Supporting information

The Role of Boron Sites in Side-chain Alkylation of Toluene with Methanol and a High Performance Composite Catalyst

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Thermodynamics analysis

Thermodynamics equilibrium data were obtained by the following five reactions which involving methanol conversion and further conversion of the generated formaldehyde during side-chain alkylation of toluene with methanol process:

(a) $CH_3OH = CH_2O + H_2$

(b) $CH_2O = CO+H_2$

(c) $CH_2O + C_7H_8 = C_8H_8 + H_2O$

(d) $CH_3OH = CO + 2H_2$

(e) $CH_3OH + C_7H_8 = C_8H_8 + H_2O + H_2$

The standard Gibbs free energy change ($\Delta_r G_m^{\theta}(T)$) of the above five reactions was calculated by the follow thermodynamic formula. The $\Delta_f H^{\theta}_{m,j}$ (298.15K), $S^{\theta}_{m,j}$ (298.15K), A, B, C and D were obtained from manual of thermodynamics.[1,2]

$$\Delta_f H_{m,j}^{\theta}(T) = \Delta_f H_{m,j}^{\theta}(298.15K) + \int_{298.15}^{T} C_{p,g,j}^{\theta} dT$$

$$S_{m,j}^{\theta}(T) = S_{m,j}^{\theta}(298.15K) + \int_{298.15}^{T} C_{p,g,j}^{\theta} dlnT$$

$$C_{p,g}^{\theta} = A + BT + CT^2 + DT^3$$

$$\Delta_r G_m^{\theta}(T) = \sum_j v_j \Delta_f H_{m,j}^{\theta}(T) - T \sum_j v_j S_{m,j}^{\theta}(T)$$

SEM images

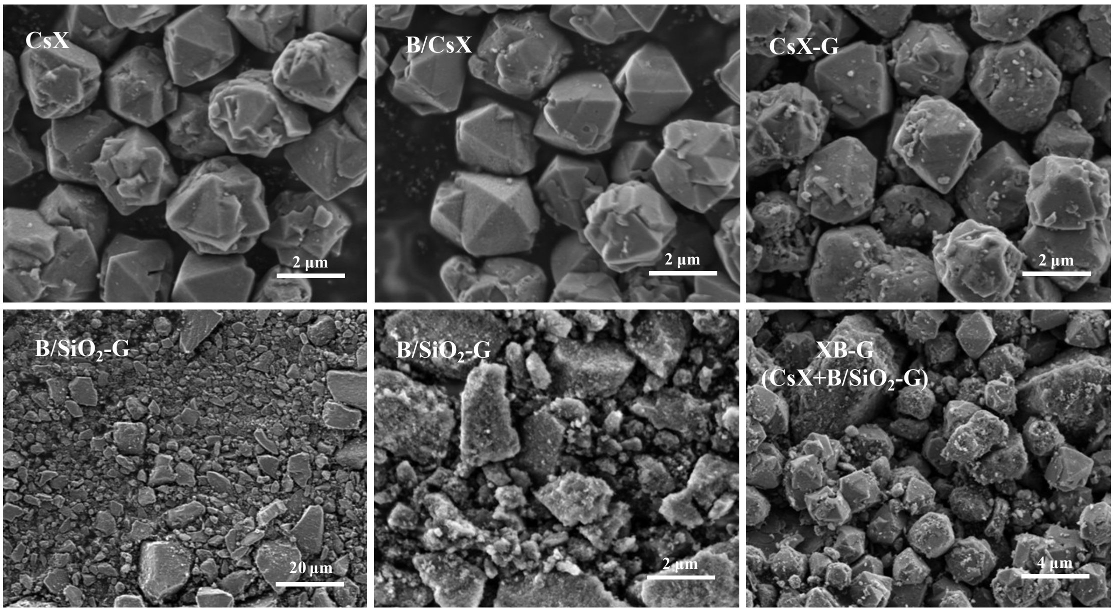

Fig. S1 SEM images of CsX, B/CsX, CsX-G, B/SiO_2-G and XB-G. G represents grinding in a mortar for 10 min.

The morphology of the catalysts was studied by SEM. As shown in Fig. S1, the particle sizes of CsX were about 2 μm, and there were no obvious changes of it in morphologies and particle sizes after impregnating with boric acid. The CsX particles were slightly broken after grinding in a mortar. However, the particles of the separated grinding B/SiO_2 were irregular, and the size of the maximum particle was about 15 μm, while some small particles were in nanometer scale. And the particles of B/SiO_2 and CsX mixed thoroughly after grinding together in a mortar (XB-G).

