Supporting Information

Highly dispersed Pt nanoparticles in the Cs-modified X zeolite with enhancement for toluene side-chain alkylation with methanol

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1. Experimental

1.1 Catalysts preparation

CsX catalysts were prepared by exchanging zeolite NaX (NanKai Catalyst Company, SiO$_2$/Al$_2$O$_3 = 2.4$) with aqueous solutions of CsOH·H$_2$O (Aladdin, 99%). Typically, 10 g of NaX zeolites were ion-exchanged at 90°C for 4 h with a 0.3 M solution of cesium ion (50 mL of solution/10 g of zeolite). The resultant samples were filtered and washed thoroughly with excess pure water. The ion-exchange process was repeated three times. The resultant samples was then dried overnight at 90°C and calcined at 540°C under a dry air flow for 4 h.

An ultrasonic assisting vacuum impregnation method was used for the preparation of the Pt/CsX catalysts. Typically, CsX was mixed with an aqueous solution of H$_2$PtCl$_6$ (0.005 M), with the volume of the latter being tuned to the target loading of Pt, and ultrasonic stirred for 0.5 h under vacuum condition. The product was then dried overnight at 80°C and calcined in air at 540°C for 4 h. The calcined catalysts were reduced in a tubular oven under H$_2$ flow (99.9%; 120 mL/min) at 250°C for 2 h. The typical catalyst prepared by above method was named as aPt/CsX-b-Rc, in which a, b and c respectively stand for the wt % loading of Pt, the calcination temperature, and the reduction temperature. In addition, the catalyst prepared with 0.5 wt% of Pt was also reduced directly at 250°C under a H$_2$ flow for 2 h after overnight drying (without calcination). This catalyst was named 0.5Pt/CsX-DR250.

1.2 Catalyst characterization
X-ray diffraction (XRD) patterns were recorded on a Bruker AXS-D8 Advance powder diffractometer with monochromatic detector equipped with CuKα radiation at 30 kV and 10 mA. The samples were scanned from 2θ of 5-60° with a step size of 0.02°. N₂ adsorption-desorption isotherms were measured on a surface analyzer (Micrometrics, ASAP 2020) at -196°C. The specific surface area was calculated using the Brunauer-Emmett-Teller (BET) method. Micropore volumes ($V_{micro}$) were determined by t-plot method.

Scanning electron microscopy (SEM) images and energy dispersive X-ray spectroscopy (EDS) mapping were taken with a Hitachi S-5500 instrument with an acceleration voltage of 5 kV. Transmission electron microscopy (TEM) images were recorded with Tecnai G2 F20. The samples were dispersed into alcohol before observation. The elemental compositions of catalysts were measured by inductively coupled plasma optical emission spectroscopy (ICP-AES, OPTIMA-3000). In detail, 0.1g sample was added to 1ml deionized water. Subsequently, 10 ml of equal mixture of HF/HCl/HNO₃ were added to the sample. After complete dissolution, 75 ml solution of boric acid (0.8 mol L⁻¹) is added to the sample, and then dilution to 100 g using deionized water.

X-ray photoelectron spectroscopy (XPS) measurements were performed on Escalab 250 (Thermo Fisher VG) with a monochromatic X-ray source of Al Kα under ultra-high vacuum (2.4×10⁻⁸ Pa). The deconvolution method of XPS spectra was fitted by Gaussian function.

Temperature-programmed desorption (TPD) profiles of CO₂ were collected on a
Micromeritics Autochem 2920 instrument in a quartz reactor with a thermal conductivity detector (TCD). 0.1 g of the sample was pretreated at 300°C for 1 h in an Ar flow at 30 ml min\(^{-1}\), then cooled to 40°C and saturated with pure CO\(_2\). After that, the sample was purged with argon for ca. 60 min to remove physically adsorbed CO\(_2\) and CO\(_2\)-TPD was carried out in the range of 40-600°C at a heating rate of 10°C min\(^{-1}\).

Thermogravimetric/differential thermal analysis (TG/DTG) curves were measured with a NETZSCH STA 449F3. The thermal analysis data were collected in the range of 30-700°C in air flow to investigate the coke deposition of catalysts.

1.3 Catalytic testing

The prepared catalyst (5.0 g) was sieved to obtain 150-200 μm particles and packed into a stainless steel tubular fixed-bed reactor with 1.5 cm inner diameter. Prior to the introduction of reactants, the catalyst was activated in situ in dry N\(_2\) flow at 480°C for 2 h and then decreased to the reaction temperature of 420°C. Pre-mixed solution of toluene (T) and methanol (M) with 3 : 1 molar ratio was pumped into the reactor (12 ml min\(^{-1}\)) at a weight hourly space velocity (WHSV) of 2.0 h\(^{-1}\) in a flowing N\(_2\) stream (60 mL min\(^{-1}\)). The products were analyzed by a gas chromatograph (Agilent Technologies GC5890) equipped with an INNOWAX capillary column (60 m length, inner diameter 0.25 mm) and a flame ionization detector (FID).

