SUPPORTING INFORMATION

Effect of the preparation methods on the physicochemical properties of indium-based catalysts and their catalytic performance for CO_2 hydrogenation to methanol

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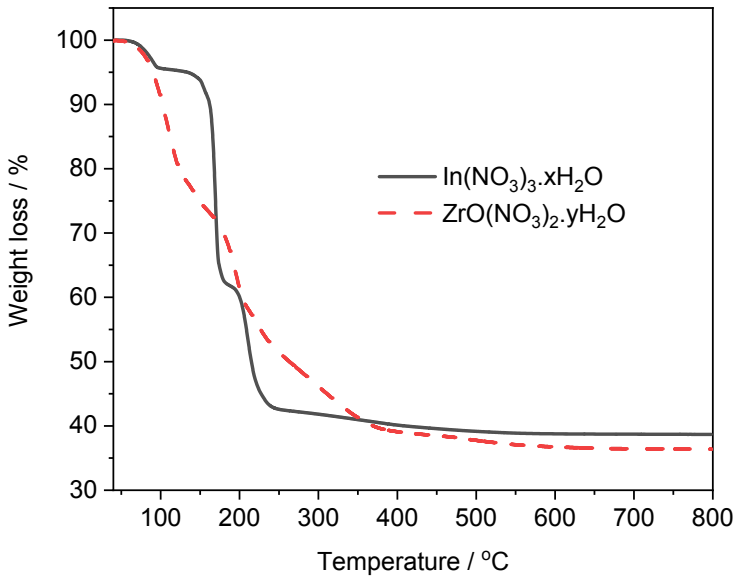


Figure S1. TGA profiles of $In(NO_3)_3 \cdot xH_2O$ and $ZrO(NO_3)_2 \cdot yH_2O$ precursors.

Figure S2. Optical image of In_2O_3 prepared by urea combustion method.

Section: Criteria for estimation of transport effects

The mass and heat transfer limitations were evaluated based on the total rate of consumption of CO_2 as guided in the textbook Catalysis From Principles to Applications (Edited by Matthias Beller, Albert Renken and Rutger A. van Santen, Wiley-VCH, 2012, pages 102 and 548). The reaction rates (taken as an average over the bed) at the standard reaction condition of 40 bar, WHSV = 6000 mL g_{cat}^{-1} h^{-1} and

feed molar H_2:CO_2 = 3:1 have been used. The calculation was performed for In_2O_3-ZrO_2 (IZ-carb) catalyst at 623 K (350 ^oC) which showed the highest conversion of CO_2 at 28%. The bulk density of In_2O_3-ZrO_2 was measured at approximately 1360 kg/m^3, and the apparent activation energy was estimated at around 77 kJ/mol. **Mears Parameter (MP)** was calculated using the equation:

For examing the absence of interphase concentration gradients:

$$MP = \frac{-r_{A\,(obs)}\,\rho_b\,R\,n}{k_c\,C_{Ab}} < 0.15 \qquad \text{(S1)}$$

For examing the absence of interphase temperature gradients:

$$MP = \frac{(-\Delta H)(r_{A\,(obs)}\,\rho_b\,R}{h\,T_b}.\frac{\mathrm{E}}{\mathrm{R}T_b} < 0.15 \qquad \text{(S2)}$$

where,

$-r_{A\,(obs)}$ = observed rate of reaction (mol/kg · s)

n = reaction order (assume n = 1 in this reaction)

Rp = average catalyst granule radius (m)

ρ_b = bulk density of catalyst bed (kg/m^3) = $(1-\Phi)\rho_c$ (Φ = porosity)

ρ_c = solid density of catalyst (kg/m^3)

C_{Ab} = bulk reactant concentration (mol/m^3)

k_c = mass transfer coefficient (m/s)

ΔH = enthalpy of reaction (J/mol)

E = activation energy of CO_2 (J/mol)

R = gas constant (8.314 J/mol.K)

Weisz Prater parameter (WP) was calculated using the equation:

For checking the absence of concentration profiles in an isothermal porous catalyst pellet:

$$WP = \frac{-r_{A\,(obs)}\,\rho_c\,R^2}{D_e\,C_{As}} < 0.6 \text{ (for n = 1)} \qquad \text{(S3)}$$

For examing the absence of intraparticle temperature gradients:

$$WP = \frac{(-\Delta H)(r_{A\,(obs)}\,R^2}{\lambda_e\,T_s}.\frac{\mathrm{E}}{\mathrm{R}T_s} < 1 \qquad \text{(S4)}$$

where,

$-r_{A\,(obs)}$ = observed rate of reaction (mol/kg · s)

ρ_c = solid density of catalyst (kg/m^3)

Rp = average catalyst granule radius (m)

D_e = effective diffusivity (m^2/s)

C_{As} = surface reactant concentration (mol/m^3)

Moreover, the Thoenes-Kramers correlation (as shown below in eq. S3) was used to estimate the packed-bed external mass transport coefficient for the Mears Parameter.

$$\left[\frac{k_c\, d_p}{D_{AB}}\left(\frac{\Phi}{1-\Phi}\right)\frac{1}{\gamma}\right] = \left[\frac{U\, d_p\, \rho}{\mu\,(1-\Phi)\,\gamma}\right]^{\frac{1}{2}}\left(\frac{\mu}{\rho\, D_{AB}}\right)^{\frac{1}{3}} \qquad \text{(S5)}$$

where,

d_p = particle diameter (m)

Φ = void fraction (porosity of packed bed)

γ = shape factor

U = superficial gas velocity through the bed (m/s)

μ = viscosity (kg/m · s)

ρ = fluid density (kg/m^3)

$\nu = \frac{\mu}{\rho}$ = kinematic viscosity (m^2/s)

D_{AB} = gas phase diffusivity (m^2/s)

k_c = mass transfer coefficient (m/s)

Weisz-Prater and Maers parameters were calculated for In_2O_3-ZrO_2 (IZ-carb) catalysts at 623 K (350 ^{o}C) which showed the highest conversion of CO_2, 28%. The Weisz-Prater and Maers parameters were WP = 0.156 and MP = 0.008, respectively for In_2O_3-ZrO_2 catalysts. The WP < 0.6 and MP < 0.15 indicating the absence of both intraparticle and interphase mass transfer limitations.

Table S1: Calculation of Weisz-Prater criterion for In_2O_3-ZrO_2 (IZ-carb) catalyst

Symbol	Term	In_2O_3-ZrO_2,
r_{obs}	Observed reaction rate at bulk concentration, mol/kg(catalyst)/s	5.966E-03
R_p	The average radius of the catalyst particle (m)	2.125E-04
C_{As}	Reactant (CO_2) concentration at external particle surface, mol/m^3	195.6
ρ_p	True bulk density of the catalyst, kg/m^3	6400
T	Reaction temperature, K	623
P	Reaction pressure, bar	40
$D_{CO2\text{-}H2}$	Diffusivity of CO_2 in a mixture of CO_2 and H_2, m^2/s	5.64E-06
De	Effective diffusivity of spherical catalyst pellets, m^2/s	5.64E-07
ϕ	Weisz-Prater Parameter $\phi = \frac{robs * \rho p * Rp2}{De * CAs}$	0.156

Table S2: Calculation of Maers criterion for In_2O_3-ZrO_2 (IZ-carb) catalyst

Symbol	Term	In_2O_3-ZrO_2,
τ_{obs}	Observed reaction rate at bulk concentration, mol/kg(catalyst)/s	5.966E-03
R_p	The average radius of the catalyst particle (m)	2.125E-04
C_{As}	Reactant (CO_2) concentration at external particle surface, mol/m^3	195.6
ρ_p	True density of the catalyst, kg/m^3	1360
T	Reaction temperature, K	623
P	Reaction pressure, bar	40
$D_{CO2\text{-}H2}$	Diffusivity of CO_2 in a mixture of CO_2 and H_2, m^2/s	5.64E-06
k_c	mass transfer coefficient (m/s)	1.18E-02
ϕ	Maers Parameter $\phi = \frac{robs * \rho p * Rp2}{De * CAs}$	0.0008

Note that the specific heat capacity (Cp) of H_2 and CO_2 was 14300 and 830 J/kg.K, respectively.