Table S1 Details of the packing modes of CsX with B/SiO_2 or SiO_2

Catalysts*	Packing modes of CsX with B/SiO_2 or SiO_2
B-X	0.2 g B/SiO_2 was loaded over 1 g CsX, and divided by quartz wool
X-B	0.2 g B/SiO_2 was loaded under 1 g CsX, and divided by quartz wool
$X(-B-X)_4$	0.2 g CsX×5 and 0.05 g B/SiO_2×4 were loaded alternately, and divided by quartz wool
XB-M	0.2 g B/SiO_2 (20~40 mush) and 1 g CsX (20~40 mush) mixed by granule-stacking
XB-G	B/SiO_2 and CsX (mass ratio 1:5) grinded in mortar for 10 min, then pressed, crushed and sieved to 20-40 mesh
XS-M	0.2 g SiO_2 (20~40 mush) and 1 g CsX (20~40 mush) mixed by granule-stacking

* X represents CsX, B represents B/SiO_2, S represents SiO_2, M represents granules mechanical mixing (20~40 mesh), G represents grinding in a mortar for 10 min

Table S2 Preparation process of binary composite catalysts containing cesium oxide modified CsX and B/SiO_2.

Catalysts*	preparation process
(4C)B-G	4CsOx/CsX and B_2O_3/SiO_2 (mass ratio: 5:1) grinded in mortar for 10 min, then pressed, crushed and sieved to 20-40 mesh
(8C)B-G	8CsOx/CsX and B_2O_3/SiO_2 (mass ratio: 5:1) grinded in mortar for 10 min, then pressed, crushed and sieved to 20-40 mesh
(16C)B-G	16CsOx/CsX and B_2O_3/SiO_2 (mass ratio: 5:1) grinded in mortar for 10 min, then pressed, crushed and sieved to 20-40 mesh

* 4C represents 4CsOx/CsX, 8C represents 8CsOx/CsX, 16C represents 16CsOx/CsX, B represents B/SiO_2, G represents grinding in a mortar.

Table S3 Preparation process of ternary composite catalysts containing CsX, cesium oxide modified CsX and B/SiO_2

Catalysts*	preparation process
X_1(8C)B-G	CsX, $8CsO_x/CsX$ and B/SiO_2 (mass ratio: 2.5:2.5:1) grinded in mortar for 10 min, then pressed, crushed and sieved to 20-40 mesh
X_3(8C)B-G	CsX, $8CsO_x/CsX$ and B/SiO_2 (mass ratio: 3.75:1.25:1) grinded in mortar for 10 min, then pressed, crushed and sieved to 20-40 mesh
X_7(8C)B-G	CsX, $8CsO_x/CsX$ and B/SiO_2 (mass ratio: 4.375:0.625:1) grinded in mortar for 10 min, then pressed, crushed and sieved to 20-40 mesh
X_3(16C)B-G	CsX, $16CsO_x/CsX$ and B/SiO_2 (mass ratio: 3.75:1.25:1) grinded in mortar for 10 min, then pressed, crushed and sieved to 20-40 mesh

* X represents CsX, 8C represents $8CsO_x/CsX$, 16C represents $16CsO_x/CsX$, B represents B/SiO_2, G represents grinding in a mortar, subscript of X represents the mass ratio of CsX without any modification to cesium oxide modified CsX.

Table S4 The acid and base amount of CsX, B/CsX, SiO_2 and B/SiO_2*

Catalysts	CsX	B/CsX	SiO_2	B/SiO_2
Acid amount (μmol g^{-1})	58.9	67.3	—	171.2
Base amount (μmol g^{-1})	170.0	131.2	—	—

*The acid amount and base amount are calculated from the amount of NH_3 and CO_2 desorption on different catalysts in NH_3-TPD and CO_2-TPD.

Table S5 Reaction behaviors of side-chain alkylation of toluene with methanol over the composite catalyst systems containing CsX and B/SiO_2

