 550 °C for 10 hours in muffle furnace.

1.2.3. Synthesis of x% G-mZ/SAPO-34

Bifunctional catalysts were prepared by physical grinding method, in which the SAPO-34 and G-mZ oxides were ground in agate mortar for 10 minutes.

1.3. Catalyst characterization

The Powder X-ray diffraction analysis (PXRD) results was performed on a Bruker D8 Advance with Cu-K α radiation in the 2θ range of 5-80 $^\circ$. N₂ sorption isotherms of samples were measured on a JK-122F instrument after they were treated at 200 $^\circ$ C for 6 hours under high vacuum. Scanning electron microscopy (SEM) imaging was performed on a ZEISS Gemini 300 field emission scanning electron microscope. Transmission electron microscopy (TEM) imaging and mapping were performed with a JEM-2100 at 200kV. The surface element content, valence state and oxygen vacancy of the catalysts were detected by X-ray photoelectron spectrometer (XPS) using Thermo Scientific Nexsa. The contents of Ga and Zr were determined by inductively coupled plasma emission spectrometer (Agilent 725 ICP-OES). Programmed temperature desorption (TPD) was recorded on the Mike AutoChem1 II 2920 instrument. In general, the 100 mg catalyst was pretreated in a high-purity He flow (30 mL/min) at 300 $^\circ$ C for 1 h, then cooled to room temperature, and CO₂ or H₂ was introduced for saturation adsorption. Temperature rise from 50 $^\circ$ C to 600 $^\circ$ C at a rate of 10 $^\circ$ C/min, and desorption CO₂ or H₂ was monitored by a heat transfer detector (TCD). In situ diffuse reflection infrared Fourier transform spectroscopy (DRIFTS) experiments have been carried out with the infrared diffuse reflection

spectrometer (Thermo, Nicolet 6700) and MCT detector. First, the catalyst was treated at 400 °C in Ar for 1 h, then the catalyst was cooled to 280 °C to obtain the background spectrum. Then, the sample was exposed to a mixture of CO₂/H₂ = 1:3, treated for 10 min and the spectrum was collected. After that, the temperature was gradually increased from 280 °C to 400 °C with 10 °C as a gradient, each temperature was maintained for about 10 minutes, and the FT-IR spectrum of the substance produced on the catalyst surface was recorded.

1.4. Catalyst evaluation

The experiment was carried out in a continuous flow fixed-bed reactor. Before each catalytic test, 0.3 g catalyst was loaded into the center of the reactor and fixed with quartz sand and quartz cotton. The catalyst was subsequently pretreated under Ar for 2 h at 673 K at a flow rate of 20 mL/min, under atmospheric pressure. Then, the gas flow was switched to the reactant mixture with V(H₂):V(CO₂):V(Ar) = 72:24:4. Ar, which does not participate in the reaction, was used as an internal standard gas to calculate the molar amount of CO₂ at the inlet. After the flow and pressure stabilized, raised the temperature to the required reaction temperature .the product was analyzed on-line using gas chromatograph equipped with thermal conductivity (TCD) and flame ionization detector (FID). The TDX-1 packed column was connected to TCD and HT-PLOT Al₂O₃/S capillary column (30 m × 0.53 mm × 25 μm) were connected to FID. Each experiment's carbon balance is above 95%. In the reaction, the selectivity of liquid products is below 0.5%*C*; therefore, liquid products are not considered when calculating product selectivity.

CO₂ conversion, CO selectivity, C_nH_m selectivity and C₂⁻-C₄⁻ yield were calculated by the

following equation:

