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## Supplementary Materials for

### Selective methylation of toluene using CO<sub>2</sub> and H<sub>2</sub> to *para*-xylene

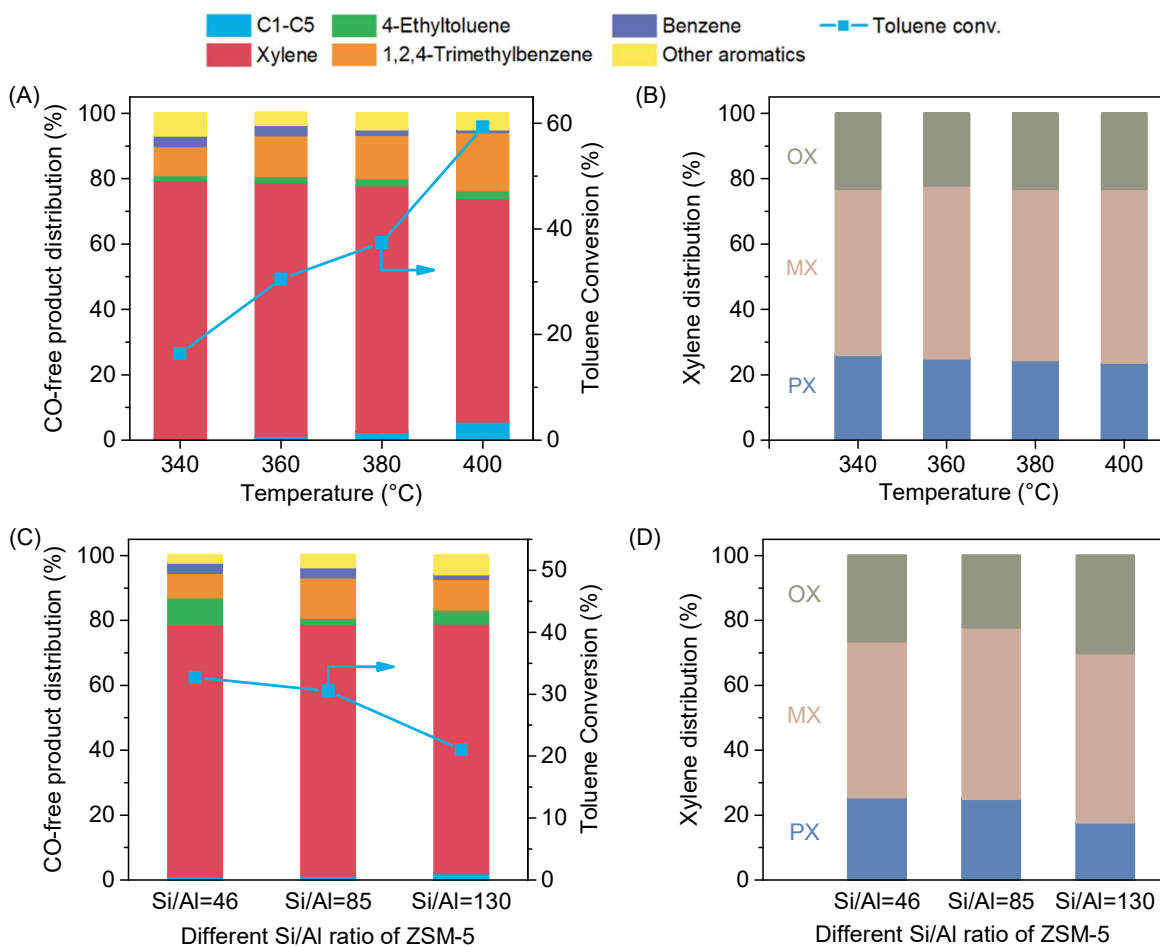
