Supporting information

Explaining the Influence of the Introduced Base Sites into Alkali Oxides modified CsX towards Side-chain Alkylation of Toluene with Methanol

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Table S1 The textural structure properties of CsX-c with different cesium oxide amount.

Catalysts	CsX-c [1]	4CsOx/CsX-c	8CsOx/CsX-c	12CsOx/CsX-c	16CsOx/CsX-c
S_{BET} (m^2/g)	542.20	468.50	398.34	356.28	295.60
V_{micro} (cm^3/g) [a]	0.196	0.155	0.128	0.116	0.088

[a] Calculated by t-plot method.

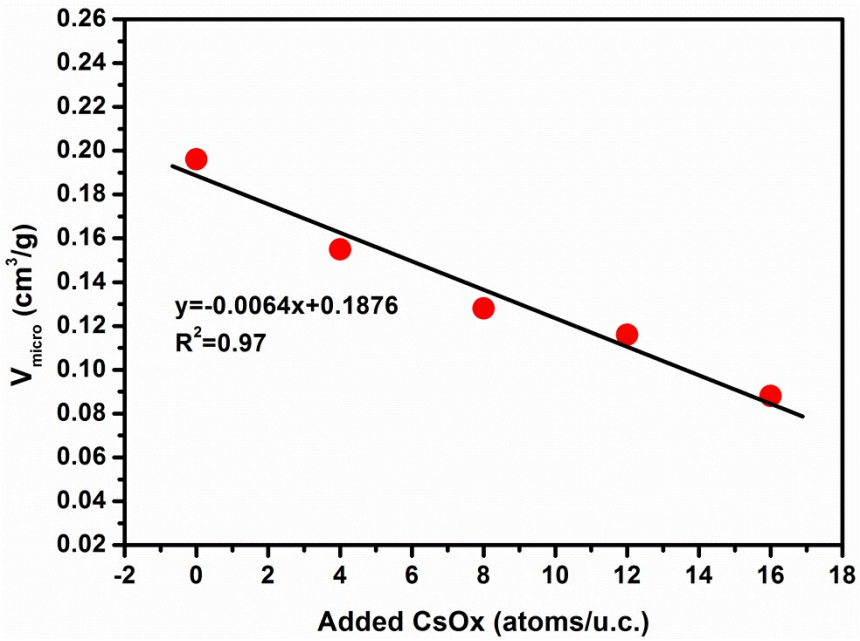

Fig. S1. The V_{micro} of the CsX-c modified with different cesium oxide amount as function of the cesium oxide loading amount.

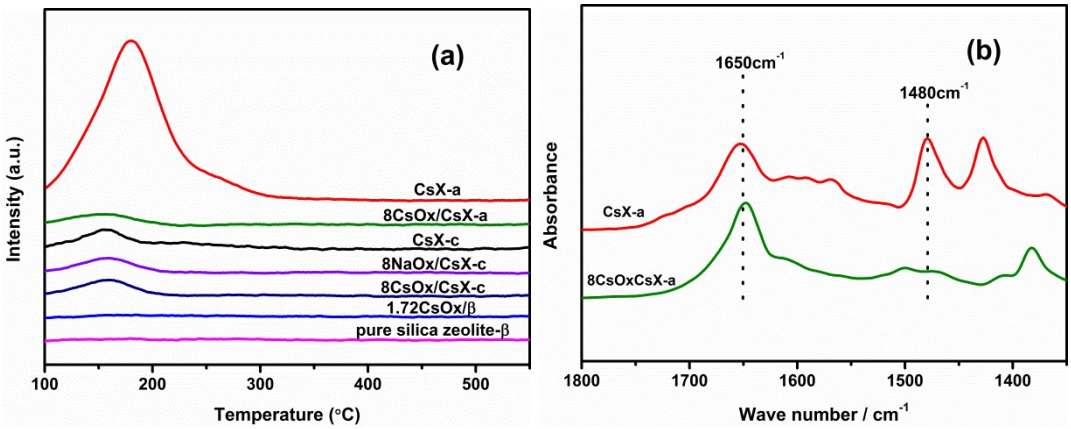

Fig. S2. (a) NH_3-TPD and (b) FT-IR of adsorbed NH_3 of the indicated catalysts.

