Supporting Information

Identifying and Controlling the Acid Site Distributions in Mordenite Zeolite for Dimethyl Ether Carbonylation Reaction by Means of Selective Ion-exchange

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Catalyst preparation

H-type mordenite zeolite with a Si/Al of 9.8 was commercially available from Jiangsu Aoke Chemical Technology Co., Ltd. The XRD pattern and SEM image of the sample were given in Fig.S2, revealing the pure MOR phase with good crystallinity. For comparison, the selective ion-exchange of low Si/Al mordenite zeolite with tetramethylammonium chloride (TMACl) was also performed as following: H-type mordenite zeolites was exchanged with 1.0 M NaCl aqueous solution (10 mL of solution per g of zeolite) at 80 °C for 4 hours three times to convert to Na-type mordenite. After filtration, the exchanged sample was washed thoroughly by deionized water to remove the residual NaCl. The Na-MOR sample was further exchanged with TMACl. Typically, 10.0 g Na-MOR was stirred in 100 mL TMACl solution (1.0 M) at 80 °C for 4 hours. The slurry was then washed by deionized water, and dried at 110 °C for 10 hours. The ion-exchange of Na-MOR with TMACl was repeated until the sodium content no longer decreased. The change of Na exchange degrees with the ion-exchange times was displayed in Fig.S3.

In situ DRIFT characterization

In situ DRIFT spectrum of TMA-exchanged H-MOR sample was collected on a Bruke Tensor 27 instrument equipped with a MCT detector. The catalyst powder was loaded in the diffuse reflectance infrared cell with ZnSe window. The sample was then dehydrated at 250 °C for 60 min in the following nitrogen. After cooling to 150 °C, in situ absorbance spectrum was collected.
Fig. S1 (a) XRD pattern of the parent mordenite (Si/Al=17), (b) N\textsubscript{2} adsorption-desorption isotherm, (c, d) SEM images of mordenite (Si/Al=17) zeolites.

Table S1. Chemical compositions and textural properties of parent MOR (Si/Al=17) sample

<table>
<thead>
<tr>
<th>Si/Al\textsuperscript{a}</th>
<th>Na (wt.%)	extsuperscript{a}</th>
<th>S\textsubscript{BET} (m\textsuperscript{2}/g)\textsuperscript{b}</th>
<th>S\textsubscript{micro} (m\textsuperscript{2}/g)\textsuperscript{c}</th>
<th>S\textsubscript{ext} (m\textsuperscript{2}/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>17</td>
<td>1.9</td>
<td>393</td>
<td>356.2</td>
<td>36.9</td>
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</tbody>
</table>

\textsuperscript{a}: determined by XRF, \textsuperscript{b}: BET surface area, \textsuperscript{c}: t-plot microporous surface area, S\textsubscript{ext}=S\textsubscript{BET} - S\textsubscript{micro}.

Fig. S2 (a) XRD pattern of the mordenite (Si/Al=9.8), (b) SEM images of mordenite zeolites (Si/Al=9.8).
Fig. S3 The ion-exchange behavior of mordenite (Si/Al = 9.8) with TMACl. Ion-exchange conditions: TMACl concentration in solution (1.0 M), temperature (80 °C), time (4 hours), volume of solution per g of zeolite (10 mL/g).

Fig. S4 The IR spectrum of 1TMA-H-MOR sample
**Fig. S5** XRD patterns of the H-MOR and TMA-exchanged H-MOR samples.

**Fig. S6** The influence of water on the DME carbonylation catalytic performance of 1TMA-H-MOR. Reaction condition: $P(\text{DME}) = 88.0 \text{ kPa}$, $P(\text{CO}) = 617.3 \text{ kPa}$, $P(\text{N}_2) = 1059.5 \text{ kPa}$, $P(\text{Ar}) = 234.5 \text{ kPa}$, $P(\text{H}_2\text{O}) = 0.2 \text{ kPa}$, $T = 200 \degree \text{C}$, $GHSV = 2550 \text{ mL/g}_{\text{cat}}\cdot\text{h}$. Water was added through a saturator using Ar as the carrier gas. The temperature of saturator was kept at 15 \degree\text{C}. 
**Fig. S7** TG-curves of H-MOR and TMA-exchanged H-MOR samples under conditions of air flow rate of 100 mL/min and ramping rate of 10 °C/min.

**Fig. S8** The long-term stability test of 3TMA-H-MOR catalyst. Reaction condition: DME/CO/N$_2$ = 5/35/60, 200 °C, 2.0 MPa, GHSV = 2250 mL/g$_{cat}$•h.
**Fig.** S9 The nitrogen adsorption-desorption isothermal curves of H-MOR and TMA-exchanged H-MOR samples.

**Fig.** S10 N$_2$ adsorption-desorption isotherm (a) and thermal analysis (b) for TEA- H-MOR sample.

**Table S2.** Textural properties of TEA-H-MOR sample.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Weight contents of TEA ions [wt.%]$^a$</th>
<th>$S_{BET}$ [m$^2$/g]$^b$</th>
<th>$V_{micro}$ [cm$^3$/g]$^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>TEA-H-MOR</td>
<td>6.9</td>
<td>35.6</td>
<td>0.004</td>
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</table>

[a] Weight loss in the temperature range of 250–700 °C. [b] BET specific surface area. [c] Single-point pore volume at $P/P_0 = 0.975$. 

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