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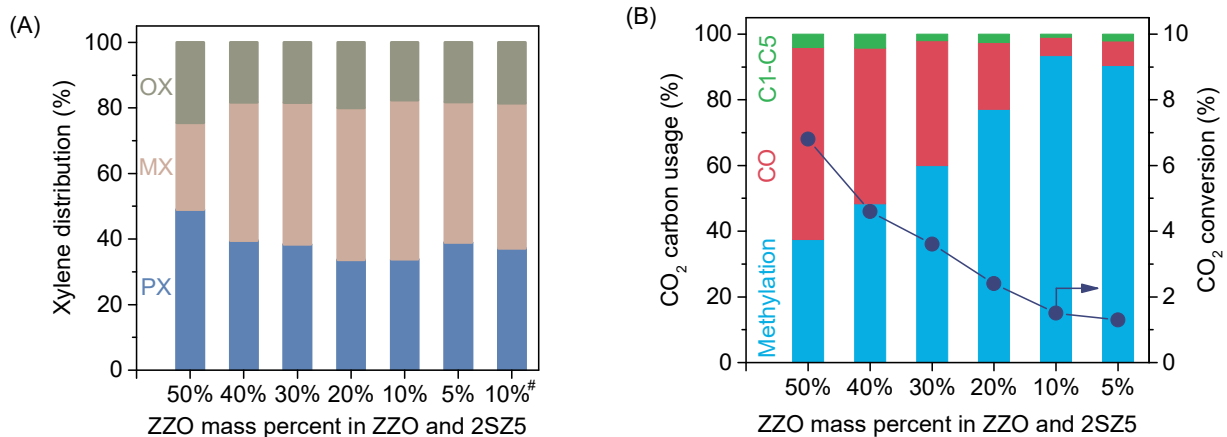
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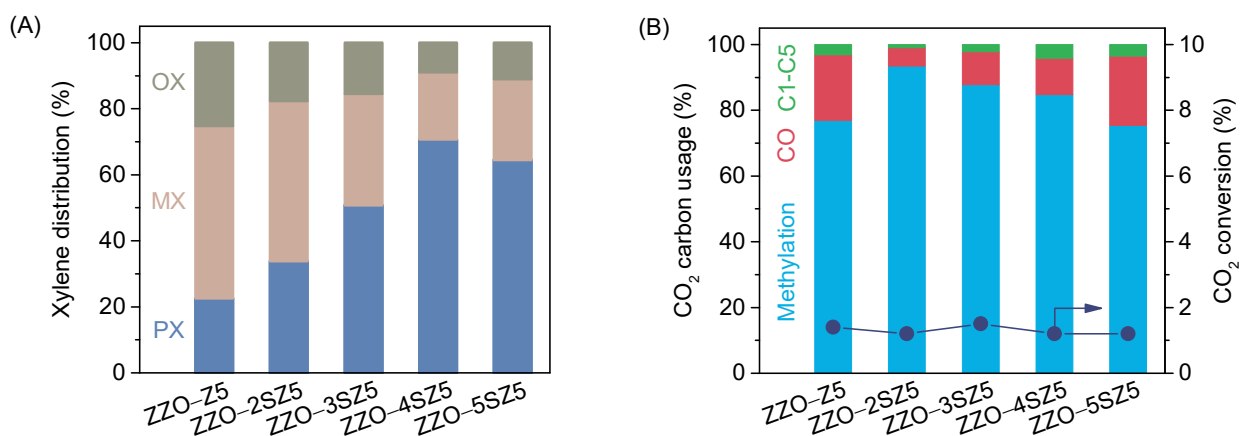
Figs. S1 to S8  
Tables S1 and S2