Thermal coefficient of H_2 and CO_2 was 0.182 and 0.017 W/m.K, respectively.

Thermal conductivity of In_2O_3-ZrO_2 was taken by average values of ZrO_2 (2.7 W/m.K, https://doi.org/10.1016/j.ijft.2023.100424) and In_2O_3 (2.5 W/m.K, https://doi.org/10.1016/j.ceramint.2021.03.129).

The heat transfer coefficient can be calculated from the mass transfer coefficient by using the Chilton-Colburn equation: $\frac{h}{kc} = \rho Cp\left(\frac{Sc}{Pr}\right)^{2/3}$ (S6)

Where Pr and Sc is the Prandtl and Schmidt number, Cp is the specific heat capacity.

The MP and WP for heat transfer examination was MP = 0.007 << 0.15 and WP = 0.0002 << 1, indicating the absence of interphase and intraparticle temperature profile.

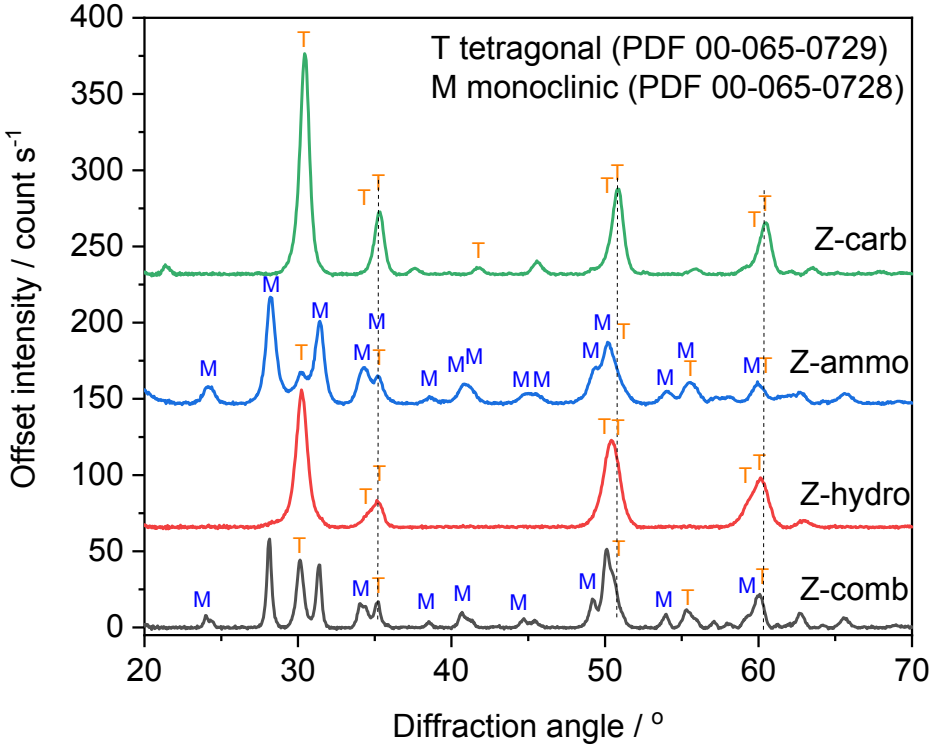


Figure S3. XRD patterns of ZrO_2 samples prepared from different methods.

