Supplementary information for

Towards maximizing the In₂O₃/*m*-ZrO₂ interfaces for CO₂-to-methanol hydrogenation

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Experimental Section

1.Materials

Indium nitrate (In(NO₃)₃.xH₂O, \geq 99.0%), zirconyl nitrate (ZrO(NO₃)₂·2H₂O, \geq 99.9%), urea (CO(NH₂)₂, \geq 99.9%), diethylenetriaminepentaacetic acid (DTPA), ethylene diamine tetraacetic acid (EDTA) and nitrilotriacetic acid (NTA) were supplied by Shanghai Aladdin Biochemical Technology. No further purification was performed on any of the chemicals before use. The H₂, CO₂, Ar and He gas are from Air Liquide (Kunshan). Nitrogen is from Shanghai Dumao'ai Purifying Gas Co., Ltd.

2.Catalyst preparation

In15/*m*-ZrO₂-*DTPA* was synthesized by chelating agent assisted impregnation (15 refer to the mass content of In₂O₃). The detailed preparation method of *m*-ZrO₂ refers to the previous work within the research group.¹ Typically, 0.689 g of indium nitrate and 0.850 g of DTPA were dissolved in 100 mL deionized water. Then 3.4 g *m*-ZrO₂ was added to the above solution at 25 °C with ultrasonication for 2 hours and the solvent was removed by rotary evaporator at 65 °C. The resulting solids were dried at 110 °C for 12 h prior to calcination in static air at 400 °C (5 °C min⁻¹) for 4 h. The In15/*m*-ZrO₂-*EDTA* and In15/*m*-ZrO₂-*NTA* were carried out by changing DTPA into EDTA or NTA, while the In15/*m*-ZrO₂ was prepared by the same procedure without adding any chelating agent.

3.Catalyst characterization

Powder X-ray diffraction (XRD) was performed using Bruker D2 with a Cu Ka radiation. N₂ sorption at 77 K was measured in a Micromeritics ASAP2020 Analyzer, following evacuation of the samples at 300 °C for 4 h. The total surface area was determined by applying the BET model. The temperature-programmed desorption of CO₂ (CO₂-TPD) and the temperature-programmed reduction with hydrogen (H₂-TPR) were carried out using a AutoChem 2920 automated chemisorption analyzer (Micromeritics Instrument Crop, USA). The CO₂-TPD measurements over the fresh catalysts encompassed *(i)* a drying step, *(ii)* a pretreatment carried out in Ar, *(iii)* isothermal exposure to CO₂ flow, and *(iv)* a temperature ramp in Ar (CO₂-TPD). The H₂-TPR analyses over the fresh catalysts comprised a drying step (like the one applied for CO₂-TPD) followed by a temperature ramp from 50 °C to 600 °C (5 °C min⁻¹) in a flow of 5 vol.% H₂ in Ar (20 mL min⁻¹).

EPR experiments were carried on a Bruker EMXplus EPR spectrometer. X-ray photoelectron spectroscopy (XPS) was conducted using a Thermo Scientific K-Alpha with Al K α radiation under an ultrahigh vacuum. The C 1s (284.8 eV) was used as the reference

to calculate the binding energies. The thermogravimetric analysis of the samples was examined by using the SDT Q600. Visible Raman spectra were measured on a Renishaw 1000 Microspectrometer using an excitation wavelength of 514 nm. HR-TEM images and EDX mappings were obtained using a JEM-2010 microscope operating at 200 kV. The AC-STEM images were from FEI Titan Themis Z microscope.

In situ DRIFTS experiments were performed using a Fourier Transform infrared spectrometer (Nicolet 6700). Before measurement, the sample was treated with 10 vol.% H₂ in Ar at 300 °C for 1 h. Then the catalyst was cooled down to the desired temperature to obtain the background spectrum. The CO₂ hydrogenation was carried out at 50-250 °C, H₂/CO₂ = 4:1 (20 mL min⁻¹), and 0.1 MPa. The intermediate species adsorption was performed at 250 °C after H₂/CO₂ = 4:1 (20 mL min⁻¹) adsorption for 30 minutes and followed by He (20 mL min⁻¹) purge for 20 minutes.