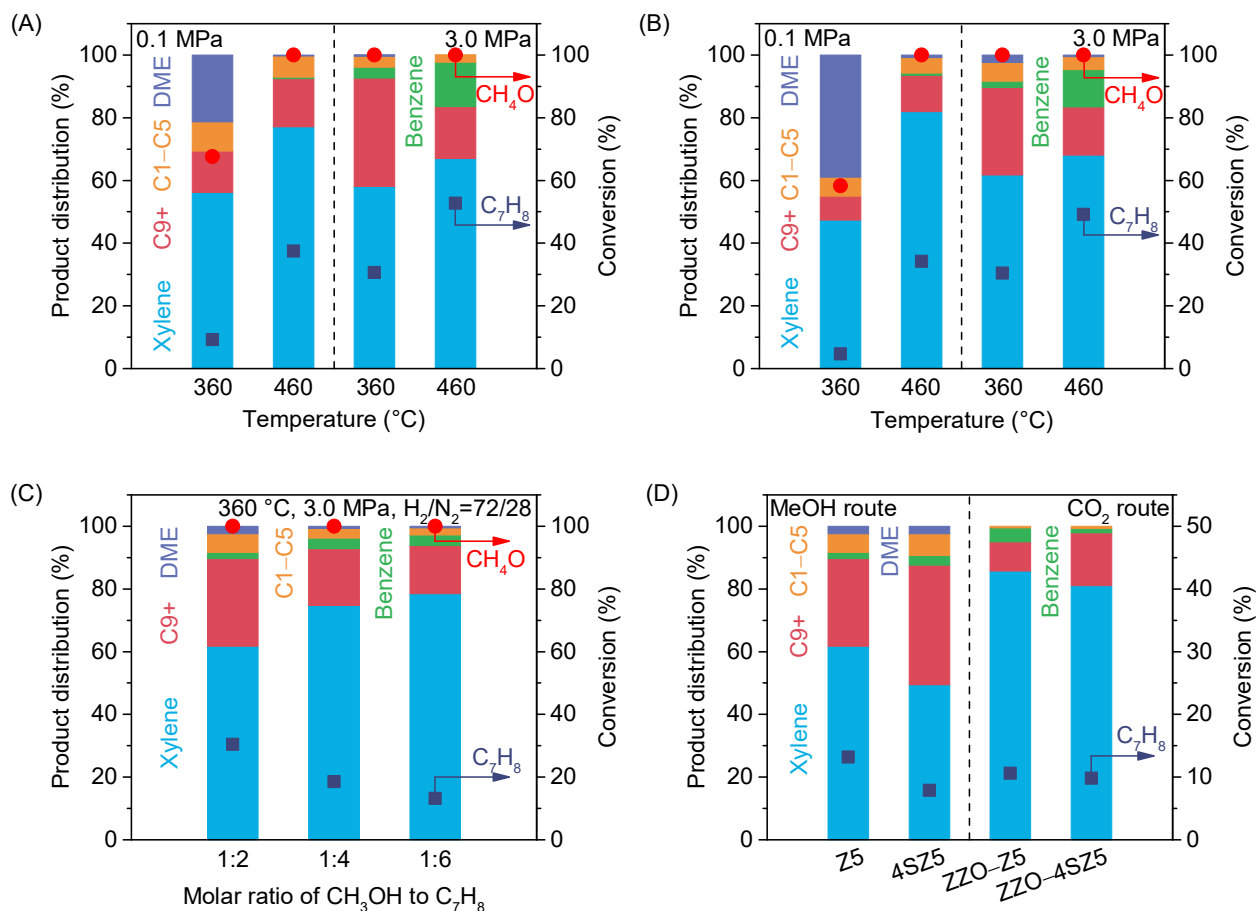
**fig. S1. Catalytic performance of toluene methylation using CO<sub>2</sub> + H<sub>2</sub> in different temperature or Z5 Si/Al ratio.** Influence of reaction temperature on (A) production distribution (CO free), and (B) xylene distribution. Influence of Si/Al ratio on (C) production distribution (CO free), and (D) xylene distribution. Catalyst: ZZO–Z5 (mass ratio of 5 : 5). Reaction conditions: 360 °C, 3.0 MPa, 12000 mL g<sup>-1</sup> h<sup>-1</sup>, H<sub>2</sub>/CO<sub>2</sub> = 3, toluene vaporized at 90 °C (toluene WHSV = 1 h<sup>-1</sup>) time on stream = 15 h.