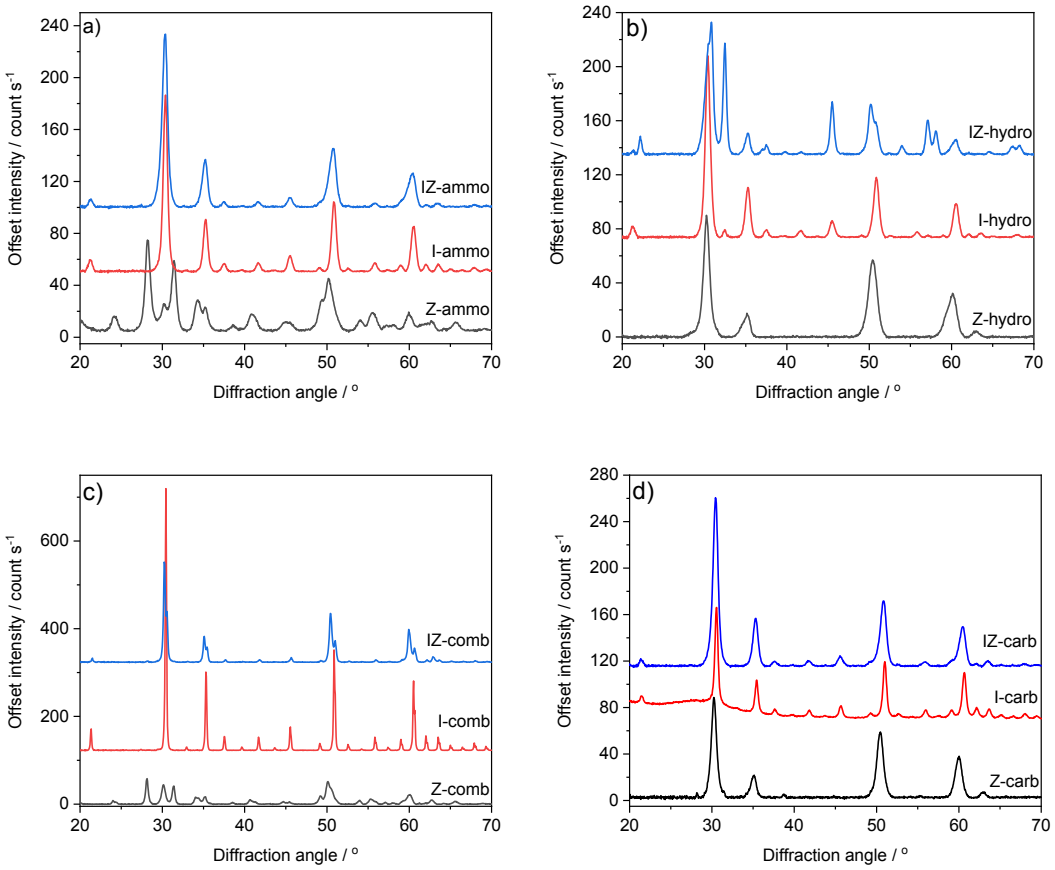
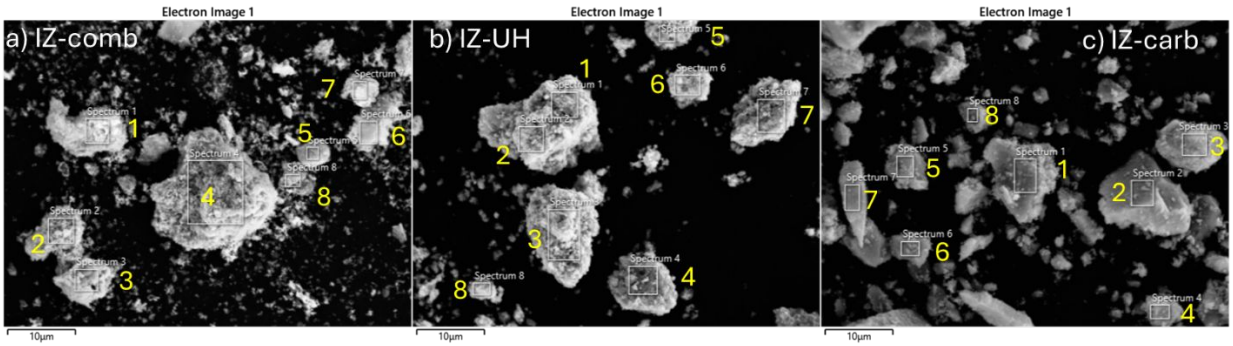


Figure S4. Comparison of XRD patterns of ZrO_2, In_2O_3, and In_2O_3-ZrO_2 prepared with the same synthesis method.