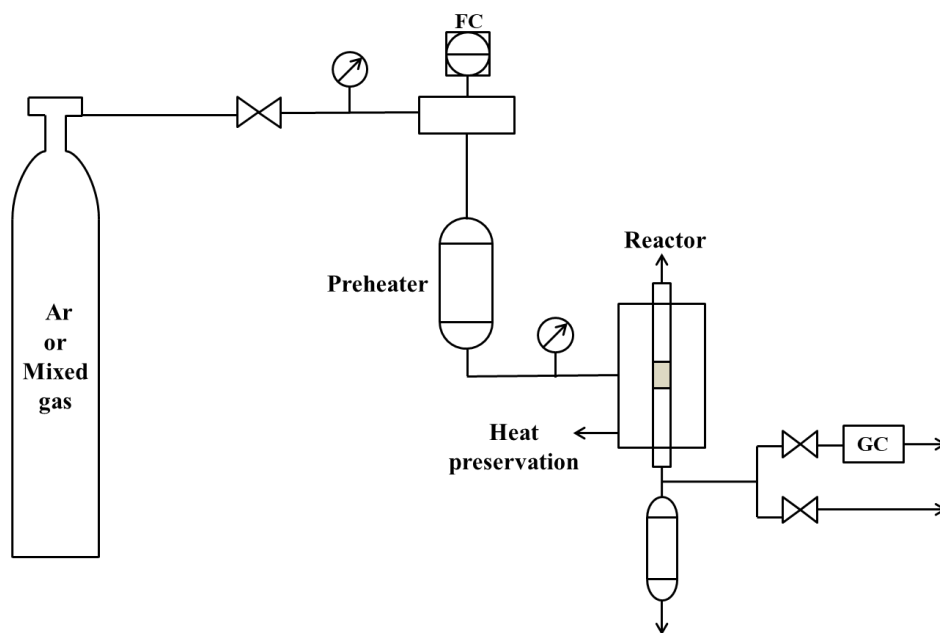
$$CO_{2 \text{ inlet}} = \frac{Ar_{\text{outlet}}}{4\%} \times 24\%$$

$$X_{CO_2} = \frac{CO_{2 \text{ inlet}} - CO_{2 \text{ outlet}}}{CO_{2 \text{ inlet}}} \times 100\%$$

$$S_{CO} = \frac{CO_{\text{outlet}}}{CO_{2 \text{ inlet}} - CO_{2 \text{ outlet}}} \times 100\%$$

$$S_{C_nH_m} = \frac{n C_nH_m}{\sum_{n=1}^i n C_nH_m} \times 100\%$$

$$Y_{C_2^-C_4^-} = X_{CO_2} \times S_{C_2^-C_4^-} \times (1 - S_{CO})$$



Scheme S1. Experimental test device diagram.

