Electronic Supplementary Material (ESI) for Nanoscale Advances.


# Supplementary Information

## Tailoring hierarchical zeolite composites with two distinct frameworks for fine-tuning product distribution in benzene alkylation with ethanol

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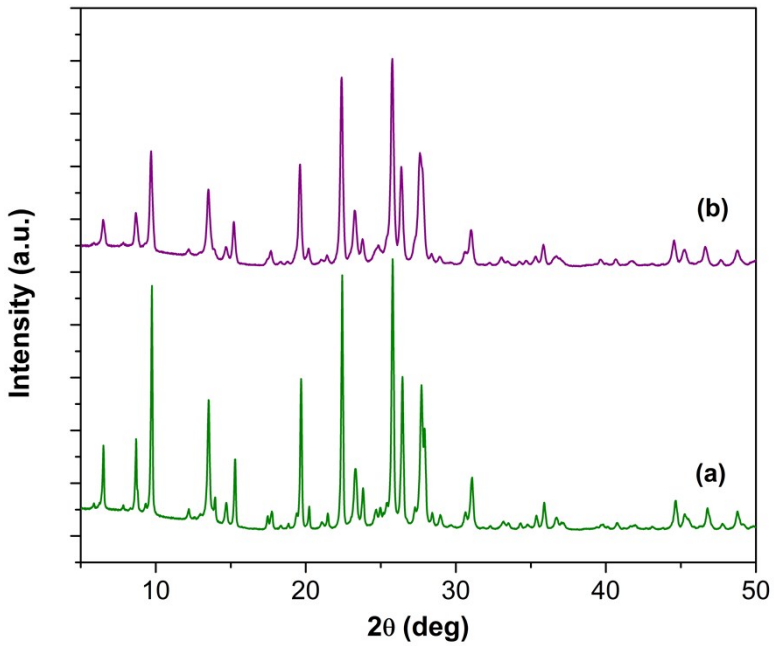



**Figure S1.** XRD patterns of (a) commercial mordenite and (b) pretreated mordenite in alkaline TBAOH solution.

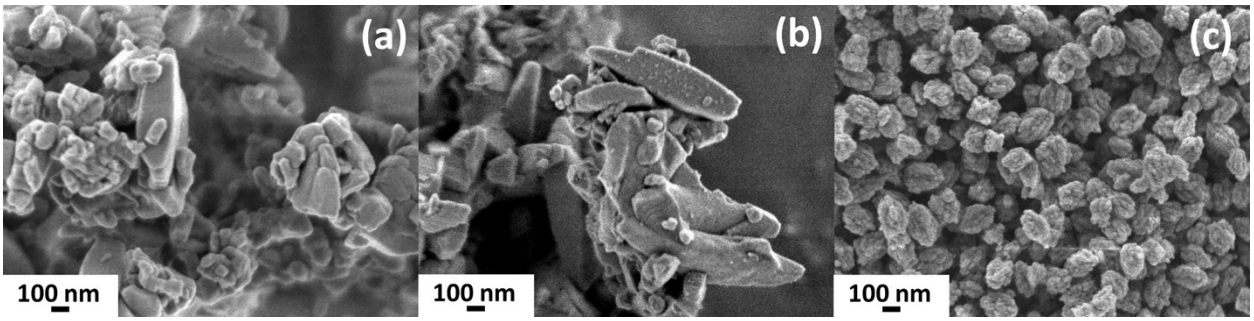



**Figure S2.** SEM images of (a) commercial mordenite, (b) pretreated mordenite in alkaline TBAOH solution, and (c) ZSM-5-NS.