The acid properties of the catalysts were studied by NH_3-TPD and FT-IR of adsorbed NH_3, and the results were shown in Fig. S2, in which the data of CsX-a and CsX-c were taken from our previous work.[1] The NH_3-TPD of the alkali modified CsX-c is similar to that of CsX-c, indicating that the introduction of alkali oxides had little effect on the acid sites of CsX-c, which was consistent with the conclusion of Alabi et al..[2] However, when CsX-a was modified with cesium oxide, both the desorption temperature and area of the NH_3 decreased obviously, and the acid properties of 8CsOx/CsX-a was similar to that of CsX-c. In our previous work, the

acid properties of NaX and CsX with different cesium exchanged degree (ED) were studied.[1] It found that Brønsted acidic hydroxyl group can be detected on NaX which could be removed by the cesium ion exchange process, and the Brønsted acid sites will disappeared entirely when the ED reaching 45.9 %. The acid properties of CsX-a and 8CsOx/CsX-a was further studied by FT-IR of adsorbed NH_3 (Fig. S2(b)). The absorption bands at 1650 cm^{-1} was assigned to the asymmetric deformation mode of NH_3 molecules adsorbed on Lewis acid sites, and 1480 cm^{-1} was attributed to the ammonium ions formed by proton transfer from Brønsted acid to ammonia molecules.[3] As shown in Fig S2(b), the Brønsted acid sites can be detected on CsX-a (ED=21.8%) as the cesium ED is lower. With the introduction of cesium oxide, the absorption band at 1480 cm^{-1} was almost disappeared on 8CsOx/CsX-a, indicating that the introduction of cesium oxide will remove the Brønsted acid sites which was consistent with the report says.[4] And the disappearance of the Brønsted acid sites should account for the weakened acid properties of CsX-a when modified with cesium oxide (Fig. S2(a)). As no Brønsted acid sites was detected on CsX-c (EB=45.9 %),[1] and the NH_3-TPD of alkali oxide modified CsX-c is similar to that of CsX-c (Fig. S2(a)), suggesting the Lewis acid sites of CsX was little influenced by the loaded alkali oxides. What's more, no NH_3 desorption peak was detected on both pure silicon zeolite β and 1.72CsOx/β, indicating that almost no acid sites on pure silicon zeolite β and no acid base sites will be introduced by loading cesium oxide.

Table S2 The composition and base properties of the indicated catalysts.

Cstalyst	composition [a]	Amount of $O^{\delta-}$ in the zeolite framework (mmol/g)	Amount of desorbed CO_2 (mmol/g)[b]	S_{int} [c]	δ_o [c]
Na_2O	Na_2O	-	-	1.3667	-0.8091
K_2O	K_2O	-	-	0.9723	-0.8922
Cs_2O	Cs_2O	-	-	0.7420	-0.9406
CsX-a	$Na_{68.9}Cs_{19.3}Al_{88.2}Si_{103.8}O_{384}$	5.66	0.0647	3.1560	-0.4128
CsX-b	$Na_{59.6}Cs_{28.4}AlO_{88}Si_{104}O_{384}$	5.31	0.1126	3.1183	-0.4324
CsX-c	$Na_{47.6}Cs_{40.4}Al_{88}Si_{104}O_{384}$	4.91	0.1700	3.0670	-0.4511
8CsOx/CsX-a	$Na_{68.9}Cs_{27.3}Al_{88.2}Si_{103.8}O_{388}$	5.28	0.1557	3.0759	-0.4493
8CsOx/CsX-b	$Na_{59.6}Cs_{36.4}Al_{88}Si_{104}O_{388}$	4.97	0.2049	3.0398	-0.4569
4CsOx/CsX-c	$Na_{47.6}Cs_{44.4}Al_{88}Si_{104}O_{386}$	4.91	0.2269	3.0283	-0.4593
8CsOx/CsX-c	$Na_{47.6}Cs_{48.4}Al_{88}Si_{104}O_{388}$	4.62	0.3394	2.9907	-0.4672
12CsOx/CsX-c	$Na_{47.6}Cs_{52.4}Al_{88}Si_{104}O_{390}$	4.49	0.4459	2.9543	-0.4749
16CsOx/CsX-c	$Na_{47.6}Cs_{56.4}Al_{88}Si_{104}O_{392}$	4.37	0.4956	2.9189	-0.4823
8NaOx/CsX-c	$Na_{55.6}Cs_{40.4}Al_{88}Si_{104}O_{388}$	4.85	0.1995	3.0233	-0.4603
8KOx/CsX-c	$Na_{47.6}K_8Cs_{40.4}Al_{88}Si_{104}O_{388}$	4.81	0.2672	3.0051	-0.4642

