

Supporting Information

For

Alkylation of benzene with methanol over hierarchical porous ZSM-

5: Synergy effects of hydrogen atmosphere and zinc modification

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Conversion of benzene and selectivity to toluene, xylene ethylbenzene and trimethylbenzene were defined as follows:

$$\text{Conversion of benzene} = \frac{\text{benzene in feed} - \text{benzene in product}}{\text{benzene in feed}} \times 100\%$$

$$\text{Selectivity of toluene} = \frac{n(\text{toluene})}{n(\text{alkyl aromatics})} \times 100\%$$

$$\text{Selectivity of xylene} = \frac{n(\text{xylene})}{n(\text{alkyl aromatics})} \times 100\%$$

$$\text{Selectivity of ethylbenzene} = \frac{n(\text{ethylbenzene})}{n(\text{alkyl aromatics})} \times 100\%$$

$$\text{Selectivity of trimethylbenzene} = \frac{n(\text{trimethylbenzene})}{n(\text{alkyl aromatics})} \times 100\%$$

Table S1 Textural properties of unmodified and ZnO modified ZSM-5 catalysts.

Catalyst	Zn content (wt%)	S_{BET} (m^2/g)	V_{micro} (cm^3/g)	V_{meso} (cm^3/g)
	XPS			
0wt% ZnO/ZSM-5	0	372	0.12	0.19
1wt% ZnO/ZSM-5	1.0	367	0.11	0.20
2wt% ZnO/ZSM-5	1.7	363	0.11	0.20
3wt% ZnO/ZSM-5	2.6	361	0.11	0.24
4wt% ZnO/ZSM-5	4.0	369	0.11	0.24

Table S2 Catalytic performance of unmodified and ZnO modified ZSM-5 catalysts in benzene alkylation with methanol under nitrogen atmosphere.

Catalyst	Conversion of benzene (%)	Selectivity (%)			
		Toluene	Ethylbenzene	Xylene	TMB
0wt% ZnO/ZSM-5	51.5	47.8	2.6	33.8	8.9
1wt% ZnO/ZSM-5	51.8	52.3	0.7	34.6	8.3
2wt% ZnO/ZSM-5	49.9	54.5	0.3	32.4	6.8
3wt% ZnO/ZSM-5	41.5	58.7	0.1	25.0	5.1
4wt% ZnO/ZSM-5	37.5	62.3	0.1	24.5	4.4

TMB: Trimethylbenzene

Table S3 Catalytic performance of unmodified and ZnO modified ZSM-5 catalysts in benzene alkylation with methanol under hydrogen atmosphere.

Catalyst	Conversion of benzene (%)	Selectivity (%)			
		Toluene	Ethylbenzene	Xylene	TMB
0wt% ZnO/ZSM-5	51.6	47.2	2.5	34.2	9.2
1wt% ZnO/ZSM-5	53.6	47.4	1.0	35.9	10.5
2wt% ZnO/ZSM-5	51.8	52.2	0.6	34.6	8.1
3wt% ZnO/ZSM-5	49.1	54.2	0.3	33.4	7.7
4wt% ZnO/ZSM-5	48.3	54.5	0.3	32.1	7.5

TMB: Trimethylbenzene

Table S4 The stability of unmodified and ZnO modified ZSM-5 catalysts under different atmospheres.

Time on stream (h)	Conversion of benzene (%)			
	0wt% ZnO/ZSM-5		1wt% ZnO/ZSM-5	
	N_2	H_2	N_2	H_2
2	51.5	51.9	53.11	53.3
4	51.4	51.3	52.89	53.2
6	51.6	51.5	51.62	53.8
8	51.2	51.9	51.18	53.9
10	51.6	51.6	50.01	53.6

TMB: Trimethylbenzene

Table S5 Products distribution of unmodified and ZnO modified ZSM-5 catalysts under different atmospheres.

Components	Catalysts and content (wt)/%			
	0wt% ZnO/ZSM-5		1wt% ZnO/ZSM-5	
	N_2	H_2	N_2	H_2
Methane	0.05	0.06	0.13	0.07
C2	0.18	0.17	0.09	0.19
C3	0.52	0.48	0.03	0.21
C4	0.24	0.21	0.00	0.05
C5	0.07	0.05	0.00	0.03
Benzene	39.09	38.98	39.73	36.82
Toluene	23.33	22.98	26.16	23.79
Ethylbenzene	1.48	1.40	0.02	0.63
Xylene	19.18	19.34	19.91	20.79
Trimethylbenzene	5.65	5.91	5.06	6.88
Other	10.21	10.42	8.87	10.36

Reaction conditions: 400 °C, 1atm, WHSV=2.0 h⁻¹, methanol to benzene molar ratio = 1:1.

Table S6 Acidic properties of unmodified and ZnO modified ZSM-5 catalysts.

<i>Catalyst</i>	<i>Acidity by type^a (mmol/g)</i>		
	<i>Brönsted</i>	<i>Lewis</i>	<i>B/L</i>
0wt% ZnO/ZSM-5	0.0291	0.0045	6.47
1wt% ZnO/ZSM-5	0.0159	0.0318	0.50
2wt% ZnO/ZSM-5	0.0127	0.0490	0.26
3wt% ZnO/ZSM-5	0.0093	0.0518	0.18
4wt% ZnO/ZSM-5	0.0063	0.0602	0.10

a: Density of the acid sites, assorted according to the acidic type, determined by Py-IR (recorded after evacuation at 400°C). B/L: the ratio of the amount of Brönsted acidic sites to that of Lewis acidic sites.