Sample	IZ-comb			IZ-UH			IZ-carb		
Point	In	Zr	In/Zr	In	Zr	In/Zr	In	Zr	In/Zr
1	19	19.3	1.0	20.3	10.6	1.9	24.5	11.8	2.1
2	19	16.2	1.2	21.1	8.1	2.6	30.9	12.5	2.5
3	15.1	13.9	1.1	18	10.4	1.7	17.2	8.4	2.0
4	19.9	16.6	1.2	33.2	10.7	3.1	15.9	7.9	2.0
5	20.6	14	1.5	21.2	10.5	2.0	22.4	10.1	2.2
6	16.6	14.5	1.1	22.5	8.3	2.7	23.1	8.2	2.8
7	30.1	4.3	7.0	26.3	8.9	3.0	22.1	8.6	2.6
8	19.9	3.3	6.0	19.5	13.1	1.5	30	11.8	2.5
Average			**1.2***			**2.3**			**2.3**
Standard deviation			**0.1***			**0.5**			**0.3**

Figure S5. SEM/EDX measurements of selected In_2O_3-ZrO_2 catalysts: a) IZ-comb; b) IZ-UH; and c) IZ-carb. The table shows molar percentages of In and Zr at 8 selected areas of each sample (the mark for each point is shown in the respective electron image). The asterisk (*) indicates that the average value was taken for only the first six points of the IZ-comb sample while it was averaged for 8 points on the IZ-UH and IZ-carb samples.