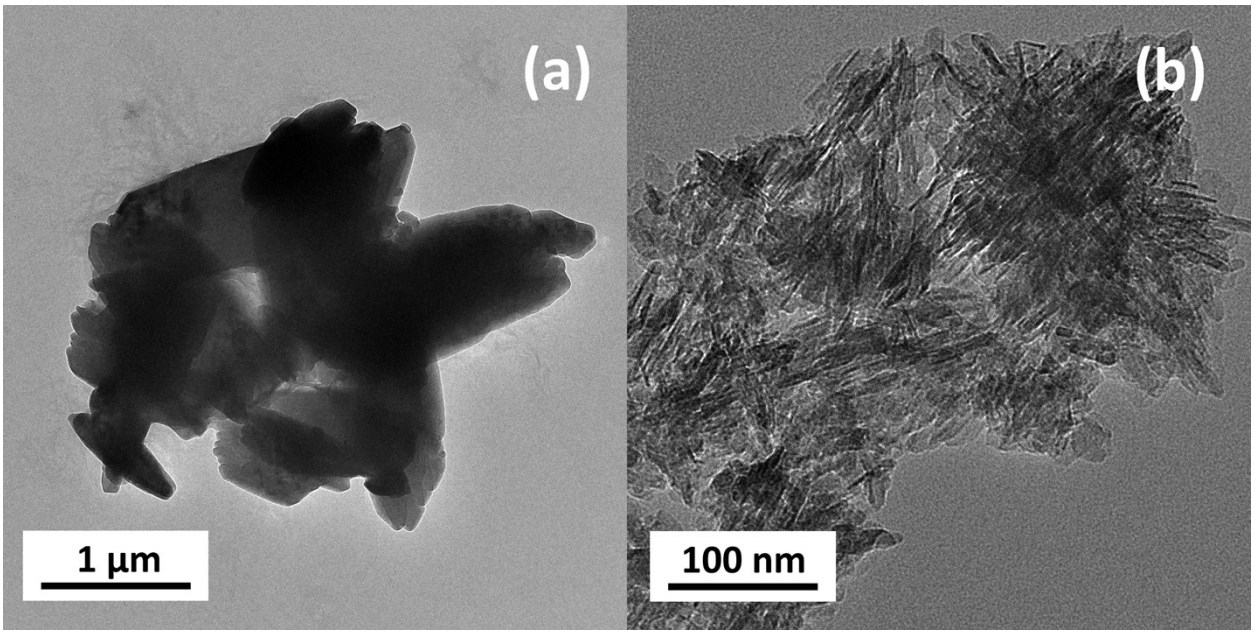



**Figure S3.** TEM images of (a) commercial mordenite and (b) ZSM-5-NS.

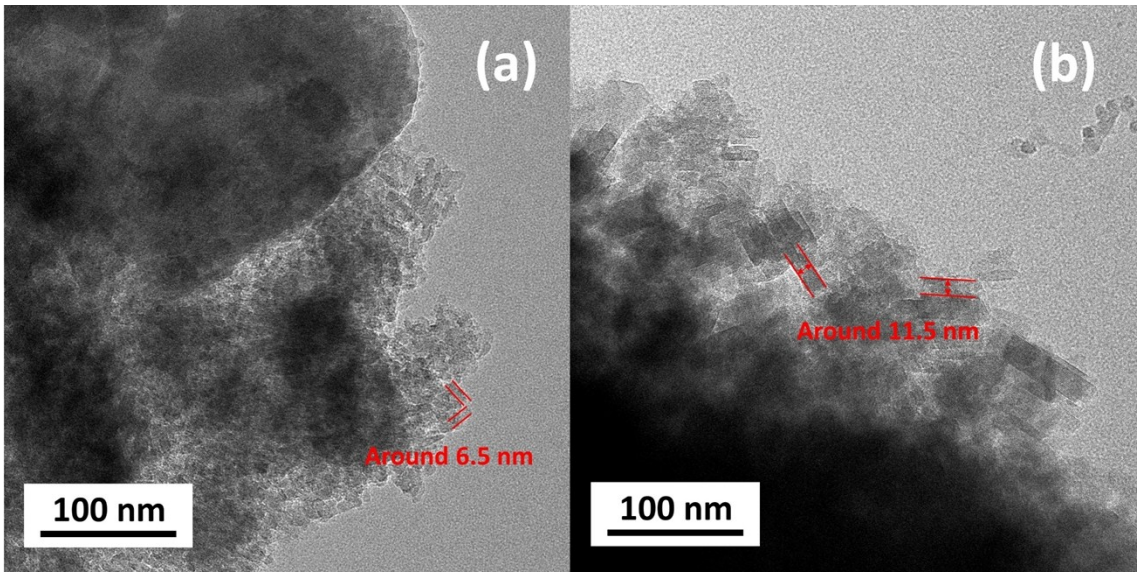
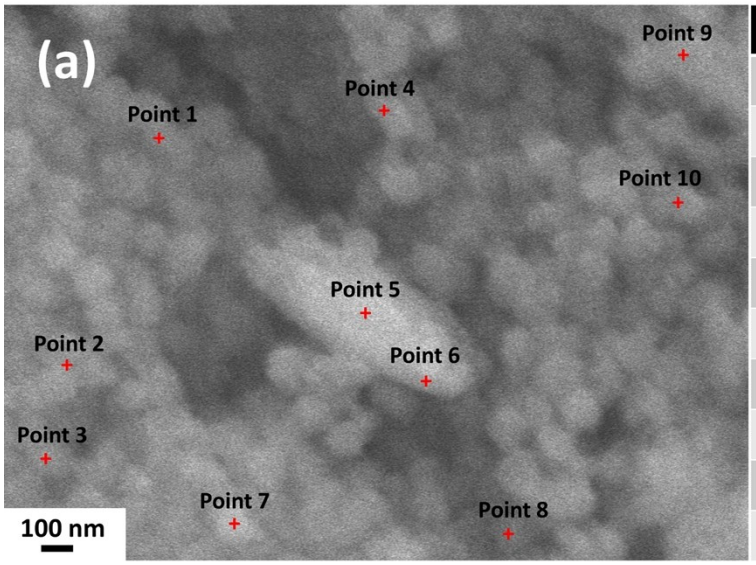
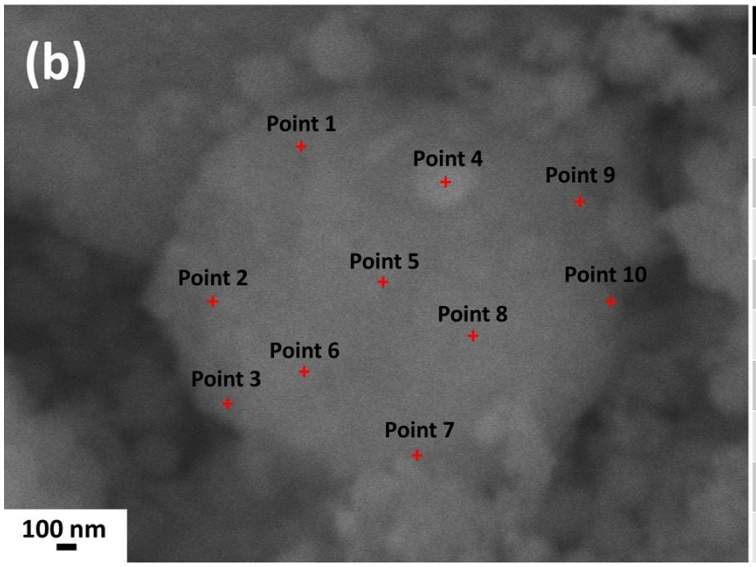



**Figure S4.** TEM images with high magnification (100 kX) of (a) MOR@ZSM-5(SS) and (b) MOR@ZSM-5(CS).




| Point No. | Si/Al ratio |
|---|---|
| 1 | 26.6 |
| 2 | 23.0 |
| 3 | 39.2 |
| 4 | 32.9 |
| 5 | 19.4 |
| 6 | 12.2 |
| 7 | 29.8 |
| 8 | 25.2 |
| 9 | 17.5 |
| 10 | 29.4 |




| Point No. | Si/Al ratio |
|---|---|
| 1 | 39.6 |
| 2 | 43.7 |
| 3 | 46.2 |
| 4 | 40.8 |
| 5 | 42.3 |
| 6 | 41.9 |
| 7 | 46.3 |
| 8 | 41.2 |
| 9 | 42.8 |
| 10 | 46.1 |

