

Supporting information

A New insight into the Reaction Behaviors of Side-chain Alkylation of Toluene with Methanol over CsX

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Fig. S1 N₂ adsorption-desorption isotherms at 77K and pore size distributions of the indicated catalysts

Fig. S2 XRD spectra of SiO₂ and H₃PO₄/SiO₂.

Fig. S3 Catalysts loading position of H₃PO₄/SiO₂ and CsX, position A for H₃PO₄/SiO₂ and position B for CsX.

Fig. S4 GC-MS analysis of hydrocarbon species trapped in zeolite pores after conversion of styrene with methanol at 430 °C for NaX, the reaction time is 50min.

Table S1 The details of cesium ion exchange process for different CsX.

Table S2. Reaction results for depolymerization of trimethylol on H₃PO₄/SiO₂.

Table S3 Details for reaction results of alkylation of toluene with methanol on indicated catalysts.

Table S1 The details of cesium ion exchange process for different CsX.

Catalysts	liquid/solid ratio (mL/g)	Temperature (°C)	ion exchange process*
CsX-1	8:1	80	Exchanged with 0.2 mol/L CsCl for 4h.
CsX-2	8:1	80	Exchanged with 0.2 mol/L CsCl for 4h, repeated one times.
CsX-3	8:1	80	Exchanged with 0.2 mol/L CsCl for 4h, repeated two more times.
CsX-4	8:1	80	Exchanged with 0.2 mol/L CsCl for 4h , repeated two more times, and then exchanged with 0.1mol/L CsCl for 1 h.
CsX-5	8:1	80	Exchanged with 0.2 mol/L CsCl for 4h , repeated two more times, and then exchanged with 0.4mol/L CsCl for 4 h.
CsX-6	8:1	80	Exchanged with 0.5 mol/L CsCl for 4h, repeated three more times.

* After each ion exchange process, the slurry was filtered and washed by a large amount of deionized water for several times.

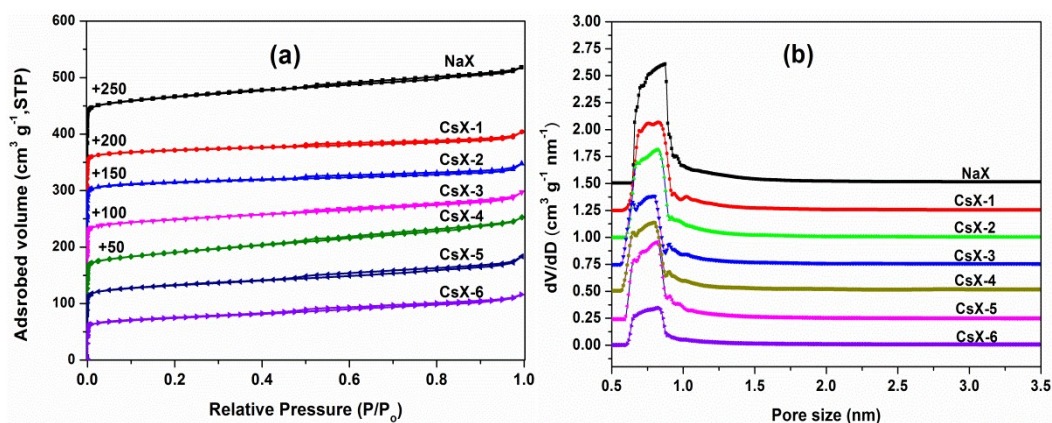


Fig. S1 N_2 adsorption-desorption isotherms at 77K (a) and pore size distributions of the indicated catalysts (b), the pore size distributions were calculated by SF method.

Depolymerization of triformol to formaldehyde

The catalyst for depolymerization of triformol was prepared by incipient-wetness impregnation of Mesoporous SiO_2 (Qingdao Ocean Chemical CO., Ltd., China.) with H_3PO_4 (Tianjin Kermel Chemical Reagent Co. Ltd., 85 %) at room temperature, after stewed overnight, dried at 110 °C for 4h and then calcined in air at 450 °C for 4h. The amount of H_3PO_4 loadings was 60 wt %, and the catalyst was named as H_3PO_4/SiO_2 .