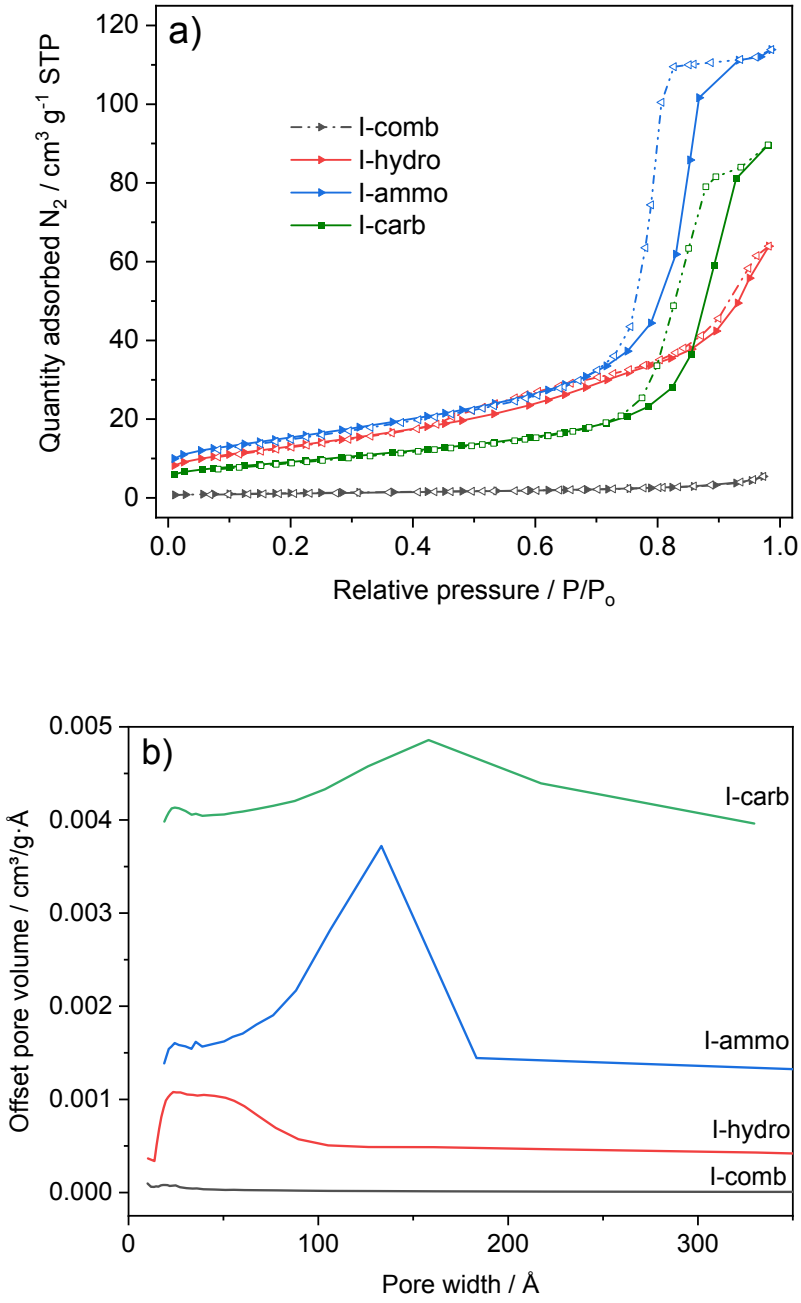


Figure S6. N_2 physisorption isotherms and pore size distribution of In_2O_3 prepared with different synthesis methods.