2. Results and Discussion

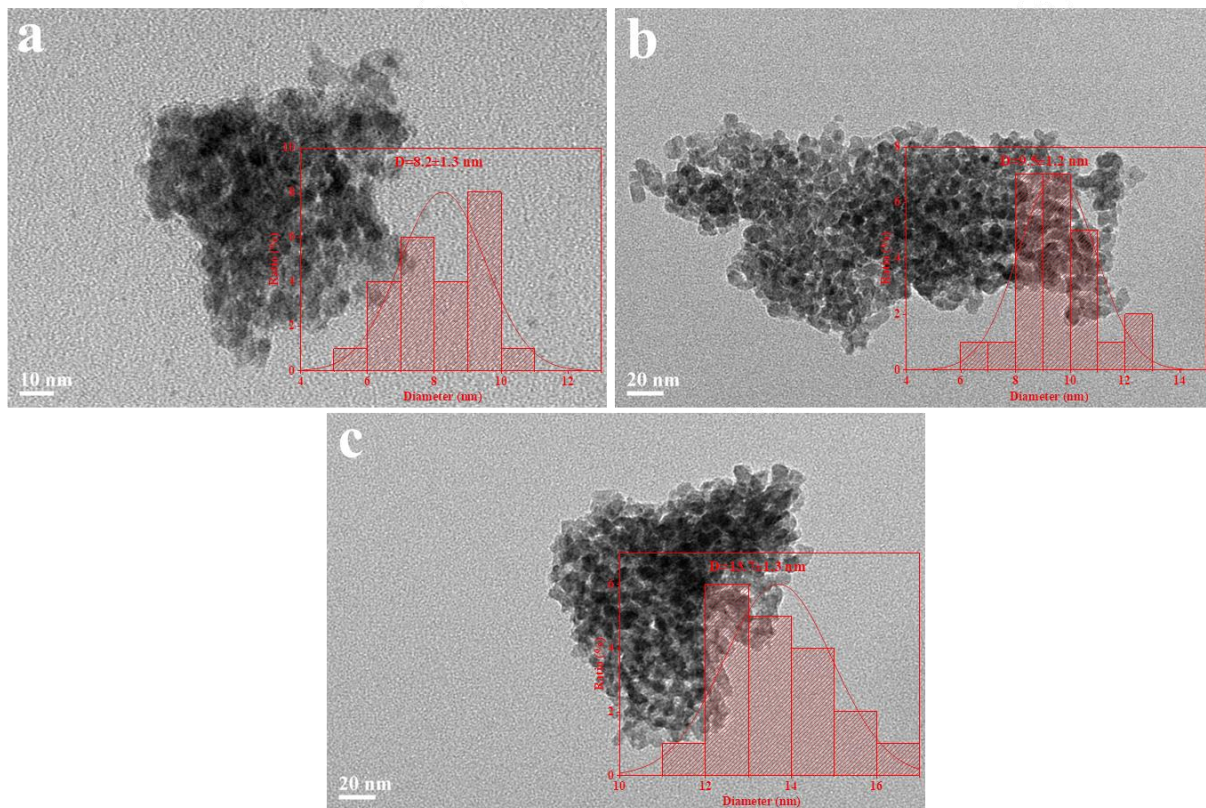


Figure S1. TEM images and the particle size distribution of GaZrO_x(C) (a), GaZrO_x(S) (b) and 15% G-tZ (c).

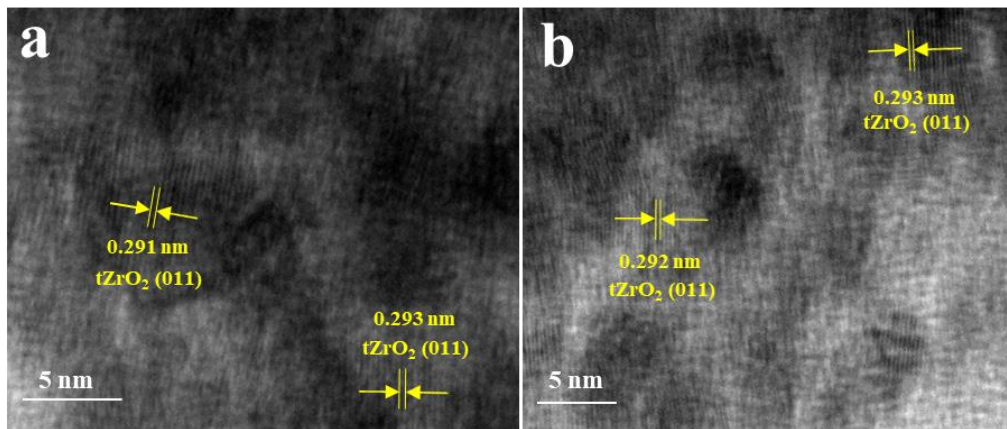


Figure S2. HRTEM images of the 15% G-*mZ*.