Catalysts	SiO_2	B/SiO_2	CsX	B-X	X-B	X(-B-X)$_4$	XB-M	XB-G	XS-M	B/CsX
Reaction Index:										
C_T (%)	0.02	0.14	2.11	2.27	2.29	2.82	2.75	2.35	2.18	2.64
C_M (%)	0.64	2.49	43.08	45.44	46.10	38.65	30.52	26.55	46.14	39.78
Y_{ST+EB} (mol%)	0.00	0.00	12.31	12.20	12.44	15.73	14.91	12.77	11.82	14.66
Y_{CO+CO2} (mol%)	0.30	0.38	25.24	22.66	23.51	13.98	6.54	5.01	25.05	16.83
ST/EB (mol/mol)	—	—	1.32	1.32	1.33	1.96	3.79	7.57	1.33	2.03
$S_{ST+EB/Aro}$ (mol%)	0.00	0.00	95.81	89.45	90.22	92.43	89.99	89.89	90.20	92.10
$Y_{ST+EB}+Y_{CO+CO2}$	0.30	0.38	37.55	34.86	35.95	29.71	21.45	17.77	36.86	31.49
Y_{ST+EB}/Y_{CO+CO2}	0.00	0.00	0.49	0.54	0.53	1.13	2.28	2.55	0.47	0.87
Carbon-containing products distribution (mol%):										
CO	22.46	17.23	60.50	54.49	55.64	39.31	23.89	21.48	58.27	45.88
CO_2	33.88	4.63	1.95	1.23	1.16	1.07	0.60	0.60	1.27	0.93
CH_4	6.85	1.01	0.67	1.04	0.95	0.83	1.12	0.85	0.83	0.66
C_2-C_5	0.00	27.80	0.15	1.92	2.25	2.27	2.58	2.64	1.87	2.01
Dimethyl ether	17.43	8.96	4.94	7.78	6.67	7.36	9.69	11.76	6.63	6.23
benzene	0.00	0.53	0.04	0.11	0.11	0.12	0.11	0.10	0.11	0.13
ethylbenzene	0.00	0.00	13.11	12.91	12.89	15.35	11.67	6.57	12.03	13.45
xylene	0.00	13.86	0.13	1.27	1.10	1.20	1.74	2.22	1.12	0.71
styrene	0.00	0.00	17.35	17.09	17.17	30.09	44.24	49.76	16.06	27.34
$C_9^{+\,a}$	19.37	26.04	1.16	2.16	2.05	2.41	4.37	4.00	1.82	2.66
Total	100	100	100	100	100	100	100	100	100	100

[a] C_9^+: aromatics with nine or more carbon atoms;

Reaction conditions: 430 ^oC, TOS=50 min, toluene and methanol (molar ratio was 6:1) was fed at a total flow rate of 0.4 mmol/min with 10 mL/min helium.

Table S6 Reaction behaviors of side-chain alkylation of toluene with methanol over the binary composite catalysts and ternary composite catalysts

Catalysts	CsX	8CsOx/ CsX	8CsOx/ B/CsX	(4C)B- G	(8C)B -G	(16C)B -G	X_1(8C) B-G	X_3(8C) B-G	X_7(8C) B-G	X_3(16 C)B-G
Reaction Index:										
C_T (%)	2.11	5.15	8.43	5.04	8.30	9.31	6.94	4.32	3.15	6.07
C_M (%)	43.08	98.52	96.40	44.73	80.60	99.37	63.33	42.24	31.77	56.16
Y_{ST+EB} (mol%)	12.31	29.92	46.80	27.92	46.12	51.74	39.45	24.24	16.91	34.26
Y_{CO+CO2} (mol%)	25.24	63.90	42.89	9.80	27.94	41.01	18.51	10.95	7.62	16.90
ST/EB (mol/mol)	1.32	0.06	0.33	1.97	0.65	0.06	1.81	3.65	5.23	0.99
$S_{ST+EB/Aro}$ (mol%)	95.81	96.16	92.93	91.89	93.02	93.51	94.21	93.32	89.93	94.27
$Y_{ST+EB}+Y_{CO+CO2}$	37.55	93.83	89.69	37.72	74.06	92.75	57.96	35.19	24.54	51.16
Y_{ST+EB}/Y_{CO+CO2}	0.49	0.47	1.09	2.85	1.65	1.26	2.13	2.21	2.22	2.03
Carbon-containing products distribution (mol%):										
CO	60.50	58.45	35.18	22.22	28.18	29.99	26.01	26.26	25.15	29.32
CO_2	1.95	8.09	10.11	1.09	6.92	11.58	3.97	1.22	0.81	1.35
CH_4	0.67	0.74	0.55	0.48	1.17	1.43	0.51	0.82	0.81	0.47
C_2-C_5	0.15	0.14	0.86	2.05	1.22	0.78	1.09	2.11	2.86	1.84
dimethyl ether	4.94	0.17	0.14	1.89	0.21	0.15	0.64	4.53	6.28	1.03
benzene	0.04	0.06	0.12	0.15	0.09	0.10	0.10	0.10	0.12	0.10
ethylbenzene	13.11	29.40	37.17	22.33	35.12	49.46	22.77	13.08	9.24	31.22
xylene	0.13	0.07	0.23	0.38	0.29	0.26	0.32	0.95	1.46	0.62
styrene	17.35	1.76	12.24	44.07	22.82	2.97	41.10	47.77	48.38	30.99
C_9^{+} [a]	1.16	1.11	3.41	5.33	3.96	3.29	3.51	3.31	4.87	3.07
Total	100	100	100	100	100	100	100	100	100	100

[a] C_9^{+}: aromatics with nine or more carbon atoms;

Reaction conditions: 430 ^{o}C, TOS=50 min, toluene and methanol (molar ratio was 6:1) was fed at a total flow rate of 0.4 mmol/min with 10 mL/min helium.

References

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