**Figure S5.** SEM-EDS elemental points of (a) MOR@ZSM-5(SS) and (b) MOR@ZSM-5(CS).

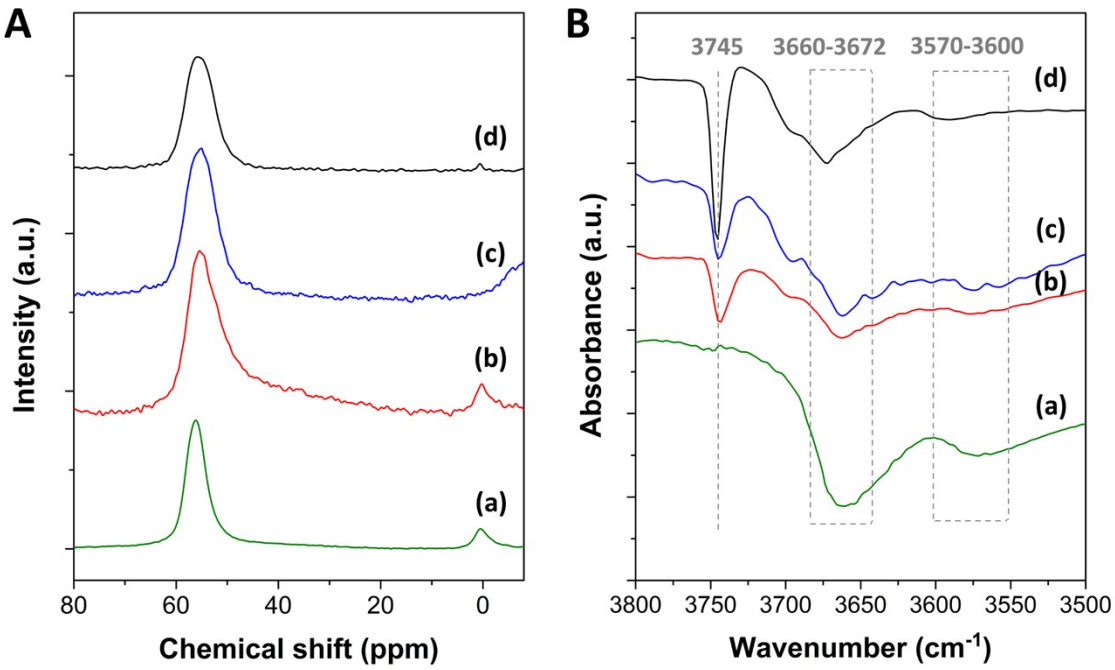



**Figure S6.** (A) $^{27}$Al MAS NMR spectra and (B) FTIR spectra of pyridine adsorption in OH region of (a) mordenite, (b) MOR@ZSM-5(SS), (c) MOR@ZSM-5(CS), and (d) ZSM-5-NS.

