Alkylation of benzene using CO_2 and H_2 over ZnZrOx/ZSM-5: the effect of Y doping

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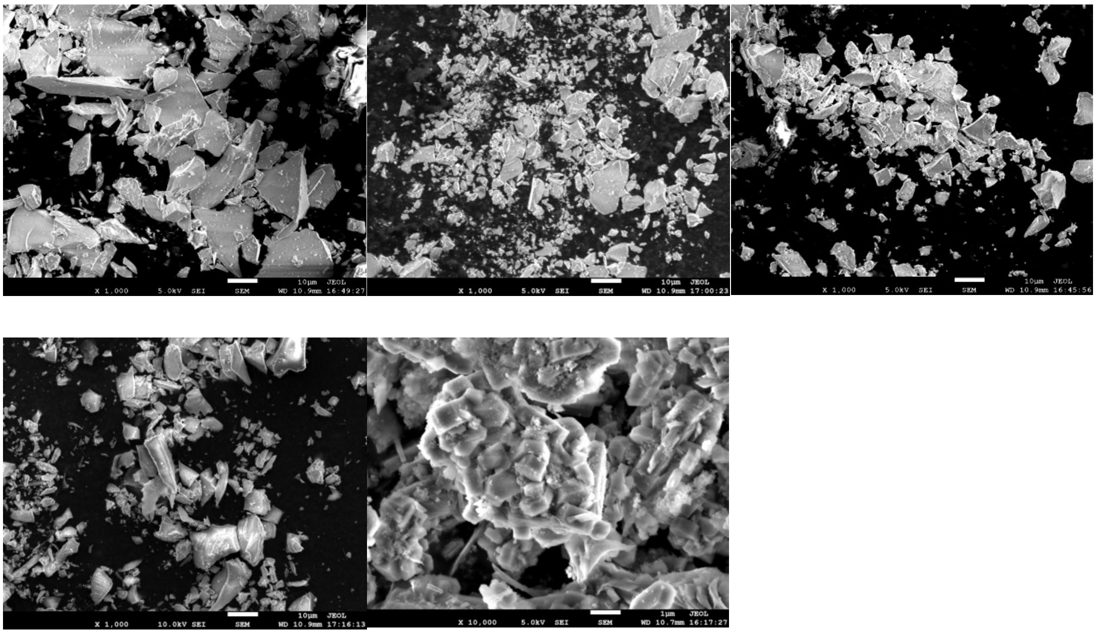

Fig.S1 Y0, Y0.05, Y0.1, Y0.3,ZSM-5 SEM images

Table S1 d-spacings of prepared catalysts calculated using the Bragg equation from XRD

	2θ / °	**d(011) (nm)**	**2θ / °**	**d(110) (nm)**	**2θ / °**	**d(020) (nm)**	**2θ / °**	**d(121) (nm)**
Y0	30.53	0.2926	35.38	0.2535	50.83	0.1795	60.4	0.1531
Y0.05	30.46	0.2932	35.28	0.2542	50.78	0.1797	60.33	0.1533
Y0.1	30.45	0.2933	35.27	0.2544	50.70	0.1799	60.23	0.1535
Y0.3	30.41	0.2937	35.15	0.2551	50.44	0.1808	59.94	0.1542

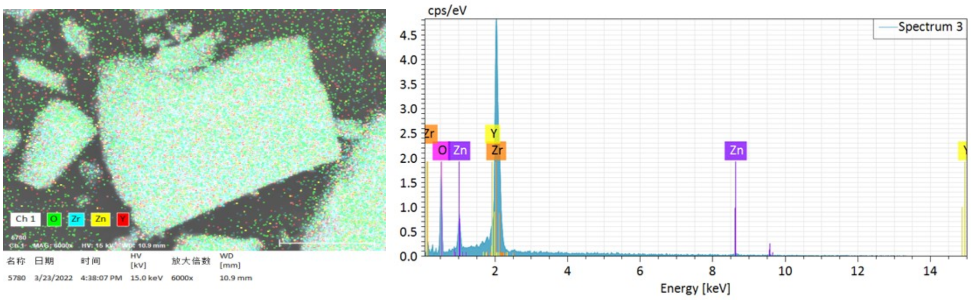

Fig.S2 EDS-mapping of Y0.1

Table S2 EDS-mapping element content analysis of Y0.1.

Element	Atomic number	Quality / %	Normalized Mass / %	Atoms / %
O	8	24.8	29.9	70.3
Zn	30	3.6	4.3	2.5
Y	39	3.8	4.6	1.9
Zr	40	50.8	61.3	25.3
		82.9	100	100