[a] CsX-a, CsX-b and CsX-c were obtained by XRF, the alkali oxide modified catalysts were calculated by plus the unite cell composition of the host zeolite and the amount of the loaded alkali oxides, the added alkali oxides were calculated in the form of Na_2O, K_2O and Cs_2O;

b Calculated by the amount of desorbed CO_2 in CO_2-TPD before 400°C;

c S_{int} and δ_o were calculated according to W. J. Mortier.[5]

Table S3 The reaction behaviors of alkylation of toluene with methanol over the indicated catalysts.*

Components	Feed	Molar flow rates of different components (mmol/h)												
		Output over different catalysts												
		CsX-a	CSX-b	CSX-c	4CsOx/CsX-c	8CsOx/CsX-c	12CsOx/CsX-c	16CsOx/CsX-c	8NaOx/CsX-c	8KOx/CsX-c	8CsOx/CsX-a	8CsOx/CsX-b	pure sillicon β	1.72CsOx/β
Carbon monoxide	——	0.266	0.618	4.520	10.975	14.627	17.298	19.433	8.910	11.302	7.158	10.694	0.008	0.013
Carbon dioxide	——	0.045	0.021	0.082	0.105	0.293	0.153	0.190	0.067	0.100	0.144	0.115	0.003	0.003
Methane	——	0.633	0.030	0.029	0.112	0.142	0.245	0.150	0.087	0.098	0.043	0.082	0.057	0.004
C_2-C_5	——	0.156	0.002	0.006	0.023	0.049	0.054	0.026	0.012	0.015	0.006	0.012	0.043	0.022
DME	——	3.687	2.145	1.420	0.606	0.349	0.203	0.128	0.542	0.566	0.878	0.514	0.184	0.052
methanol	25.643	15.979	20.326	17.097	10.661	7.411	5.645	3.872	13.665	10.860	15.238	11.855	24.938	25.413
benzene	——	0.004	0.001	0.008	0.004	0.004	0.003	0.004	0.004	0.004	0.005	0.004	0.000	0.000
Toluene	12.821	11.511	12.485	11.925	11.021	10.405	10.656	11.128	11.252	10.948	11.559	11.000	12.647	12.820
Ethylbenzene	——	0.010	0.034	0.408	1.594	2.069	1.897	1.418	1.299	1.605	0.822	1.515	0.000	0.000
Xylene	——	0.952	0.187	0.013	0.005	0.002	0.004	0.005	0.002	0.002	0.009	0.002	0.064	0.001
Styrene	——	0.011	0.087	0.446	0.203	0.137	0.043	0.029	0.227	0.195	0.384	0.218	0.000	0.000
C_9^+	——	0.245	0.027	0.046	0.081	0.173	0.144	0.207	0.064	0.091	0.047	0.079	0.093	0.004
Total	38.464	33.498	35.964	36.001	35.390	35.660	36.345	36.591	36.129	35.785	36.293	36.089	38.036	38.331
[CH_2O]	——	0.332	0.759	5.457	12.878	17.125	19.391	21.070	10.503	13.202	8.509	12.541	0.011	0.016
[H]		1.285	2.796	20.119	47.915	64.088	73.685	81.386	38.959	49.208	31.622	46.701	0.041	0.062
$X_{toluene}$ (mol%)		10.220	2.622	6.992	14.038	18.845	16.886	13.203	12.241	14.611	9.843	14.202	1.358	0.010
$X_{methanol}$ (mol%)		8.931	4.002	22.253	53.703	68.377	76.399	83.899	42.487	53.236	33.728	49.759	1.316	0.489
Y_{ST+EB} (mol%)		0.163	0.939	6.667	14.022	17.204	15.130	11.287	11.902	14.035	9.408	13.511	0.003	0.004
Y_{CO+CO2} (mol%)		1.212	2.492	17.948	43.208	58.181	68.055	76.524	35.007	44.465	28.477	42.153	0.039	0.060
ST/EB (mol/mol)		1.176	2.591	1.094	0.128	0.066	0.022	0.020	0.175	0.121	0.467	0.144	0.000	0.000
Y_{xylene} (mol%)		7.422	1.460	0.105	0.041	0.018	0.029	0.039	0.018	0.017	0.072	0.016	0.501	0.010
$X_{(CH2O\text{-}to\text{-}ST)}$ (mol%)		6.315	15.856	15.663	13.961	12.880	10.004	6.868	14.529	13.631	14.177	13.812	4.004	3.012
$Y_{[CH2O]}$		1.294	2.961	21.281	50.219	66.782	75.620	82.167	40.958	51.483	33.181	48.908	0.041	0.062