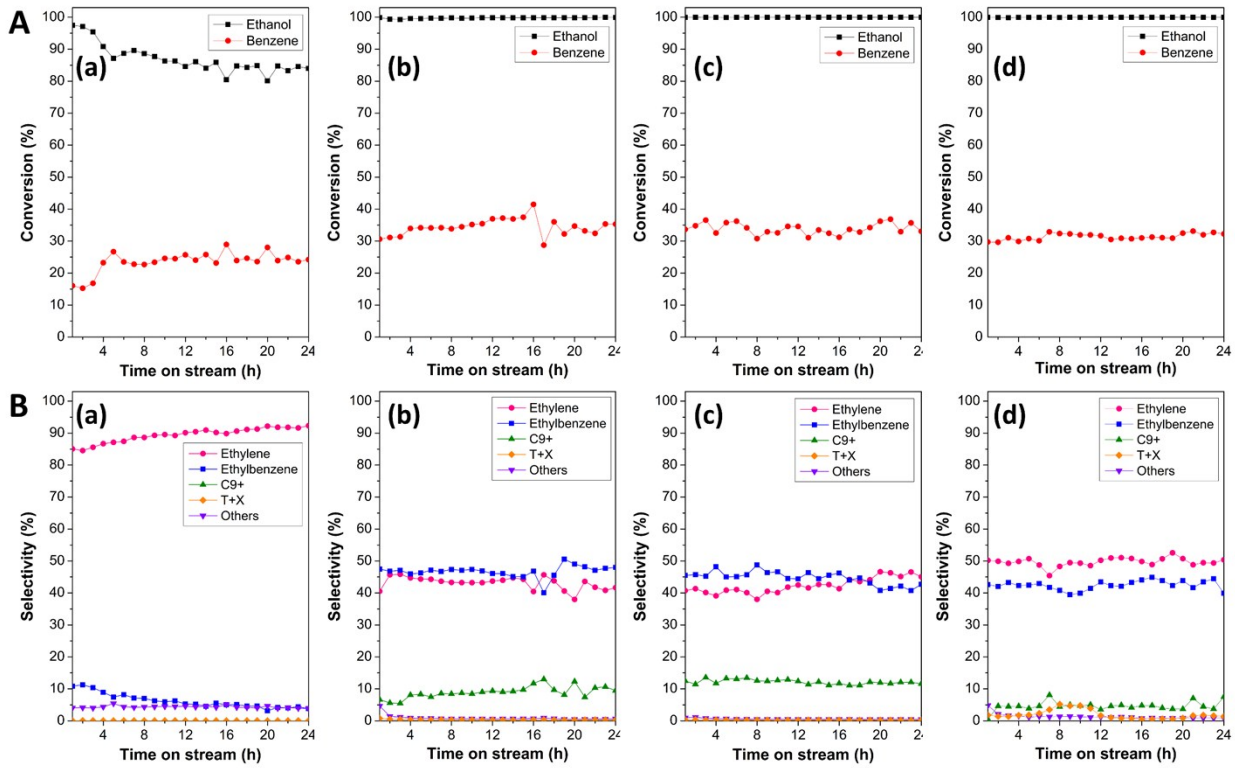



**Figure S7.** (A) Reactant conversion (%) and (B) Product selectivity (%) obtained over (a) mordenite, (b) MOR@ZSM-5(SS), (c) MOR-ZSM-5(mix), and (d) ZSM-5-NS in benzene alkylation at 450 °C as a function of time on stream (TOS) for 24 h.