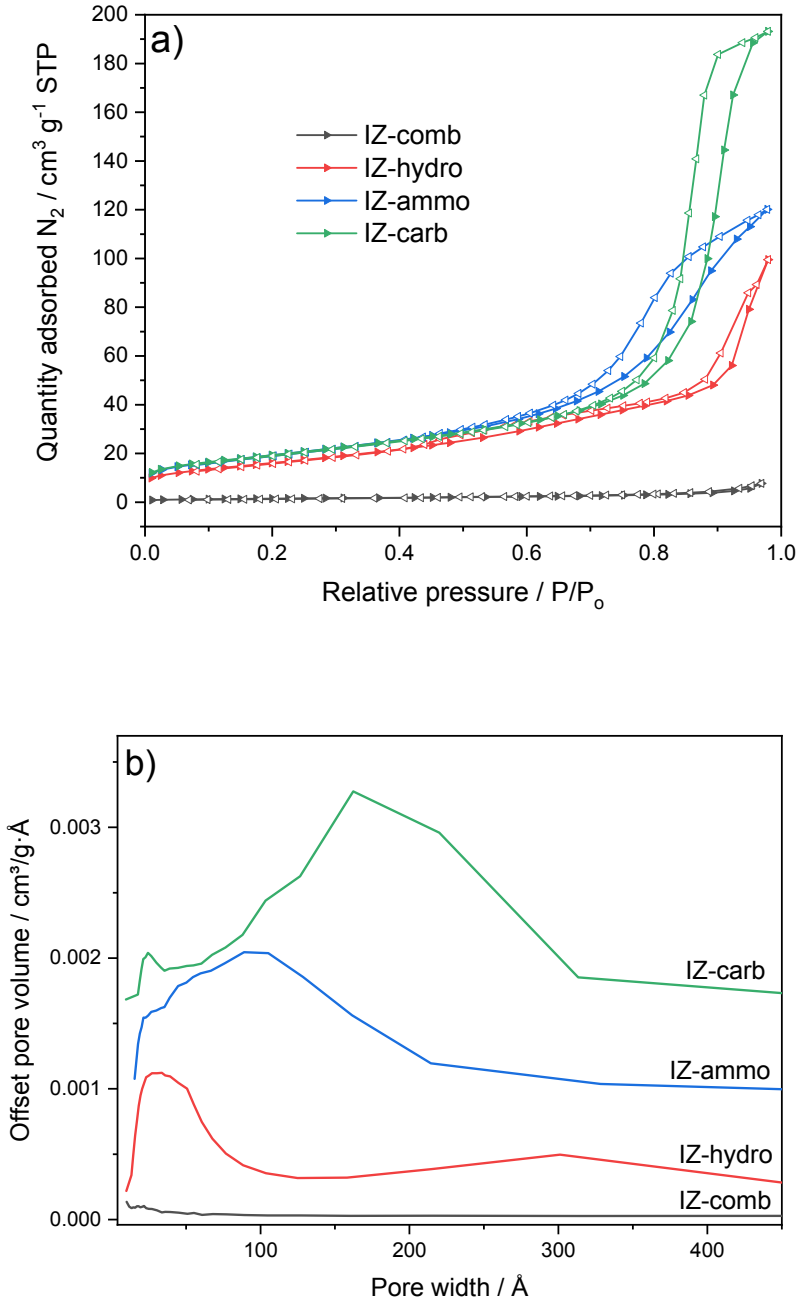


Figure S7. N_2 physisorption isotherms and pore size distribution of In_2O_3-ZrO_2 prepared with different synthesis methods.

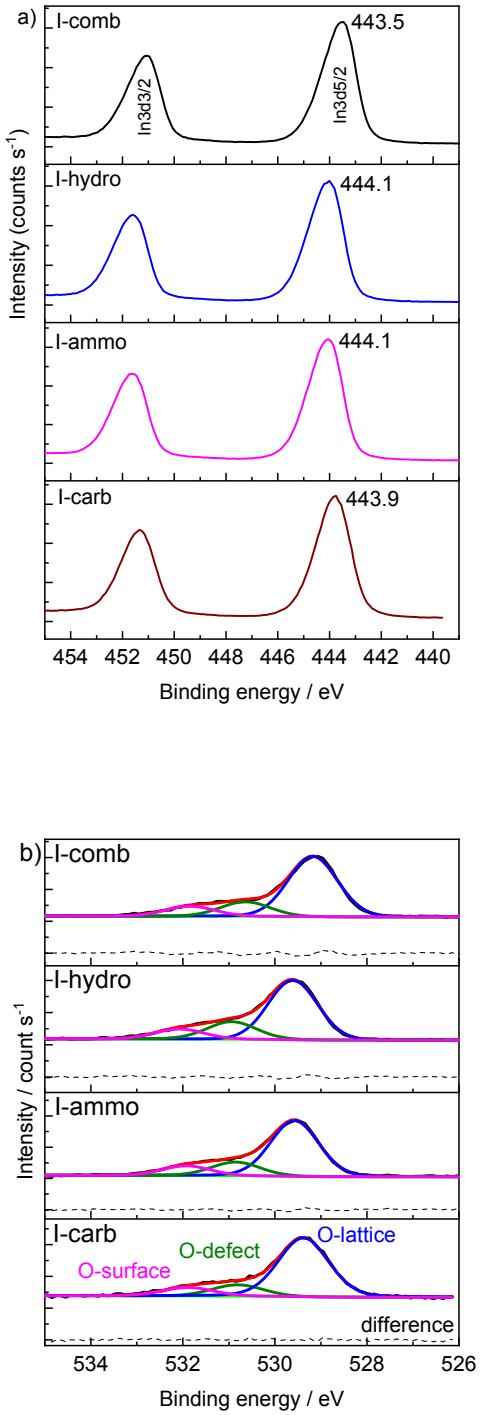


Figure S8. XPS spectra of In_2O_3 catalyst prepared by different methods: a) In3d and b) O1s core level.

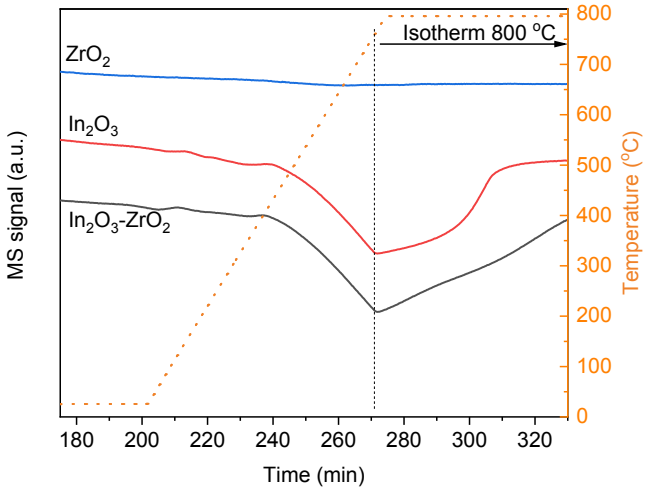


Figure S9. Comparison of H_2-TPR profile of ZrO_2, In_2O_3, and In_2O_3-ZrO_2 synthesized by the urea hydrolysis method.