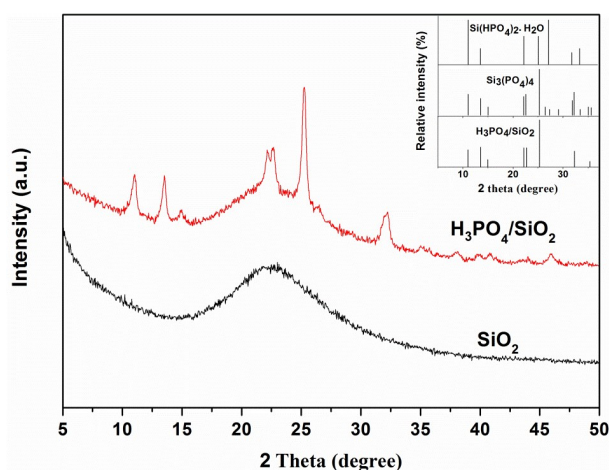


Fig. S2 XRD spectra of SiO_2 and H_3PO_4/SiO_2 .

XRD patterns of SiO_2 and H_3PO_4/SiO_2 are in Fig. 2. Only a broad peak around 22° can be detected on the XRD spectrum of SiO_2 , which can be attributed to

amorphous SiO₂. After loading of H₃PO₄, a series of new peaks appeared with the position matching well with Si₃(PO₄)₄ (PDF NO. 22-1380) in the inset figure. Actually, the peak position of Si₃(PO₄)₄ and Si(HPO₄)₂•H₂O (PDF NO. 18-1168) is very similar with each other. The existence of Si(HPO₄)₂•H₂O species can not be omitted.¹ Thus, it is reasonable to suggest that both Si(HPO₄)₂•H₂O and Si₃(PO₄)₄ were formed on H₃PO₄/SiO₂.

Reference

1Y. Maki, K. Sato, A. Isobe, N. Iwasa, S. Fujita, M. Shimokawabe and N. Takezawa, Appl. Catal. A: Gen., 1998,**170**, 269-275.

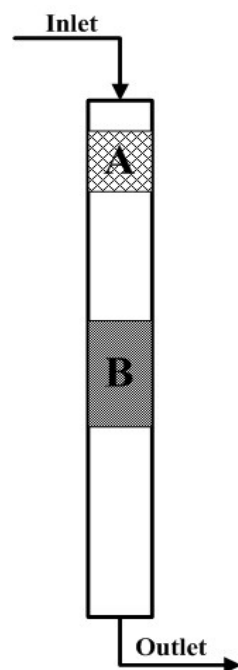


Fig. S3 Catalysts loading position of H₃PO₄/SiO₂ and CsX, position A for H₃PO₄/SiO₂ and position B for CsX.

Formaldehyde employed in this work was produced by depolymerization of trimethylol using a H₃PO₄/SiO₂ catalyst. The packing structure of H₃PO₄/SiO₂ (A) and CsX (B) catalysts is shown in Fig. S3.

The H₃PO₄/SiO₂ catalyst was activated in-situ at 335 °C under a flow of air (40 mL/min) for 90 min and then cooled to the reaction temperature of 295 °C. Before the

side-chain alkylation of toluene with formaldehyde, a liquid mixture of toluene and triformol with molar ratio of 18:1 was pumped into A at a weight hourly space velocity (WHSV) of 2 h⁻¹ with helium at a flow rate of 10 mL/min (run number 1). Before the styrene conversion with formaldehyde, the feedstock is benzene, styrene and triformol with a molar ratio of 16:1:1 (run number 2). The reaction results were shown in Table S2.

Table S2 Reaction results for depolymerization of triformol on H₃PO₄/SiO₂.