4.Catalyst evaluation

The catalyst was evaluated in a fixed bed reactor (internal diameter of 8 mm). 100 mg catalyst (40-60 mesh) diluted with quartz (40-60 mesh) was packed in the constant temperature zone of the fixed-bed reactor. The catalyst was pretreated in a stream of 5 vol.% H₂ in N₂ at 300 °C for 2 h. The reaction was conducted under reaction conditions of 5.0 MPa, 180~300 °C, H₂/CO₂ = 4:1, and GHSV = 24,000~48,000 mL g_{cat}⁻¹ h⁻¹. The products were analyzed by an online gas chromatograph (Agilent GC 8860) equipped with a TCD and a flame ionization detector (FID). The CO₂ conversion, methanol selectivity, and methanol space-time yield can be calculated as follows:

$$X(C_{CO2}) = \frac{f_{CH3OH} \times \frac{A_{CH3OH}}{A_{CH4}} + f_{CO} \times \frac{A_{CO}}{A_{CH4}}}{f_{CO2} \times \frac{A_{CO2}}{A_{CH4}} + f_{CH3OH} \times \frac{A_{CH3OH}}{A_{CH4}} + fCO \times \frac{A_{CO}}{A_{CH4}}}$$

$$S(CH_{3}OH) = \frac{f_{CH3OH} \times \frac{A_{CH3OH}}{A_{CH4}}}{f_{CH3OH} \times \frac{A_{CH3OH}}{A_{CH4}} + fCO \times \frac{A_{CO}}{A_{CH4}}}$$

$$F_{CO2} * X_{CO2} * S_{CH3OH} * 32 * 60$$
(4)

$$STY(CH_3OH) = \frac{co2}{22.4 * m_{cat}}$$
 (5)

Xco2 is the conversion of CO₂. S_x is the selectivity of x species in products. To measure the

methanol production, we use $S(CH_3OH)$, which is the ratio of methanol output to catalyst weight and reaction time. We also use a chromatograph that gives us the peak area A_x and the response factor f_x for each component.

Figure S1-S13



Figure S1. XRD patterns of (a) Inx/m-ZrO₂-*DTPA*, (b) Inx/m-ZrO₂ and (c) Comparison of catalysts obtained by two impregnation methods with standard card for indium and zirconium oxides.



Figure S2. HR-TEM images of (a), (b)In15/*m*-ZrO₂, (c), (d) In15/*m*-ZrO₂-*DTPA* and (e), (f) In10/*m*-ZrO₂.



Figure S3 AC-STEM images of $15 \text{In}/m\text{-}ZrO_2\text{-}DTPA$ catalyst insets in a depict the lattice distance of $m\text{-}ZrO_2$ phase in Fourier-transformed space and some areas containing potential overlayers of In_2O_3 growth, which is evidenced by the line profile.^{2, 3}



Figure S4. Elemental mapping results of (a) – (f) $In15/SiO_2$ -based catalysts, (g) – (l) $In15/TiO_2$ -based catalysts and (m) – (r) $In15/Al_2O_3$ -based catalysts.



Figure S5. XRD patterns of In₂O₃ dispersion on various oxide supports.



Figure S6. In-situ (a) (b) thermogravimetry of catalysts' precursors as In15/m-ZrO₂ with different chelating agent and (c) (d) mass spectrometry of In15/m-ZrO₂-*DTPA* and In15/m-ZrO₂ precursors.



Figure S7. XPS spectra of (a) In15/m-ZrO₂-*DTPA*, (b) In15/m-ZrO₂ and (c) *c*-In₂O₃ before and after CO₂-to-methanol reaction.⁴



Figure S8. H₂-TPR profiles of In10/m-ZrO₂ and In15/m-ZrO₂-*DTPA*-calcined in Ar flow at 500 °C for 2 hours.



Figure S9. Catalytic performance under intermittent reaction conditions, displaying the methanol yield with time on stream over 2 switch off. Reaction conditions, 260 °C, $H_2/CO_2 = 4$, 5 MPa, and GHSV = 48,000 mL $g_{cat}^{-1}h^{-1}$. The length of the initial reaction was 3800 min. The duration of each "switch off" process was 180 min under N_2 atmosphere.



Figure S10. Activity of different complexing agent precursors. Reaction conditions: T = 260 °C, 5.0 MPa, H₂/CO₂ = 4, GHSV = 48,000 mL g_{cat} ⁻¹ h ⁻¹.



Figure S11. Correlation between the (a) degree of reduction (DOR), (b) percentage of OVs and the methanol space-time yield (STY) on In15/m-ZrO₂-based catalysts.



Figure S12. Arrhenius plots for (a) methanol and (b) CO formation rates over In15/m-ZrO₂ based catalysts.



Figure S13. Dependence of methanol formation rates on CO_2 partial pressure over In15/m- ZrO_2 basedcatalysts.