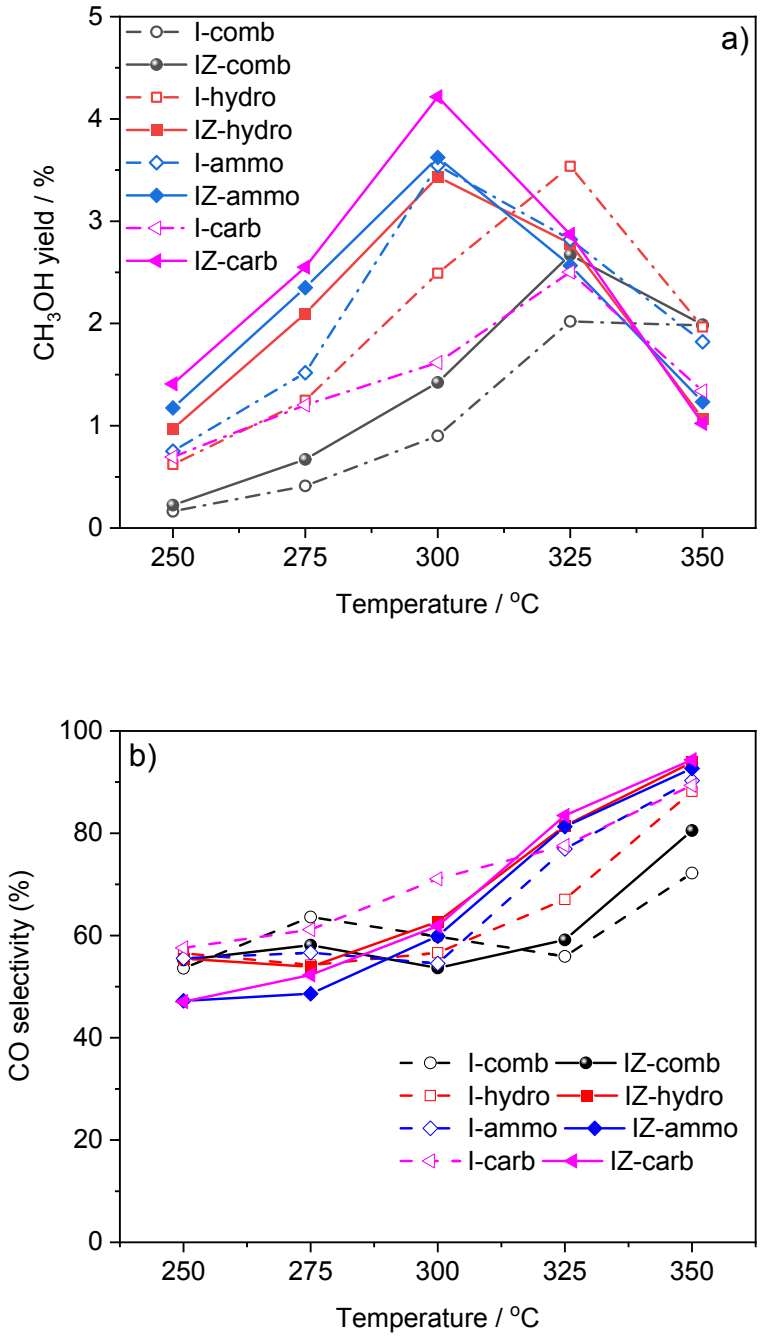


Figure S10. Comparison of In_2O_3 and In_2O_3-ZrO_2 catalysts on (a) CH_3OH yield and (b) CO selectivity.