Run number	Conversion of triformol (mol%)	Yield of formaldehyde (mol%)	Y _{ST+EB} ^a	X _(StoEB) ^b	molar ratio of main compounds in outlet	
					toluene: formaldehyde	benzene: styrene: formaldehyde
1	99.31	96.29	0.0013	-	6.1: 1	-
2	99.48	96.71	-	0.034	-	15.7: 1: 2.9

^aY_{ST+EB}, yield of styrene and ethylbenzene, calculated by
$$Y_{ST+EB} = \frac{\text{styrene and ethylbenzene}_{outlet}}{3 \times \text{triformol}_{inlet}} \times 100\%$$
 ;

^bX_(STtoEB), conversion of styrene to ethylbenzene, calculated by
$$X_{(ST\ to\ EB)} = \frac{\text{ethylbenzene}_{outlet}}{\text{styrene}_{inlet}} \times 100\%$$
 .

As shown in Table S2, the conversion of triformol reaches 99%, and yield of formaldehyde is higher than 96% for both run number 1 and 2 experiments. Y_{ST+EB} in run number 1 and X_(ST-to-EB) in run number 2 is close to zero. The molar ratio of toluene to formaldehyde in outlet of run number 1 is 6.1:1, which is close to that of toluene to methanol used in Table 3. And the molar ratio of benzene, styrene and formaldehyde in outlet of run number 2 is 15.7: 1: 2.9, which is close to the molar ratio inlet of benzene, styrene and methanol in conversion of styrene with methanol used in Fig.10. Thus, it is reasonable to employ this experiment system to investigate the reaction behaviour of toluene and formaldehyde and conversion of styrene with formaldehyde.

Table S3 Details for reaction results of alkylation of toluene with methanol on indicated catalysts.*

Components	Molar flow rates of different components (mmol/h)							
	Reactor feed	Output over different catalysts						
		NaX	CsX-1	CsX-2	CsX-3	CsX-4	CsX-5	CsX-6
Carbon monoxide	-	1.079	0.266	0.618	2.560	4.520	7.221	10.335
Carbon dioxide	-	0.172	0.045	0.021	0.068	0.082	0.139	0.263
Methane	-	0.618	0.633	0.030	0.028	0.029	0.042	0.071
C ₂ -C ₅	-	0.312	0.156	0.002	0.004	0.006	0.008	0.012
DME	-	3.298	3.687	2.145	1.813	1.420	0.964	0.984
methanol	25.643	15.443	15.979	20.326	18.500	17.097	14.913	10.672
benzene	-	0.013	0.004	0.001	0.002	0.008	0.005	0.006
Toluene	12.821	11.524	11.511	12.485	12.268	11.925	11.360	10.792
Ethylbenzene	-	0.015	0.010	0.034	0.166	0.408	0.810	1.487
Xylene	-	0.884	0.952	0.187	0.070	0.013	0.009	0.007
Styrene	-	0.007	0.011	0.087	0.314	0.446	0.573	0.488
C ₉ ⁺	-	0.279	0.245	0.027	0.041	0.046	0.057	0.077
Total	38.464	33.643	33.498	35.964	35.833	36.001	36.102	35.195
[HCHO]	-	1.273	0.332	0.759	3.109	5.457	8.744	12.574
X _{toluene} (mol%)		10.119	10.220	2.622	4.312	6.992	11.392	15.829
X _{methanol} (mol%)		14.056	8.931	4.002	13.716	22.253	34.326	50.704
Y _{ST+EB} (mol%)		0.172	0.163	0.939	3.748	6.667	10.787	15.406
Y _{CO+CO₂} (mol%)		4.878	1.212	2.492	10.249	17.948	28.705	41.331
ST/EB (mol/mol)		0.482	1.176	2.591	1.887	1.094	0.707	0.329
S _{Side-chain} (mol%)		2.436	2.155	39.144	87.321	98.450	99.322	99.642
Y _{xylene} (mol%)		6.895	7.422	1.460	0.544	0.105	0.074	0.055
X _(HCHO to ST+EB) (mol%)		1.734	6.315	15.856	15.457	15.663	15.817	15.709
Y _[HCHO]		4.964	1.294	2.961	12.123	21.281	34.098	49.034
X _(ST to EB)		67.474	45.966	27.847	34.644	47.765	58.589	75.269

*Reaction conditions: T=430°C; WHSV=2h⁻¹; n(toluene)/n(methanol)=1:2.