Figure S14. In situ DRIFTS spectra of (a), (b) In15/*m*-ZrO₂, (c), (d) In15/*m*-ZrO₂-*DTPA* catalysts during CO₂ hydrogenation followed by He sweep after reaction. Reaction conditions: 0.1 MPa, 250 °C, 50 mL⁻¹ min, H₂/CO₂ = 4.⁵



Figure S15. (a) CO₂-TPD and (b) H₂-TPD of c-In₂O₃, m-ZrO₂, In15/m-ZrO₂, In15/m-ZrO₂-DTPA.



Figure S16. Activity at (a) 300 °C, 320 °C, (b) different pressure and (c) different GHSV of In15/*m*-ZrO₂ and In15/*m*-ZrO₂-*DTPA*.



Figure S17. Infrared spectrum of In-DTPA impregnated m-ZrO₂ and as-calcined In15/m-ZrO₂-DTPA.



Figure S18. N₂ sorption isothermals of c-In₂O₃, m-ZrO₂, In15/m-ZrO₂, In15/m-ZrO₂-DTPA.

Table S1-S5

Catalysts	BET surface area ^[a] (m ² /g)	BJH pore Volume ^[a] (cm ³ /g)	d _{In2O3} ^[b] [nm]	In/wt% [c]
<i>m</i> -ZrO ₂	89.8	0.27	-	-
In15/ <i>m</i> -ZrO ₂	87.1	0.14	8	14.8
In15/m-ZrO ₂ -DTPA	89.4	0.12	-	15.2
$c-In_2\Theta_3$	24.4	0.14	-	-
In15/ <i>m</i> -ZrO ₂ -used	84.3	0.12	8	14.4
In15/m-ZrO ₂ -DTPA-used	88.1	0.11	-	15.1

Table S1. Characterization of the supported catalysts after CO₂ hydrogenation.

[a] N₂ sorption. [b] Determined by Sherrer equation using XRD. [c] ICP-OES.

Sample description	B. E.	Surface concentration (%)					
	3d _{3/2} (eV)	3d _{5/2} (eV)	In	Zr	0	С	In/Zr
c-In ₂ O ₃	452.1	444.4	-	-	-	-	-
In15/ <i>m</i> -ZrO ₂	452.1	444.4	3.7	24.2	45.0	27.1	15.2
In15/ m -ZrO ₂ - $DTPA$	452.1	444.4	7.0	21.7	43.5	27.8	32.4

 Table S2. XPS results of indium-based catalysts.

Catalyst	Hydrogen consumption	Reducibility
	$(\text{mmol}_{\text{H2}} \text{ g}_{\text{In2O3}}^{-1})$	(%)
$c-In_2O_3$	10.87	100
In15/ <i>m</i> -ZrO ₂	9.38	86.3
In15/ <i>m</i> -ZrO ₂ - <i>DTPA</i>	5.63	60
In15/m-ZrO ₂ -EDTA	5.81	61.9
In15/ m -ZrO ₂ - NTA	6.89	73.4
	Catalyst c-In ₂ O ₃ In15/m-ZrO ₂ In15/m-ZrO ₂ -DTPA In15/m-ZrO ₂ -EDTA In15/m-ZrO ₂ -NTA	Catalyst Hydrogen consumption (mmol _{H2} g _{In2O3} ⁻¹) c-In ₂ O ₃ 10.87 In15/m-ZrO ₂ 9.38 In15/m-ZrO ₂ -DTPA 5.63 In15/m-ZrO ₂ -EDTA 5.81 In15/m-ZrO ₂ -NTA 6.89

 Table S3. Degree of reduction (DOR).