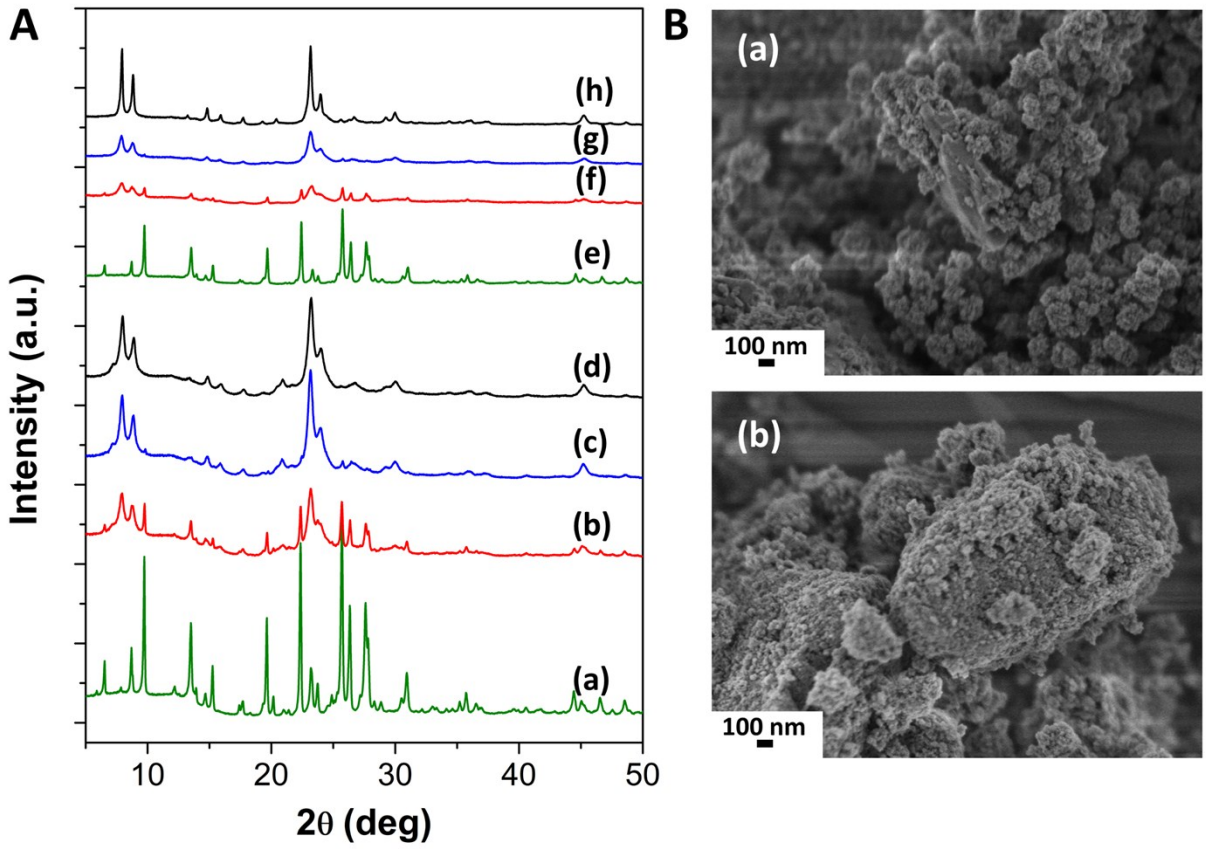



**Figure S8.** (A) XRD patterns of fresh (a) mordenite, (b) MOR@ZSM-5(SS), (c) MOR@ZSM-5(CS), and (d) ZSM-5-NS and spent (e) mordenite, (f) MOR@ZSM-5(SS), (g) MOR@ZSM-5(CS), and (h) ZSM-5-NS and (B) SEM images of spent (a) MOR@ZSM-5(SS) and (b) MOR@ZSM-5(CS).