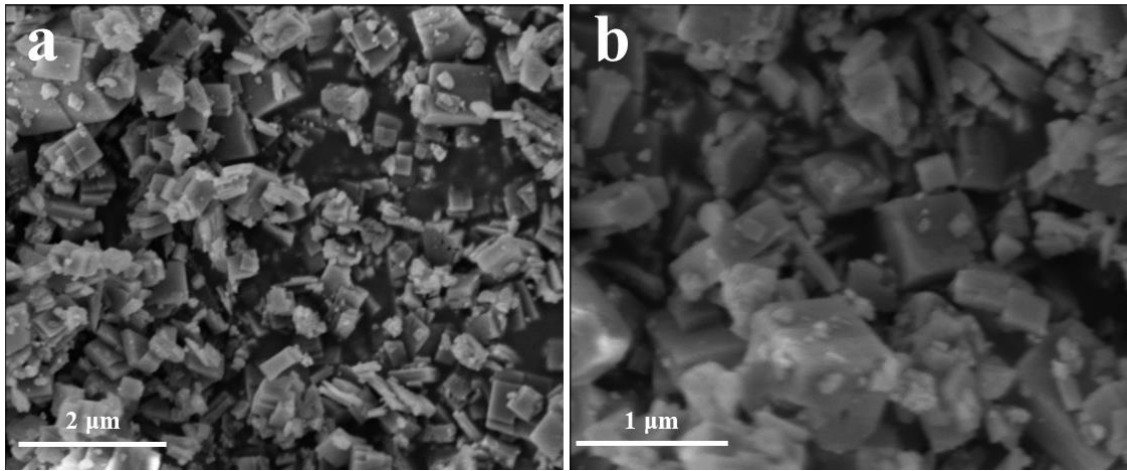


Figure S3. SEM of the 15% G-mZ/SAPO-34 after reaction.

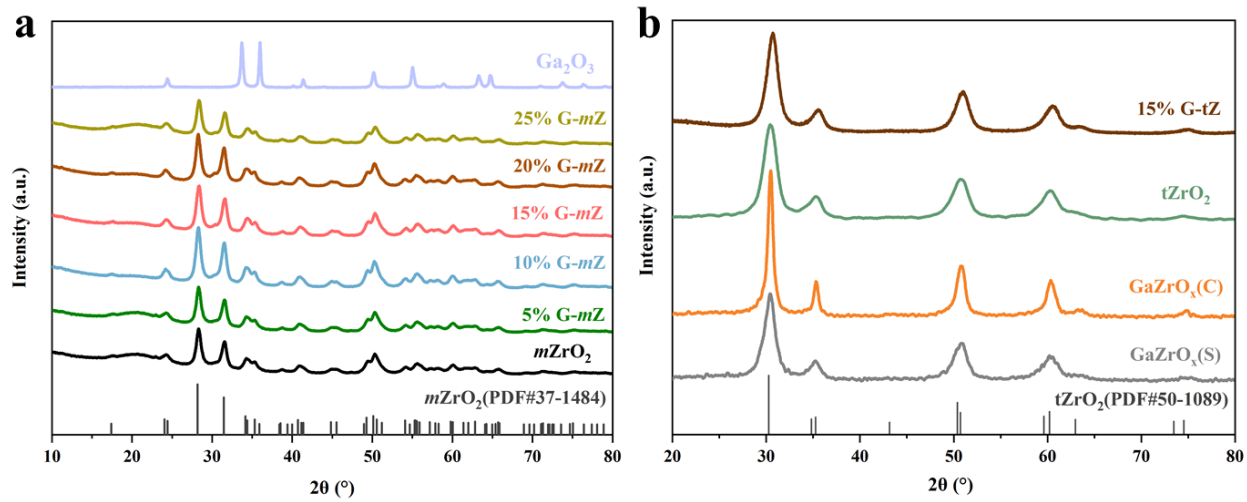


Figure S4. Powder X-ray diffraction patterns of the prepared oxides.

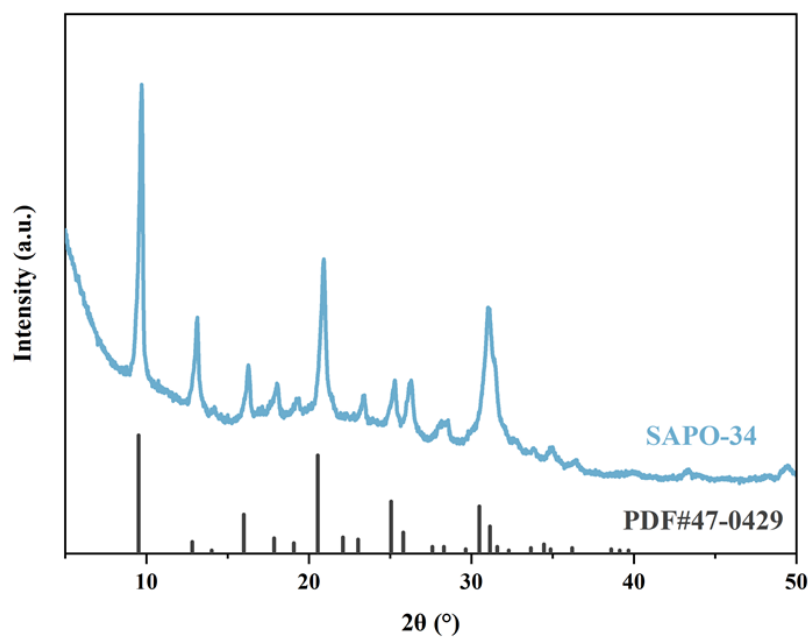


Figure S5. Powder X-ray diffraction patterns of SAPO-34.