**fig. S2. Catalytic performance for different ZZO and 2SZ5 mass ratios.** Influence of the ZZO mass percent in ZZO and 2SZ5 on (A) xylene distribution, and (B) conversion and carbon usage of CO<sub>2</sub>. 10%# means ZZO was directly deposited on Z5 powder. Reaction conditions are the same as those in fig. S1.



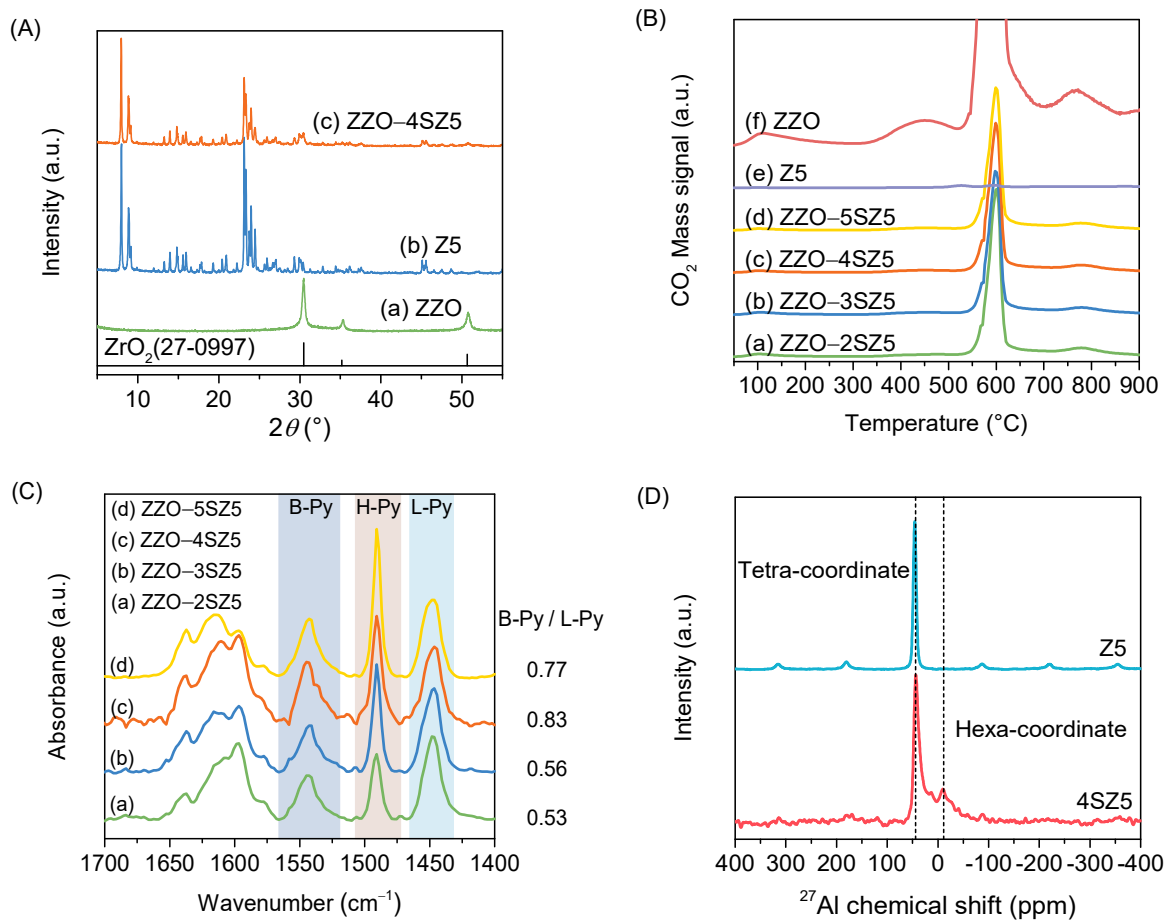
**fig. S3. Catalytic performance for different Z5 modifying times.** Influence of Z5 modified times by TEOS on (A) xylene distribution, and (B) conversion and carbon usage of CO<sub>2</sub>. Reaction conditions are the same as those in fig. S1.