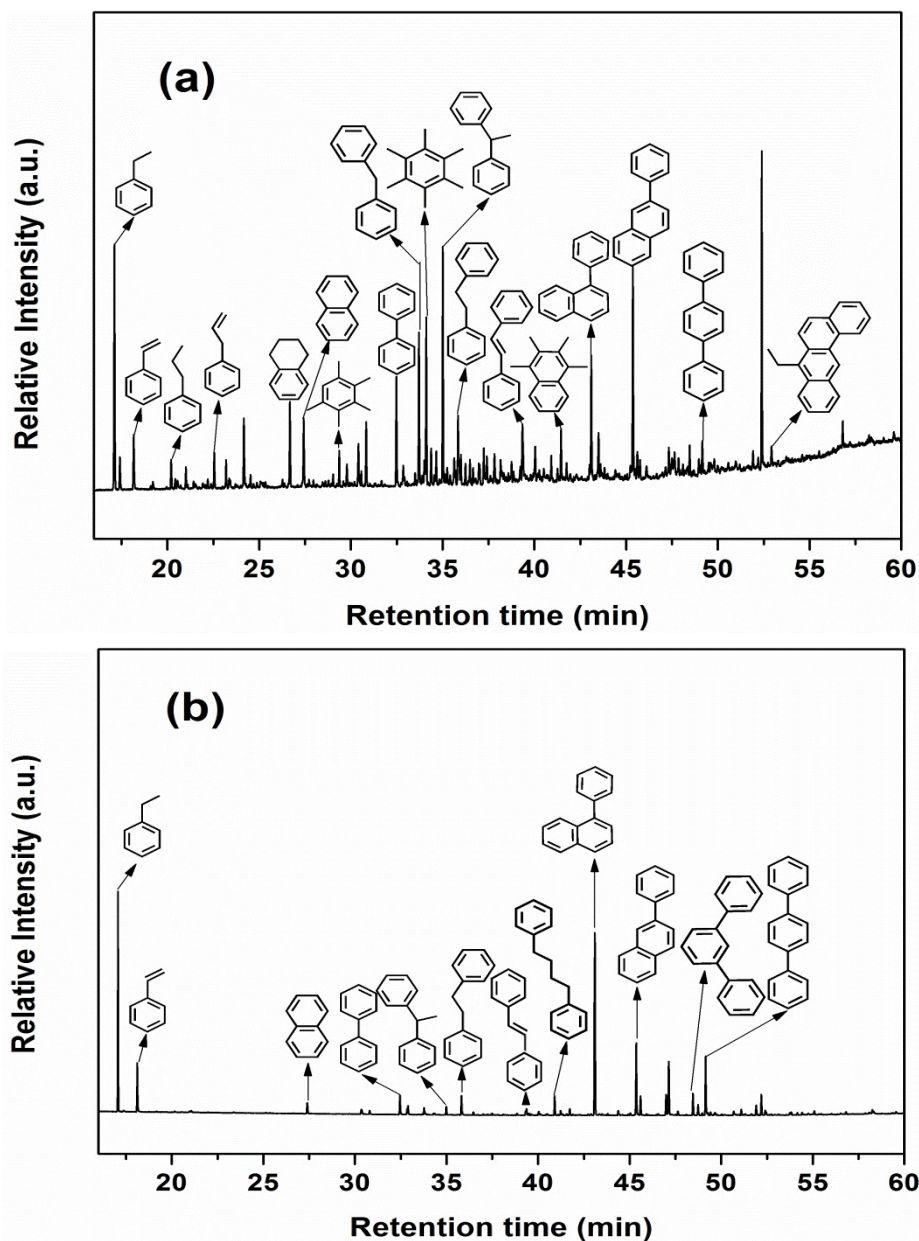


Fig. S4. GC-MS analysis of hydrocarbon species trapped in zeolite pores after conversion of styrene with methanol at 430 °C for NaX (a) and CsX-6 (b), the reaction time was 50min.

The hydrocarbon species trapped in the pores of NaX and CsX-6 after reaction between styrene and methanol was analyzed by an Agilent 7890A/7000B GC/MSD. The results are shown in Fig. S4. The retained hydrocarbon species were obtained by dissolving the catalyst in 15% HF in a screw-cap Teflon vial, and then extracted by CH_2Cl_2 .