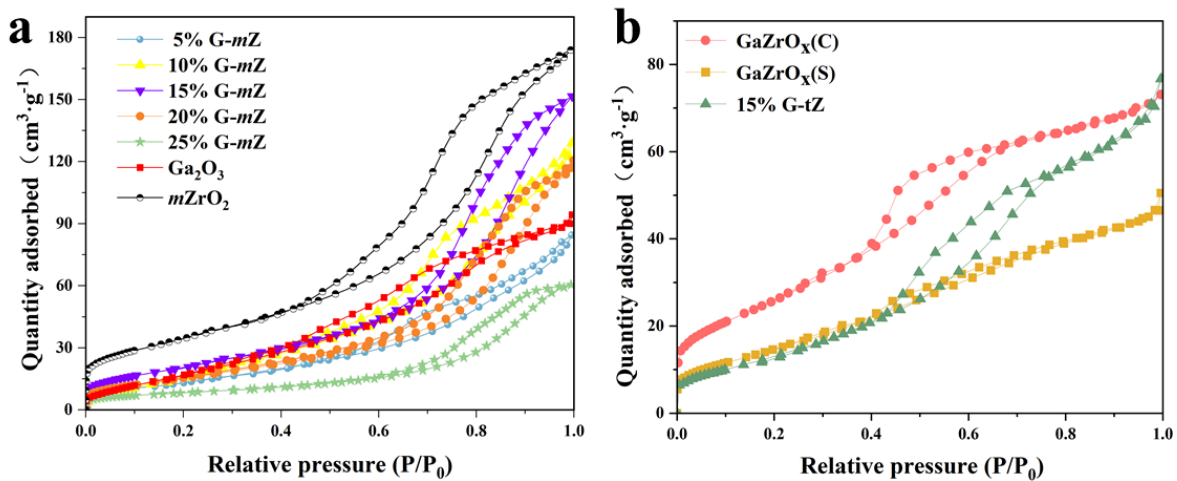


Figure S6. N_2 adsorption-desorption isothermal curves of $mZrO_2$, Ga_2O_3 and $x\%$ G-mZ (a), $GaZrO_x(C)$, $GaZrO_x(S)$ and 15% G-tZ (b).

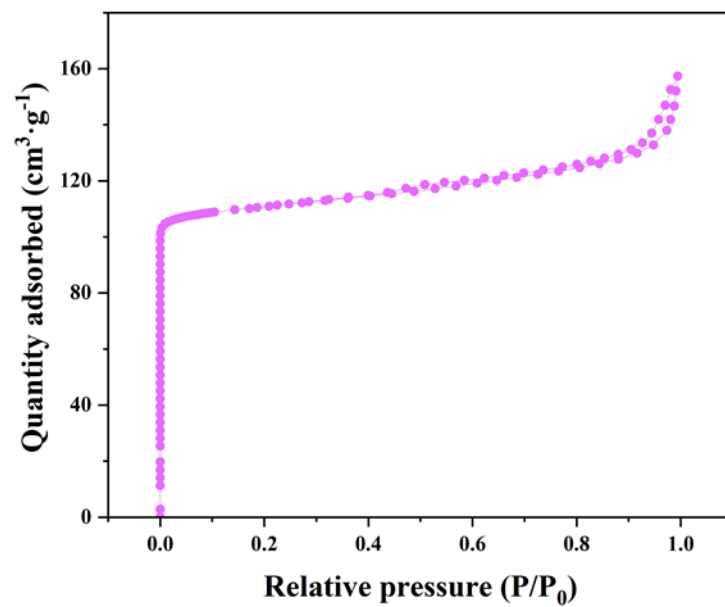


Figure S7. N₂ adsorption-desorption isothermal curves of SAPO-34.