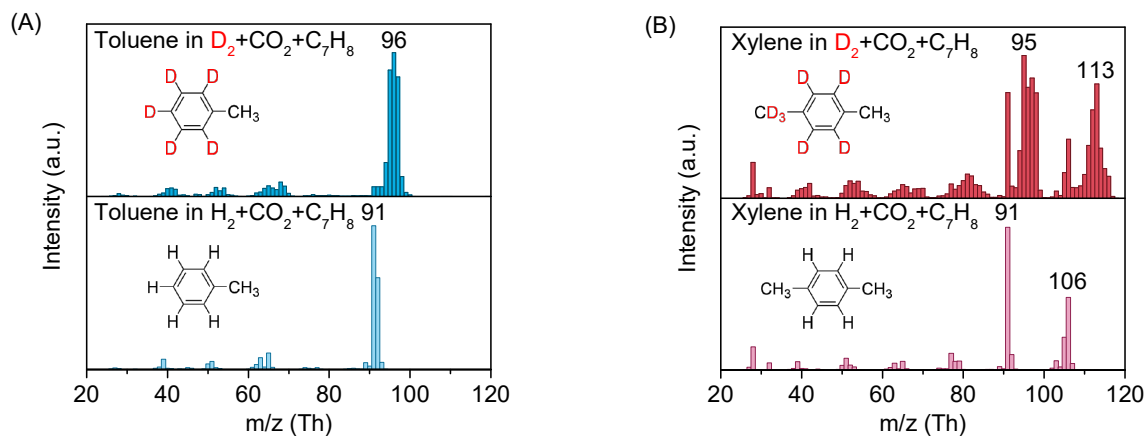
**fig. S4. Catalytic performance of methanol route and the comparison of that in  $CO_2$  route.** (A) Catalytic performance while using  $N_2$  as carrier gas. (B) Catalytic performance while using  $H_2/N_2$  (72/28, v/v) as carrier gas. (C) Influence of the molar ratio of  $CH_3OH$  to  $C_7H_8$  on catalytic performance. (D) The comparison of catalytic performance via methanol route and  $CO_2$  route. Typical reaction conditions for methanol route: toluene WHSV = 0.9  $h^{-1}$ ,  $C_7H_8/CH_3OH = 2$ , carrier gas GHSV = 12000  $ml\ g^{-1}\ h^{-1}$ , time on stream = 15 h. Typical catalyst: Z5.

Here, in order to compare the two methylation routes meaningfully, firstly, controlled experiments where toluene was methylated by methanol over Z5 at different parameters (temperature, pressure, carrier gas and  $CH_3OH/C_7H_8$  ratio) were conducted. Then, the molar ratio of  $CH_3OH$  to  $C_7H_8$  is adjusted to decrease toluene conversion to 13.2% (fig. S4C), which is approach to that in  $CO_2$  route.