Catalyst	T (°C)	P (MPa)	$GHSV$ (mL $g_{cat}^{-1} h^{-1}$)	CO ₂ Conv. (%)	CH3OH Select. (%)	CH ₃ OH STY (mg g _{cat} ⁻¹ h ⁻¹)	CH ₃ OH STY (g g _{In} ⁻¹ h ⁻¹)
c-In ₂ O ₃ ²	280	5	24,000	3.9	84	220	0.27
c-In ₂ O ₃ ⁶	330	4	15,000	7.1	39.7	118	0.14
$5 In_2 O_3 / m - Zr O_2, WI^2$	280	5	48,000	2.6	94	340	8.2
$5In_2O_3/m$ -ZrO ₂ ,WI ²	280	5	24,000	4.8	84	270	6.5
$7.5 In_2O_3/t$ -ZrO ₂ ,WI ²	280	5	24,000	0.6	83	50	0.81
h-In ₂ O ₃ ⁷	300	4	20,000	6.7	99.5	365	0.44
<i>c</i> -In ₂ O ₃ ,FSP ⁸	280	5	48,000	N.A.	N.A.	180	0.22
5In ₂ O ₃ -ZrO ₂ ,FSP ⁸	280	5	48,000	N.A.	N.A.	360	8.7
9In ₂ O ₃ / <i>m</i> -ZrO ₂ ,WI ⁸	300	5	16,000	5.2	99.8	295	4.0
In15/m-ZrO ₂ - DTPA ^a	280	5	24,000	6.7	78.2	351	2.8
In15/ m -ZrO ₂ - $DTPA^a$	280	5	48,000	5.5	82.6	596	4.8
In15/ <i>m</i> -ZrO ₂ - <i>DTPA</i> ^{<i>a</i>}	260	5	48,000	2.9	91.3	341	2.7
(a: refer to	this	work,	Reaction	n	condition:	H ₂ /CO	=4)

Table S4. Comparative performance of heterogeneous catalysts under similar reactionconditions for CO_2 hydrogenation to methanol.

Surface species	Adsorption peak position ^{5, 9-13} (cm ⁻¹)			
Formate	2977, 2975, 2878, 2875, 2850, 2736,			
	1595, 1385			
Methoxy	2930, 1145			
Carboxylate	1595			

Table S5. Summary of infrared band of the surface species for CO_2 -to-methanol reaction on Inx/m-ZrO₂ based catalysts at 0.1 MPa.

REFERENCES

- Q.-Y. Bi, J.-D. Lin, Y.-M. Liu, H.-Y. He, F.-Q. Huang and Y. Cao, J. Power Sources, 2016, 328, 463-471.
- M. S. Frei, C. Mondelli, A. Cesarini, F. Krumeich, R. Hauert, J. A. Stewart, D. Curulla Ferré and J. Pérez-Ramírez, ACS Catal., 2019, 10, 1133-1145.
- 3. X. Zhang, A. V. Kirilin, S. Rozeveld, J. H. Kang, G. Pollefeyt, D. F. Yancey, A. Chojecki, B. Vanchura and M. Blum, *ACS Catal.*, 2022, **12**, 3868-3880.
- 4. M. Chen, J. Xu, Y. Cao, H.-Y. He, K.-N. Fan and J.-H. Zhuang, J. Catal., 2010, 272, 101-108.
- K. Larmier, W. C. Liao, S. Tada, E. Lam, R. Verel, A. Bansode, A. Urakawa, A. Comas-Vives and C. Coperet, *Angew. Chem., Int. Ed.*, 2017, 56, 2318-2323.
- K. Sun, Z. Fan, J. Ye, J. Yan, Q. Ge, Y. Li, W. He, W. Yang and C.-j. Liu, J. CO₂ Util., 2015, 12, 1-6.
- D. Shanshan, Q. Bin, Y. Yong, W. Hui, C. Jun, H. Yong, L. Shenggang, G. Peng and S. Yuhan, *Sci. Adv.*, 2020, 6, eaaz2060.
- T. Pinheiro Araujo, C. Mondelli, M. Agrachev, T. Zou, P. O. Willi, K. M. Engel, R. N. Grass, W. J. Stark, O. V. Safonova, G. Jeschke, S. Mitchell and J. Perez-Ramirez, *Nat. Commun.*, 2022, 13, 5610.
- T.-y. Chen, C. Cao, T.-b. Chen, X. Ding, H. Huang, L. Shen, X. Cao, M. Zhu, J. Xu, J. Gao and Y.-F. Han, ACS Catal., 2019, 9, 8785-8797.
- M. Yang, J. Yu, A. Zimina, B. B. Sarma, L. Pandit, J. D. Grunwaldt, L. Zhang, H. Xu and J. Sun, Angew. Chem., Int. Ed., 2023, 62, e202216803.
- 11. M.-Y. He, J. M. White and J. G. Ekerdt, J. Mol. Catal., 1985, 30, 415-430.
- 12. S. Kattel, B. Yan, Y. Yang, J. G. Chen and P. Liu, J. Am. Chem. Soc., 2016, 138, 12440-12450.
- H. Chang, F. Gao, A. Luo, Y. Liu, Y. Zhu, H. He and Y. Cao, *Chem. Commun.*, 2023, 59, 7647-7650.