Supplementary Information

Tandem catalytic methylation of naphthalene using CO₂ and H₂

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Experimental Details

Catalyst preparation

The *og*-ZnZrO_x catalyst was prepared by an oxalate-gel co-precipitation method. Typically, 12 mmol of Zr(NO₃)₄·5H₂O (\geq 99.0%, Sinopharm Chemical Reagent) and 3 mmol of Zn(NO₃)₂·6H₂O (\geq 99.0%, Sinopharm Chemical Reagent) were dissolved in 150 mL of ethanol. Then 50 mL of the alcoholic solution containing 20% access of oxalic acid (32 mmol) was injected into the above solution with a drop rate of 2.5 mL/min under vigorous magnetic stirring at room temperature. The suspension was continuously stirred for 2 h, after which the resultant gel-like precipitate was separated by filtration and washed for three times with ethanol. The filtered sample was dried at 110 °C overnight, then grinded and sieved into fine powder, which was calcinated at 500 °C in static air for 8 h with a ramping rate of 5 °C/min to obtain the final catalyst. The ZrO₂ and ZnO were prepared according to the same recipe. Reference catalyst named as *im*-ZnZrO_x was prepared by the common incipient impregnation method using Zn(NO₃)₂·6H₂O as the precursor and ZrO₂ as the substrate. Another reference catalyst named as *cp*-ZnZrO_x was prepared by a previously reported (NH₄)₂CO₃-

coprecipitation method,¹ Cu-Zn-Al with a Cu/Zn/Al molar ratio of 6/3/1 was prepared by a similar Na₂CO₃-coprecipitation method. The molar ratio of Zn/Zr in each catalyst was fixed at 1/4. H-Beta (Si/Al=12.5, CP814E*), H-Beta (Si/Al=19, CP814C*), H-Beta (Si/Al=150, CP811C-300), H-ZSM-5 (Si/Al=40, CBV8014), H-Y (Si/Al=2.6, CBV500), H-MOR (Si/Al=10, CBV21A) were purchased from Zeolyst International Company. H-MCM-22 (Si/Al=15, NKF-10) were purchased from Nankai University Catalyst Company. For the preparation of the two additional *og*-ZnZrO_x/H-Beta tandem catalysts with different integration manners, one was obtained by ball-milling the powdery mixture of *og*-ZnZrO_x and H-Beta in the QM-3SP04 planetary grinding mill for 2 h, the other was prepared by the pre-blending of H-Beta with the alcoholic solution of Zn(NO₃)₂ and Zr(NO₃)₄ before the addition of oxalic acid after which the washing and calcination processes were kept same as used for the preparation of *og*-ZnZrO_x alone.

Catalyst characterization

Transmission electron microscopy (TEM) images were taken with a JEOL JEM 2011 electron microscope operating at 200 kV. Before being transferred into the TEM chamber, the samples dispersed with ethanol were deposited onto a carbon coated copper grid and then quickly moved into the vacuum evaporator. X-ray diffraction (XRD) analysis was carried out on a Germany Bruker D2 Phaser X-ray diffractometer using nickel filtered Cu K α radiation with a scanning angle (2 θ) of 5–90° at 40 kV and 40 mA. Raman spectra were collected on a Horiba LabRAM HR Evolution spectrometer by using a laser at 532 nm. The data were collected between 100 and 800 nm. All samples were analyzed as powders without any pretreatment.

Catalyst evaluation

A mixture of naphthalene (designated amount), zeolite (designated amount), oxide (designated amount) and solvent (15 mL) were charged into a 50 mL high-pressure reactor. The reactor was sealed and purged with CO_2 and H_2 to the designed pressure. Then the reaction mixture was heated to the required temperature and kept for the given reaction time under mechanical stirring (400 rpm). After completion of the reaction, the reactor was cooled to room temperature. The catalyst was separated by centrifuge. The liquid products were collected and analyzed by an Agilent 7820A gas chromatograph with a flame ionization detector. The gas products were collected using an air bag

and analyzed by Agilent 8860 gas chromatograph with a thermal conductivity detector. All the products were identified by gas chromatography-mass spectrometry (GC-MS). The recycling test was performed after the regeneration of catalyst used in the prior batch. After each reaction cycle, the catalyst was separated by centrifuge and washed with ethanol several times. The catalyst was then dried at 110 °C overnight and calcined at 500 °C for 4 h before being used for the next reaction. For the hydrogenation of CO₂ in the fixed-bed flow reactor, 100 mg of the *og*-ZnZrO_x (40-60 mesh) diluted with 400 mg quartz (40-60 mesh) were packed in the constant temperature zone of the reaction tube with internal diameter of 8 mm. Before the reaction the catalyst was pretreated in a N₂ stream (20 mL/min) for 2 h at reaction temperature. Then the reaction gas with a H₂/CO₂ ratio of 4/1 were introduced into the reactor. Argon with a concentration of 4% was used as an internal standard. Reaction was conducted under the conditions of 2.0 MPa, 310-350 °C, GHSV = 24000 mL·g⁻¹·h⁻¹. The reactor lines from reactor outlet to chromatographic inlet was maintained at 150 °C. The effluent gas analysis was conducted using a gas chromatograph (Agilent 8860) equipped with thermal conductivity and flame ionization detectors.