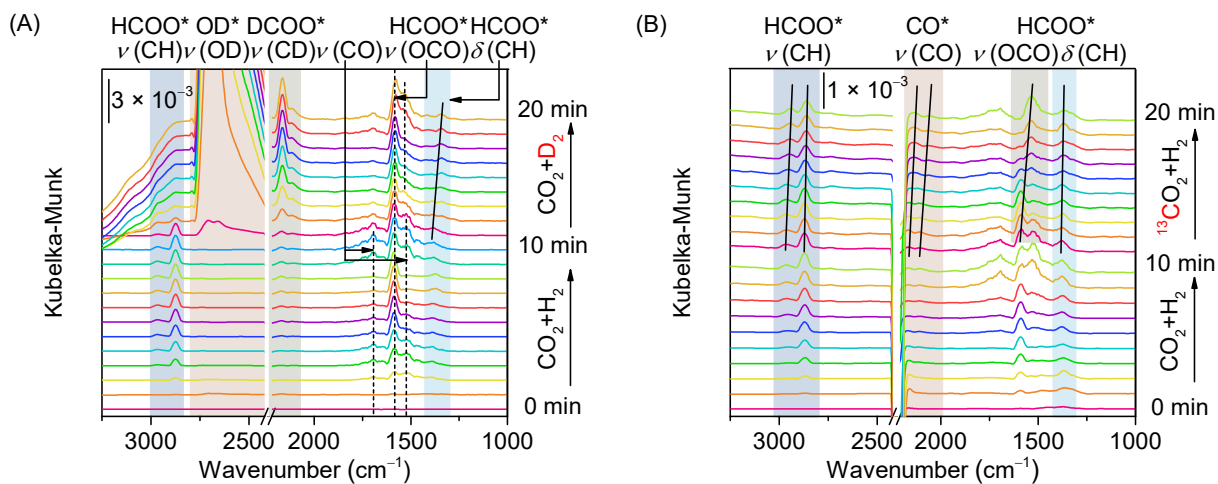
It can be seen that while the reaction pressure increased from 0.1 MPa to 3.0 MPa, toluene conversion increases and DME in production decreases at 360 °C whatever  $N_2$  or  $H_2/N_2$  (72/28, v/v) as carrier gas, which may be because that higher pressure leads to higher reactant partial pressure and longer contact time between reactants and catalyst. While at 460 °C, the toluene conversion slightly exceeds the theoretical value of 50%, due to the remarkable toluene disproportionation reaction. Compared with the case of using different carrier gases, the selectivity of C1-C5 is lower while  $H_2/N_2$  (72/28, v/v) instead of  $N_2$  as carrier gas, indicating that  $H_2$  is beneficial to inhibit carbon deposition. However, a higher C1-C5 selectivity is obtained when  $H_2/N_2$  (72/28, v/v) as carrier gas at 3.0 MPa. It may be because that methanol-to-hydrocarbons (MTH) reaction is promoted at high pressure.



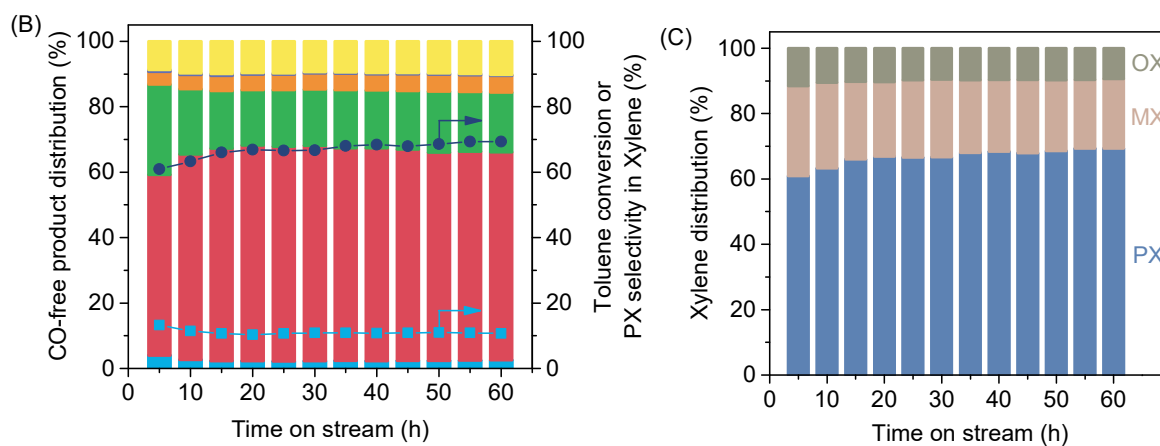
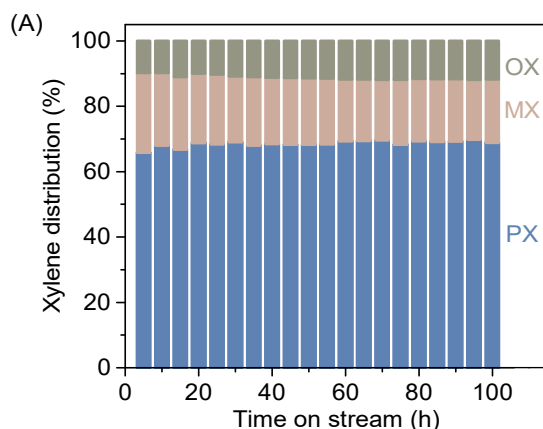
**fig. S5. XRD, CO<sub>2</sub>-TPD, Pyridine-FTIR, and <sup>27</sup>Al MAS NMR characterizations of dual-functional catalysts.** (A) XRD patterns of (a) ZZO, (b) Z5 and (c) ZZO-4SZ5. (B) CO<sub>2</sub>-TPD curves of ZZO, Z5 and ZZO-Z5 series dual-functional catalysts according to mass spectrometry signal. (C) Pyridine-FTIR spectrums of ZZO-Z5 series dual-functional catalysts. (D) <sup>27</sup>Al MAS NMR profiles of Z5 and 4SZ5.