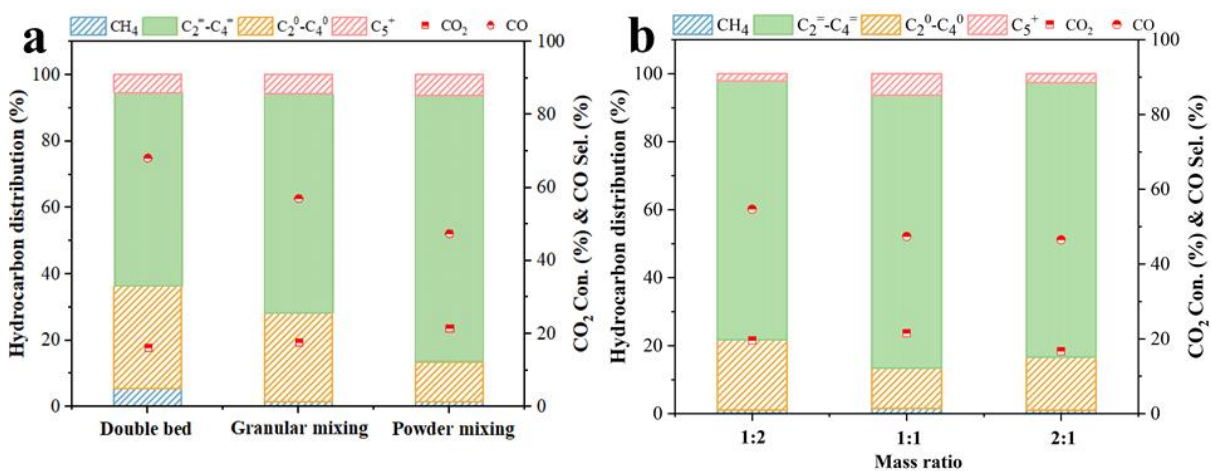


Figure S8. Effect of operating conditions on catalytic performance over 15% G-mZ/SAPO-34. Adjusting the integration manners of 15% G-mZ and SAPO-34(a), Adjusting the weight ratio of 15% G-mZ to SAPO-34 (b).