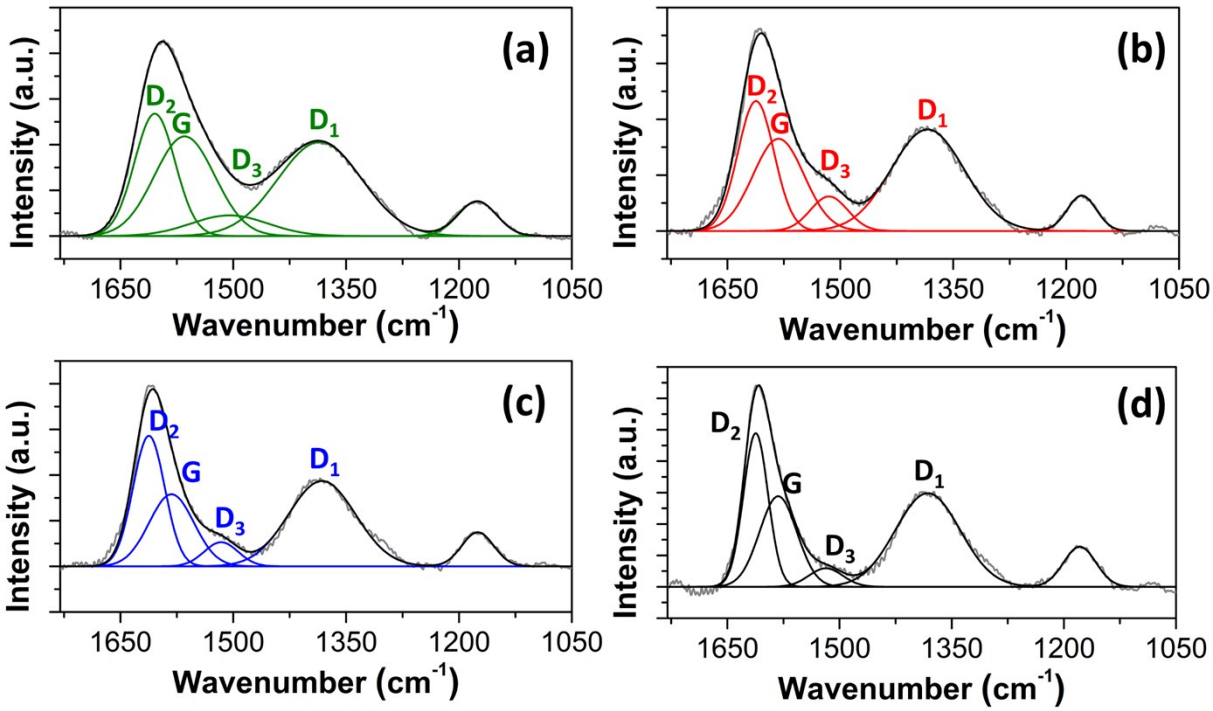



**Figure S9.** Raman spectra of spent catalysts: (a) mordenite, (b) MOR@ZSM-5(SS), (c) MOR@ZSM-5(CS), and (d) ZSM-5-NS taken after the catalytic test for alkylation of benzene with ethanol at 450 °C for 24 h.

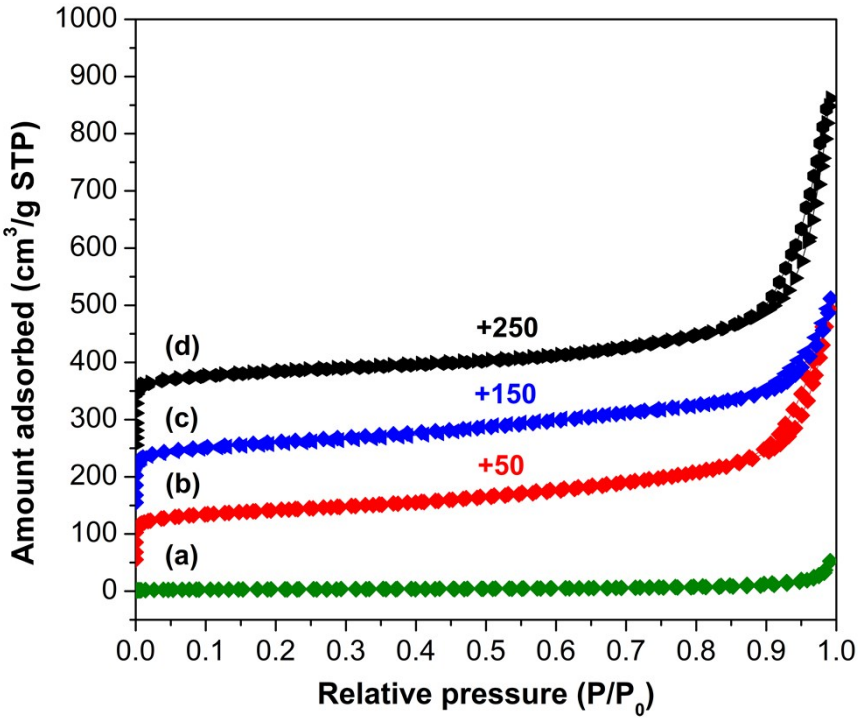



**Figure S10.** $N_2$ adsorption/desorption isotherms of spent (a) mordenite, (b) MOR@ZSM-5(SS), (c) MOR@ZSM-5(CS), and (d) ZSM-5-NS.