Fig. S1 Gibbs free energy changes at different temperatures for CO_2 hydrogenation to methanol, naphthalene methylation with methanol, and naphthalene methylation with CO_2/H_2 . The calculation was based on HSC6 Chemistry software.



Fig. S2 Raman spectra of *og*-ZnZrO_x catalyst. Five bands recorded at 146, 267, 317, 462, and 644 cm⁻¹ were identified as the characteristic signals for t-ZrO₂.²

Entry	Temperature	CO ₂ Conv.	Selectivity (%)	
	(°C)	(%)	CH ₃ OH	СО
1	310	4.9	84.2	15.8
2	330	7.3	81.1	18.9
3	350	8.5	62.5	37.5
4	310	3.0	76.2	23.8
5	330	8.6	58.9	41.1
6	350	13.2	32.0	68.0

Table S1 Results of CO₂ hydrogenation to methanol over *og*-ZnZrO_x catalyst.

Reaction conditions: for entries 1-3 which were performed in a fixed bed flow reactor, 100 mg *og*-ZnZrO_x, $H_2/CO_2 = 4/1$ (2 MPa), GHSV = 24000 mL·g⁻¹·h⁻¹; for entries 4-6 which were performed in a batch reactor, 150 mg *og*-ZnZrO_x, 15 mL cyclohexane, $H_2/CO_2 = 4/1$ (5 MPa), 3 h.

Table S2 Comparison of productivities of aromatic methylation using CO_2/H_2 over reported systems and *og*-ZnZrO_x/H-Beta in this work.

Ref.	Catalyst	Temp.	Pressure	H ₂ /CO ₂	Substrate	Productivity	
		(°C)	(MPa)		Substrate	$(\text{mmol}_{\text{Mono-Me}} \cdot g_{\text{cat}}^{-1} \cdot h^{-1})$	
		1(0	0	2/1	0.5 mmol 1,3,5-	0.12	
3	Ku(acac) ₃	160	8	3/1	trimethoxybenzene	~0.12	
4	Re/TiO ₂ -H-Beta	230	6	5/1	1 mmol NAP	~0.036	
5	ZnZrO _x -H-ZSM-5	360	3	3/1	WHSV of toluene 1 h ⁻¹	~0.71	
6	ZnCrO _x -H-ZSM-5	390	4	3/1	WHSV of toluene 0.87 h ⁻¹	~0.83	
This work	og-ZnZrO _x /H-Beta	330	5	4/1	30 mmol NAP	3.4	
This work	og-ZnZrO _x /H-Beta	330	5	4/1	10 mmol NAP	3.0	

Note: The data point at 20 h in the reaction profile of ref. 4 was selected to calculate the productivity because it reached the comparable yield level (~18% mono-methylated NAP) to that in our work (22.5%). For ref. 5 and ref. 6, reaction results under the standard conditions were adopted to calculate the productivities, which refer in particular to the production of para-xylene.

Entry	Catalyst	NAP		S	Selectivity (%)	
		Conv. (%)	2-MN	1-MN	Poly-MNs	Dearomatized-NAPs
1	Cu-Zn-Al	82.8	3.5	1.6	0.5	94.4
2	<i>im</i> -ZnZrO _x	14.6	56.3	35.8	7.9	-
3	<i>cp</i> -ZnZrO _x	18.9	57.1	36.4	6.5	-

Table S3 Reaction results over H-Beta integrated with other methanol synthesis catalysts.

Reaction conditions: 150 mg methanol synthesis catalyst, 100 mg H-Beta, 15 mL cyclohexane, 10 mmol NAP, 5 MPa H₂/CO₂ (4:1), 330 °C, 3 h.

Table S4 Comparison between CO₂/H₂ and CH₃OH as methylation reagent.

Methylation	NAP	Selectivity (%)		
reagent	Conv. (%)	2-MN	1-MN	Poly-MNs
CO ₂ /H ₂	36.0	51.5	34.3	14.2
CH ₃ OH	38.9	29.3	16.9	53.8

Reaction conditions: For CO_2/H_2 methylation, 150 mg *og*-ZnZrO_x, 100 mg H-Beta, 15 mL cyclohexane, 10 mmol NAP, 5 MPa H₂/CO₂ (4:1), 330 °C, 6 h; For CH₃OH methylation, 100 mg H-Beta, 15 mL cyclohexane, 10 mmol NAP, 10 mmol CH₃OH, 1 MPa N₂, 330 °C, 3 h.



Fig. S3 Recycling results of *og*-ZnZrO_x/H-Beta catalyst. Reaction conditions: 150 mg *og*-ZnZrO_x, 100 mg H-Beta, 15 mL cyclohexane, 10 mmol NAP, 5 MPa H_2/CO_2 (4:1), 330 °C, 3 h.





Fig. S5 TEM images of *og*-ZnZrO_x.



Fig. S6 TEM images of H-Beta.



Fig. S7 TEM images of regenerated og -ZnZrO_x/H-Beta catalysts.

References

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