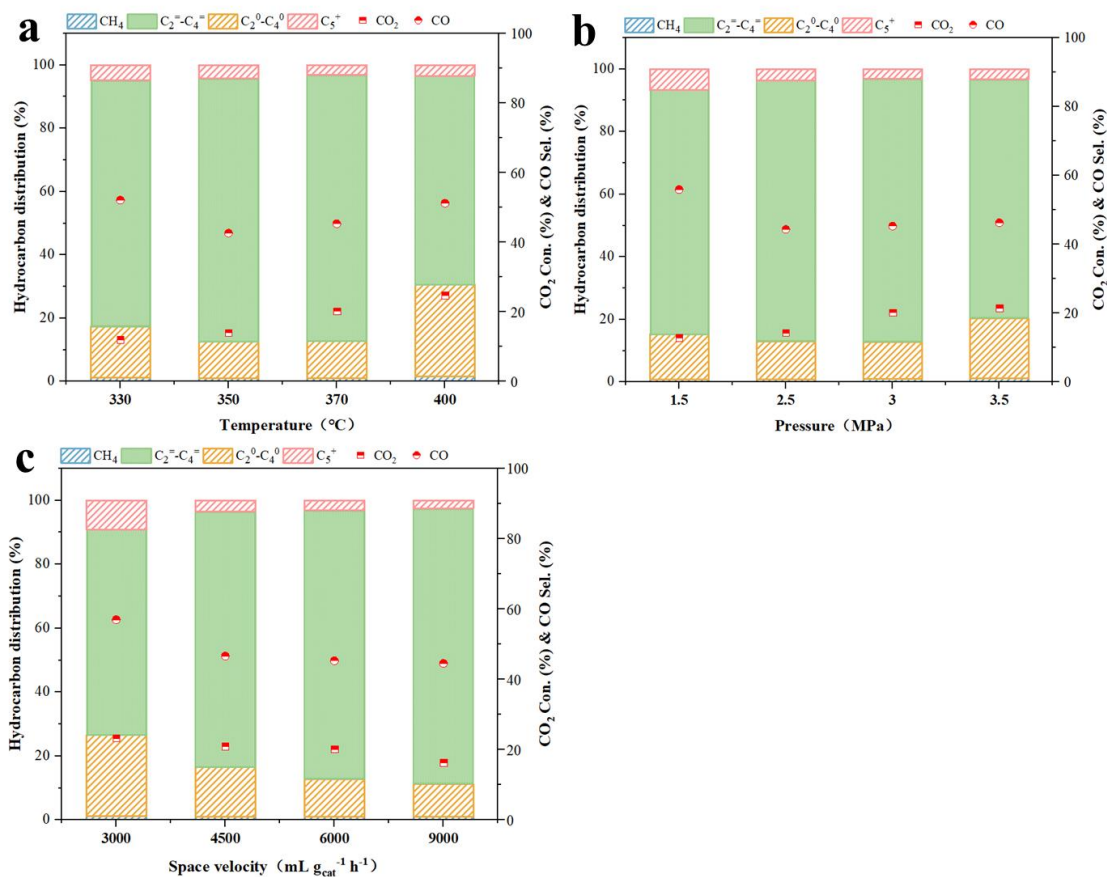


Figure S9. Effect of operating conditions on catalytic performance over 15% G-mZ/SAPO-34. Adjusting the reaction temperature range 330~400 °C (a), Adjusting the reaction pressure range 1.5~3.5 MPa (b) and adjusting the space velocity range 3000~9000 mL g_{cat}⁻¹ h⁻¹ (c).

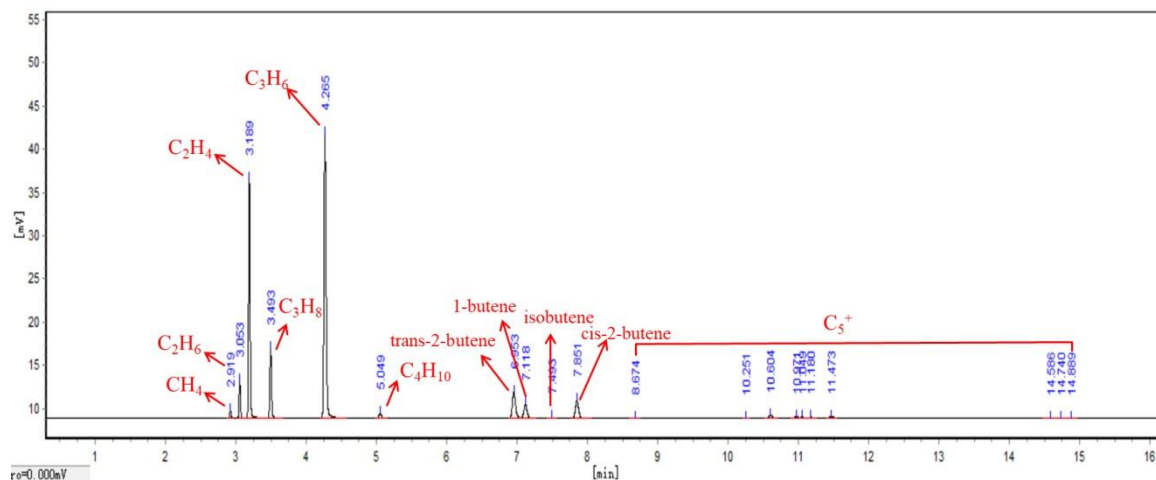


Figure S10. GC chromatograms for CO₂ hydrogenation over 15% G-*m*Z/SAPO-34 catalysts. Reaction conditions: H₂/CO₂ = 3:1, 370 °C, 3.0 MPa and GHSV = 6000 mL g_{cat}⁻¹ h⁻¹.