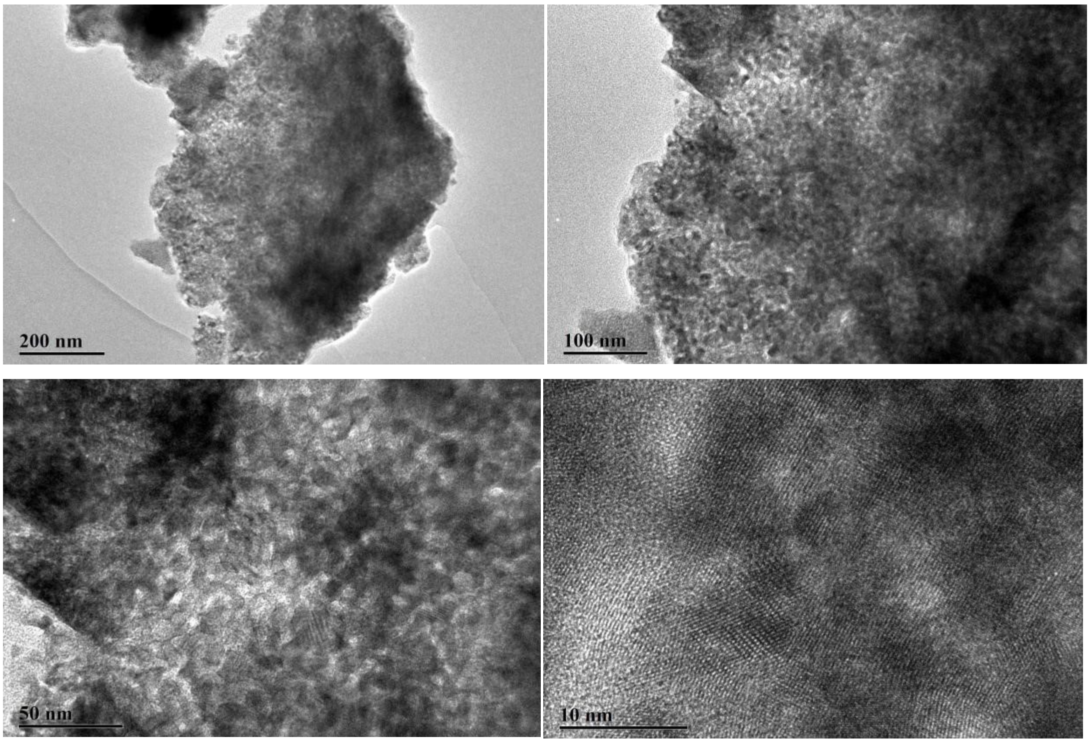

Fig. S3 Y0.1TEM images of different magnifications

Table S3 Deconvolution results of O 1s XPS peaks.

Catalyst	O_{OH} / %	O_V / %	O_L / %
Y0	13.1	17.8	69.1
Y0.05	11.0	24.7	64.3
Y0.1	13.6	25.7	60.7
Y0.3	17.3	20.2	62.5

Table S4 Y-doped ZnZrOx/HZSM-5 catalyzed alkylation of CO_2 and benzene.

Catalyst	Conv.	Conv.	Selectivity/%			
	CO_2/%	benz./%	M_B	E_B	X_B	Other
Y0/ZSM-5	10.0	19.7	73.6	3.0	14.3	9.1
Y0.05/ZSM-5	10.2	22.7	61.8	2.6	12.4	23.2
Y0.1/ZSM-5	17.3	30.8	56.5	2.5	15.0	26.0
Y0.3/ZSM-5	14.5	18.3	73.3	3.0	11.5	12.2

Table S5 Liquid phase product distribution

Catalyst	Conv.	Liquid phase product distribution / %				
	benz. / %	M_B	E_B	X_B	C_{9+}	
Y0/ZSM-5	19.7	80.2	3.3	15.5	1.0	
Y0.05/ZSM-5	22.7	79.8	3.3	16.1	0.7	
Y0.1/ZSM-5	30.8	74.8	3.3	20.0	1.9	
Y0.3/ZSM-5	18.3	81.5	3.3	12.8	2.3	
Zn0.1Ti/ZSM-5(30)	23.8	77.4	2.8	16.1	3.7	Ref.[1]

Table S6 Different mixing methods of Y0.1/HZSM-5 catalyzed alkylation of CO_2 and benzene.

	Conv.	Conv.	Selectivity/%			
	CO_2/%	benz./%	M_B	E_B	X_B	Other
dual-bed	12.8	9.33	56.8	5.9	6.2	31.1
granule-mixing	14.8	28.5	58.0	2.1	14.4	26.5
powder-mixing	17.3	30.8	56.5	2.5	15.1	25.9

Table S7 Gas phase products of Y0.1/ZSM-5 and Y0.1 for CO_2 hydrogenation to methanol

Catalyst	**Conv. CO_2/%**	**Selectivity/%**						
		Methane	**Ethylene**	**Ethane**	**Propylene**	**Propane**	**Butane**	**CO**
Y0.1/ZSM-5	17.3	1.4	0.1	0.2	0.3	0.3	0.3	56.3
Y0.1	13.5	3.7	0	0	0	0	0	91.8

Table S8 H_2 consumption amount of various catalysts.

Catalysts	**ZnY-O-Zr / mmol/g**	**ZrO_2 / mmol/g**	**(ZnY-O-Zr)/(ZnY-O-Zr+ZrO_2)**
Y0	0.08	0.52	0.13
Y0.05	0.18	0.58	0.24
Y0.1	0.24	0.34	0.41
Y0.3	0.11	0.54	0.17

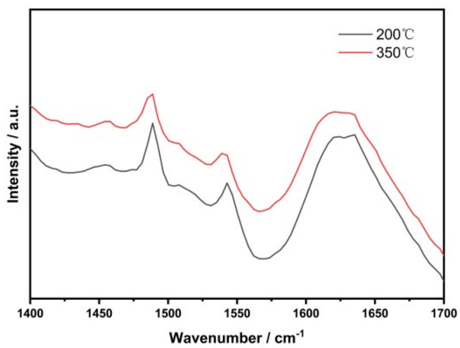

Fig. S4 IR spectra of the ZSM-5 after pyridine desorption

	BET Surface Area / m²/g	**Pore Volume / cm³/g**	**Pore Size / nm**
Y0	28	0.03	3
Y0.05	33	0.04	3
Y0.1	29	0.04	3
Y0.3	14	0.01	3
ZSM-5	346	0.09	6

Table S9 Catalyst bet specific surface area, pore volume and pore size

1. Liu, X.; Pan, Y.; Zhang, P.; Wang, Y.; Xu, G.; Su, Z. *Frontiers of Chemical Science and Engineering* **2021,** *16* (3), 384-396.