*Reaction conditions: T=430℃; WHSV=2h^{-1}; n(toluene)/n(methanol)=1:2.

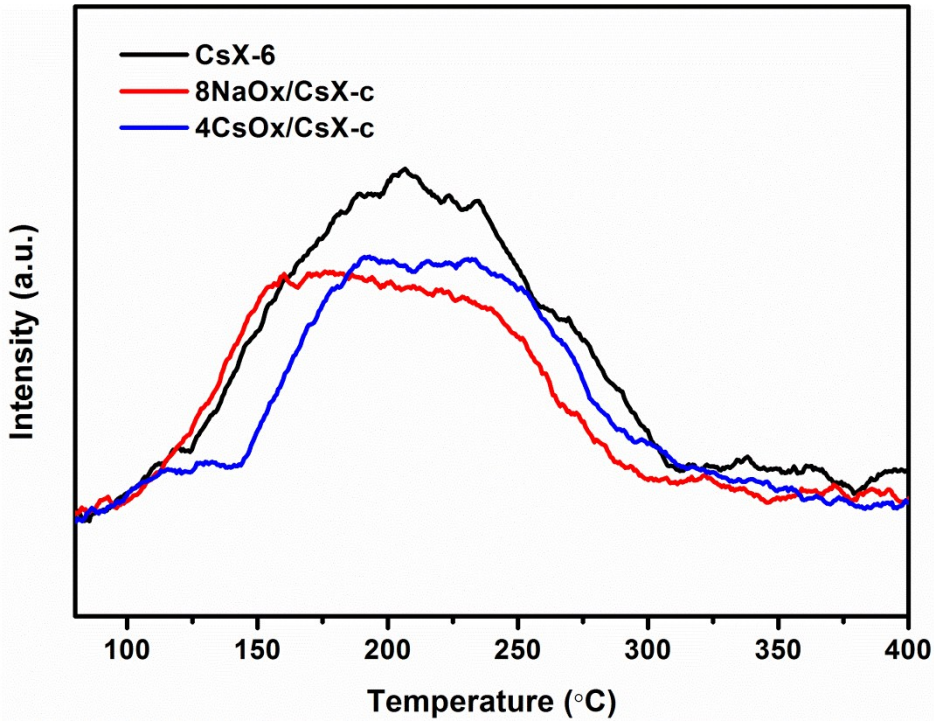

Fig. S3 the comparison of CO_2-TPD curves of the indicated catalysts with similar S_{int}.

The CO_2-TPD of CsX-6 (cesium exchanged degree is 59.2 %) was taken from our preceding paper to compare with 8NaOx/CsX-c and 4CsOx/CsX-c,[1] as the S_{int} for the three catalysts is similar to each other.

Reference

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