**Table S1.** The crystallinity and Si/Al ratio of commercial and pretreated mordenite.

| Sample | Si/Al ratio[a] | Crystallinity[b] (%) | Amorphous[b] (%) |
|---|---|---|---|
| commercial mordenite | 9.3 | 87.9 | 12.1 |
| pretreated mordenite | 9.1 | 75.2 | 24.8 |

[a]estimated from XRF, [b]obtained from XRD pattern.

**Table S2.** The average reactant conversion and product selectivity obtained at 24 h of TOS for alkylation of benzene with ethanol at 450 °C over different catalysts.

| Sample | Conversion (%) | | Selectivity (%) | | | | |
|---|---|---|---|---|---|---|---|
| | Ethanol | Benzene | EB | Ethylene | Heavy aromatics ($C_9^+$) | T + X[a] | Others[b] |
| mordenite | 86.9 | 23.5 | 6.2 | 89.4 | 0 | 0.1 | 4.3 |
| MOR@ZSM-5(SS) | 99.8 | 34.4 | 46.7 | 43.1 | 8.9 | 0.4 | 0.9 |
| MOR@ZSM-5(CS) | 99.6 | 44.9 | 59.3 | 23.7 | 15.1 | 0.5 | 1.4 |
| MOR-ZSM-5(mix) | 100.0 | 33.9 | 44.7 | 42.3 | 12.2 | 0.2 | 0.6 |
| ZSM-5-NS | 99.9 | 31.4 | 42.4 | 49.7 | 4.6 | 2.0 | 1.3 |

[a]T + X: toluene and xylenes, [b]other products: ethane, propane, propylene, butylene, pentane, and diethyl ether.

**Table S3.** The amount of coke formed on different spent catalysts.

| Sample | Amount of coke[a] (mmol/g) |
|---|---|
| mordenite | 0.82 |
| MOR@ZSM-5(SS) | 0.37 |
| MOR@ZSM-5(CS) | 0.34 |
| ZSM-5-NS | 0.24 |

[a]estimated from $O_2$-TPO data.

**Table S4.** Representative parameters of the Raman bands and in-plane correlation length (*La*) calculated by Ferrari-Robertson expression.

| Sample | $G_p$ ($cm^{-1}$) | $G_w$ ($cm^{-1}$) | $D_1/G$ | *La*[a] (nm) |
|---|---|---|---|---|
| mordenite | 1565 | 94 | 1.34 | 1.56 |
| MOR@ZSM-5(SS) | 1582 | 80 | 1.58 | 1.69 |
| MOR@ZSM-5(CS) | 1582 | 70 | 1.75 | 1.78 |
| ZSM-5-NS | 1582 | 59 | 1.83 | 1.83 |

[a]calculated by $D_1/G = 0.55\ La^2$.

**Table S5.** Textural properties of different spent zeolite samples after the catalytic test for alkylation of benzene with ethanol at 450 °C for 24 h.

| Sample | $S_{BET}$[a] ($m^2/g$) | $S_{micro}$[b] ($m^2/g$) | $S_{ext}$[c] ($m^2/g$) | $V_{total}$[d] ($cm^3/g$) | $V_{micro}$[e] ($cm^3/g$) | $V_{ext}$[f] ($cm^3/g$) | %Loss of $V_{micro}$[g] |
|---|---|---|---|---|---|---|---|
| spent mordenite | 12 | 1 | 11 | 0.08 | 0 | 0.08 | 100.0 |
| spent MOR@ZSM-5(SS) | 331 | 146 | 185 | 0.68 | 0.06 | 0.62 | 60.0 |
| spent MOR@ZSM-5(CS) | 398 | 271 | 127 | 0.54 | 0.14 | 0.4 | 36.4 |
| spent ZSM-5-NS | 496 | 234 | 262 | 0.89 | 0.09 | 0.8 | 25.0 |

[a]BET specific surface area, [b]microporous surface area, [c]external surface area, [d]total pore volume, [e]micropore volume, [f]$V_{ext} = V_{total} – V_{micro}$, [g]Loss of microporous volume = $[(V_{micro,\ fresh} – V_{micro,\ spent})/ V_{micro,\ fresh}] \times 100$.