The conversion of toluene (C\(_T\)), the selectivity of styrene (S\(_{ST}\)), and the total
The selectivity of styrene and ethylbenzene ($S_{ST + EB}$) were estimated by the following equations:

$$C_T(\%) = \frac{\text{toluene}_{\text{in}} - \text{toluene}_{\text{out}}}{\text{toluene}_{\text{in}}} \times 100\%$$

$$S_{ST}(\%) = \frac{\text{styrene}_{\text{out}}}{\text{toluene}_{\text{in}} - \text{toluene}_{\text{out}}} \times 100\%$$

$$S_{ST + EB}(\%) = \frac{\text{styrene}_{\text{out}} + \text{ethylbenzene}_{\text{out}}}{\text{toluene}_{\text{in}} - \text{toluene}_{\text{out}}} \times 100$$

The normalized reaction rate can be calculated by the following equation:

$$\text{rate (r)} = \frac{[\text{toluene}]_{\text{in}} x V_{\text{in}}}{n_{Cs}}$$

where $[\text{toluene}]_{\text{in}}$ is the concentration of toluene in the inlet; $x$, the conversion of toluene within the differential kinetic regime (toluene conversion less than 10%, and not affected by heat or mass transport limitations); $V_{\text{in}}$, the total molar flow rate; $n_{Cs}$, the molar quantity of Cs per gram of the catalysts. The apparent activation energy ($E_{app}$) is determined from Arrhenius plots, and tested by tuning the temperature between 390°C and 450°C.

The deactivation parameter $k_d$ was estimated by the following equation $^1$:

$$k_d = \frac{100 - x_{\text{end}}}{\ln\frac{100 - x_{\text{end}}}{x_{\text{end}}} - \ln\frac{100 - x_{\text{in}}}{x_{\text{in}}}}$$
where \( t \) is the reaction time (h), \( x_{\text{end}} \) is the toluene conversion at end of reaction, \( x_{\text{in}} \) is the initial toluene conversion.

**The transport effect and product inhibition effect**

In order to make sure that the obtained kinetic parameters were not significantly influenced by interphase or intra-particle transfer limitations, the transport effects over 0.5Pt/CsX-540-R250 catalyst were investigated by using Madon-Boudart criterion.\(^2\) Herein, the effect of interphase transport was experimentally evaluated by employing different flow rates of reactants at constant WHSV of 2.0 h\(^{-1}\). It was shown in Fig. S7a that there was no significant change in toluene conversion by varying the flow rate of reactants ( > 10 ml/h). Thus, the interphase diffusion limitation can be excluded at a feed flow rate of 12ml/h during the reaction in this study. The internal diffusion mainly depends on the particle size of catalyst. With small particle size, the conversion of toluene is chemically controlled and independent of the particle size. Fig. S7b showed the variation of toluene conversion with the different particle sizes of 0.5Pt/CsX-540-R250 catalyst, where no significant change in the toluene conversion was observed in the range of 150-200 μm of the particle size. Thus, the effect of internal diffusion can be excluded in the experimental range.

Ignoring product inhibition when it is in fact present may produce inaccurate kinetic data such as apparent reaction orders and activation energies. Plotting the natural logarithm of toluene conversion versus the natural logarithm of the space time is a simple way to check for product inhibition. As shown in Fig. S7c, the slope of the plot is 0.97, which imply that the product inhibition showing small impact in this
reaction system.\textsuperscript{3} Moreover, the dependence of rate on the concentration of styrene products was investigated (Fig. S7d). It can be seen that the relatively low concentration of styrene product has little effect on reaction rates.
**Table S1** Textural properties of the samples.