As can be seen from Figure S10, most of the products are ethylene and propylene, and few alkanes, especially methane.

Table S1. The content of composition of $m\text{ZrO}_2$ and $t\text{ZrO}_2$ in each Ga-Zr oxide.

Samples	$m\text{ZrO}_2$ (%)	$t\text{ZrO}_2$ (%)
15% G- $m\text{Z}$	95.2	4.8
GaZrO _x (C)	0	100
GaZrO _x (S)	0	100
15% G- $t\text{Z}$	0	100

Table S2. The specific surface area and pore volume of catalysts.

Samples	S_{BET} ($\text{m}^2 \text{g}^{-1}$)	V_{total} ($\text{cm}^3 \text{g}^{-1}$)
5% G- <i>m</i> Z	54.6	0.163
10% G- <i>m</i> Z	55.6	0.223
15% G- <i>m</i> Z	72.7	0.228
20% G- <i>m</i> Z	82.7	0.241
25% G- <i>m</i> Z	58.2	0.193
Ga_2O_3	58.6	0.163
<i>m</i> ZrO ₂	120.1	0.267
GaZrO _x (C)	90.2	0.112
GaZrO _x (S)	51.0	0.072
15% G- <i>t</i> Z	45.5	0.114
SAPO-34	595.2	0.357

Specific surface area (S_{BET}) values determined by N₂-Brunauer-Emmett-Teller method.

Total pore volume (V_{total}) determined by Barrett-Joyner-Halenda (BJH) method.

Table S3. The proportion of each component in the oxides.

Catalyst	Ga ₂ O ₃ content		mZrO ₂ content	
	nominal [wt%]	measured [wt%]	nominal [wt%]	measured [wt%]
5% G-mZ	4.8	2.9	95.2	97.1
15% G-mZ	13.0	11.3	87.0	88.7
25% G-mZ	20.0	17.1	80.0	82.9
GaZrO _x (C)	13.0	12.1	87.0	87.9
GaZrO _x (S)	13.0	11.9	87.0	88.1

$$\text{Ga}_2\text{O}_3 \text{ content measured} = \frac{m(\text{Ga}_2\text{O}_3)}{m(\text{Ga}_2\text{O}_3) + m(\text{ZrO}_2)} \times 100\%$$

$$m(\text{Ga}_2\text{O}_3) = \frac{\text{measured } (m(\text{Ga}))}{2M(\text{Ga})} \times M(\text{Ga}_2\text{O}_3); \quad m(\text{ZrO}_2) = \frac{\text{measured } (m(\text{Zr}))}{M(\text{Zr})} \times M(\text{ZrO}_2)$$

Table S4. Comparison of catalytic performance over different bifunctional catalysts for CO₂ hydrogenation to light olefins.

Catalyst	Reaction conditions				X(CO ₂) (%)	S(CO) (%)	S(C ₂ ⁻ -C ₄ ⁻) (%)	Ref.
	<i>T</i>	<i>P</i>	H ₂ /CO ₂	GHSV				
	(°C)	(MPa)	ratio	(mL g _{cat} ⁻¹ h ⁻¹)				
ZnO-ZrO ₂ /SAPO-34	400	2.0	3.0	3600	18.0	65.0	80.0	2
ZnAl ₂ O ₄ /SAPO-34	370	3.0	3.0	5400	15.0	49.0	87.0	4
ZnO-Y ₂ O ₃ /SAPO-34	390	4.0	4.0	1800	27.6	85.0	83.9	5
ZnGa ₂ O ₄ /SAPO-34	400	3.0	3.0	5400	22.0	66.0	80.0	6
In ₂ O ₃ -ZnZrO _x /SAPO-34	380	3.0	3.0	9000	17.0	55.8	85.0	7
ZnZrO ₂ @Al ₂ O ₃ @SAPO-34	380	3.0	3.0	3500	21.0	45.0	75.0	8
CuZnZr@(Zn-)SAPO-34	400	2.0	3.0	3000	19.6	58.6	60.5	9
15% G- <i>m</i> Z/SAPO-34	370	3.0	3.0	6000	20.2	45.3	84.1	This work

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