**fig. S6. Mass spectra of toluene and xylene.** (A) Mass spectra of toluene in H/D exchange reaction. (B) Mass spectra of xylene in H/D exchange reaction.



**fig. S7. Isotope effect studies of CO<sub>2</sub> hydrogenation step.** (A) In situ DRIFTS spectra over ZZO-4SZ5 catalyst exposed the stream of  $CO_2 + H_2$  and subsequently switched to  $CO_2 + D_2$ . (B) In situ DRIFTS spectra over ZZO-4SZ5 catalyst exposed the stream of  $CO_2 + H_2$  and subsequently switched to  $^{13}CO_2 + H_2$ .



**fig. S8. The fresh and regenerated catalyst stability tests for ZZO-4SZ5.** (A) Xylene distribution for fresh ZZO-4SZ5. (B) The stability test for regenerated ZZO-4SZ5. (C) Xylene distribution for regenerated ZZO-4SZ5. Reaction conditions are the same as those in fig. S1.

**table S1. Pore structure of Z5 and ZZO-*n*SZ5 catalysts.**

	BET surface area (m <sup>2</sup> /g)	t-Plot micropore area (m <sup>2</sup> /g)	t-Plot external area (m <sup>2</sup> /g)	t-Plot volume (cm <sup>3</sup> /g)
Z5	360	300	60	0.1244
ZZO-2SZ5	283	237	46	0.0983
ZZO-3SZ5	261	208	53	0.0856
ZZO-4SZ5	260	212	48	0.0869
ZZO-5SZ5	253	200	53	0.0821



**table S2. DRIFTS peak assignments of the surface species in the process of CO<sub>2</sub> hydrogenation, toluene methylation, and isotope effect study.**

Peaks (cm <sup>-1</sup> )	Assignment	Species
2968	$\nu_{\text{as}}(\text{CH})$	HCOO*
2876	$\nu_{\text{s}}(\text{CH})$	
1584	$\nu(\text{OCO})$	
1382	$\delta(\text{CH})$	
2166	$\nu_{\text{as}}(\text{CD})$	DCOO*
2120	$\nu_{\text{s}}(\text{CD})$	
2942	$\nu_{\text{as}}(^{13}\text{CH})$	H <sup>13</sup> COO*
2862	$\nu_{\text{s}}(^{13}\text{CH})$	
1535	$\nu(\text{O}^{13}\text{CO})$	
1369	$\delta(^{13}\text{CH})$	
1525	$\nu(\text{CO})$	CO <sub>3</sub> *
2170	$\nu_{\text{as}}(\text{CO})$	CO*
2105	$\nu_{\text{s}}(\text{CO})$	
2141	$\nu_{\text{as}}(^{13}\text{CO})$	<sup>13</sup> CO*
2056	$\nu_{\text{s}}(^{13}\text{CO})$	
3080	$\nu(\text{CH})$	Benzene ring
3035		
1503		
2935	$\nu_{\text{as}}(\text{CH})$	CH <sub>3</sub> *
2884	$\nu_{\text{s}}(\text{CH})$	
1437	$\delta_{\text{as}}(\text{CH})$	
2709	$\nu_{\text{as}}(\text{OD})$	OD*
2662	$\nu_{\text{s}}(\text{OD})$	