<table>
<thead>
<tr>
<th>Samples</th>
<th>$S_{\text{BET}}^a$ (m$^2$ g$^{-1}$)</th>
<th>$V_{\text{micro}}^b$ (cm$^3$ g$^{-1}$)</th>
<th>$V_{\text{total}}^c$ (cm$^3$ g$^{-1}$)</th>
<th>Si/Al $^d$</th>
<th>Cs content $^d$ (wt %)</th>
<th>Pt content $^d$ (wt %)</th>
<th>Pt average diameters (nm) $^e$</th>
<th>Pt dispersion (%) $^f$</th>
<th>Total Basicity ($\mu$mol g$^{-1}$) $^g$</th>
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<tbody>
<tr>
<td>NaX</td>
<td>705</td>
<td>0.29</td>
<td>0.34</td>
<td>1.25</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>99</td>
</tr>
<tr>
<td>CsX</td>
<td>529</td>
<td>0.18</td>
<td>0.23</td>
<td>1.24</td>
<td>27.68</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>304</td>
</tr>
<tr>
<td>0.5Pt/CsX-540</td>
<td>516</td>
<td>0.16</td>
<td>0.22</td>
<td>1.22</td>
<td>27.35</td>
<td>0.514</td>
<td>5.4</td>
<td>20.9</td>
<td>294</td>
</tr>
<tr>
<td>0.5Pt/CsX-540-R250</td>
<td>503</td>
<td>0.16</td>
<td>0.21</td>
<td>1.24</td>
<td>27.23</td>
<td>0.507</td>
<td>1.8</td>
<td>62.3</td>
<td>299</td>
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<tr>
<td>0.5Pt/CsX-DR250</td>
<td>477</td>
<td>0.14</td>
<td>0.21</td>
<td>1.22</td>
<td>26.77</td>
<td>0.491</td>
<td>6.6</td>
<td>17.1</td>
<td>282</td>
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</tbody>
</table>

$^a$ BET surface area calculated using BET method.

$^b$ Micropore surface area and micropore volume calculated using t-plot method.

$^c$ Total pore volume calculated at $p/p_0 = 0.99$.

$^d$ Determined by ICP-AES results.
\(^e\) Determined by TEM results.

\(^f\) Calculated by the following equation \(^4\): \(D = 6 \times (V_m/A_m)/d_{pt}\), where \(V_m\) and \(A_m\) are the parameters related to Pt, and \(d_{pt}\) is average diameter of Pt particle.

\(^g\) Determined by CO\(_2\)-TPD results.

**Table S2** Surface valence distribution of Pt (4f) and Cs (3d\(_{5/2}\)) species over different catalysts derived from XPS analyses

<table>
<thead>
<tr>
<th>Samples</th>
<th>Pt species assignment (%)</th>
<th>Cs species assignment (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Pt(^0)</td>
<td>Pt(^{2+})</td>
</tr>
<tr>
<td>0.5Pt/CsX-540</td>
<td>-</td>
<td>77.3</td>
</tr>
<tr>
<td>0.5Pt/CsX-540-R250</td>
<td>68.9</td>
<td>31.1</td>
</tr>
<tr>
<td>0.5Pt/CsX-DR250</td>
<td>71.6</td>
<td>28.4</td>
</tr>
<tr>
<td>CsX</td>
<td>-</td>
<td>-</td>
</tr>
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</table>
Fig. S1 \( \text{N}_2 \) adsorption/desorption isotherms of NaX, CsX and Pt-modified CsX catalysts.

Fig. S2 (a) XRD patterns of the samples and (b) local enlargement of (a).
Fig. S3 SEM images of (a) CsX, (b) 0.5Pt/CsX-540, (c) 0.5Pt/CsX-540-R250, (d) 0.5Pt/CsX-DR250.

Fig. S4 CO$_2$-TPD profiles of the samples.
Fig. S5 EDS elemental mapping of 0.5Pt/CsX-540-R250 (Cs, Si and Al are indicated in blue, red and green, respectively).

Fig. S6 Methanol conversion over NaX, CsX and Pt-modified CsX catalysts in the side-chain alkylation reaction. Reaction conditions: 430°C, toluene/methanol ratio = 3.0, WHSV = 2.0h⁻¹.
Fig. S7 Catalytic performance of Pt/CsX-540-R250 catalysts with different Pt loadings (0.1-2%). Reaction conditions: 430°C, toluene/methanol ratio = 3.0, WHSV = 2.0h⁻¹, TOS = 1h.

Fig. S8 (a) Variation of toluene conversion with the flow rate of reactants on 0.5Pt/CsX-540-R250 catalyst; (b) Variation of toluene conversion with the different particle sizes of 0.5Pt/CsX-540-R250 catalyst; (c) Natural log of toluene conversion as a function of the natural log of space time (mass of catalyst ranged from 0.5 to 3 g); (d) The dependence of toluene conversion rate on the concentration of styrene products (1.23-5.88 mol%). Reaction conditions: 430°C, toluene/methanol ratio = 3.0, TOS = 1h.
**Fig. S9** Durability of 0.5Pt/CsX-540-R250 and CsX catalysts in the side-chain alkylation reaction. Reaction conditions: 430°C, toluene/methanol ratio = 3.0, WHSV = 2.0h⁻¹.

**Fig. S10** TG curves of 0.5Pt/CsX-540-R250 and CsX catalysts after 100 h reaction for toluene side-chain alkylation with methanol.
Scheme S1 the possible synergistic reaction mechanism of toluene alkylation with methanol in the presence of added Pt species.
References:


