## Electronic Supplementary Information

# Precise control of the sizes of zeolite B-ZSM-5 based on seed surface crystallization 

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Fig. S1 XRD patterns of the silicalite-1 nanoparticle synthesized with different temperatures, a-80 ${ }^{\circ} \mathrm{C}$ -
$74 \mathrm{~nm}, \mathrm{~b}-100^{\circ} \mathrm{C}-111 \mathrm{~nm}, \mathrm{c}-120^{\circ} \mathrm{C}-141 \mathrm{~nm}$.





Fig. S2 Particle size distributions of B-ZSM-5 based on measurements of 100 particles by SEM. (a) B-ZSM-5 zeolite synthesized in the absence of seed, (b-d) the amount of seed addition was $1 \%$ and the seed size was 74,111 and 141 nm , respectively.


Fig. S3 XRD patterns of the B-ZSM-5 nanoparticle synthesized with different seed sizes. (a) 14.2 $\mu \mathrm{m}$, (b) 336 nm , (c) 536 nm , (d) 691 nm .


Fig. S4 $\mathrm{N}_{2}$ adsorption/desorption isotherms at 77 K of B-ZSM-5 samples with different sizes. The isotherms of each sample in one diagram are offset vertically by $10 \mathrm{~cm}^{3} / \mathrm{g}$.

Table S1 Specific surface area and porosity characteristics of the samples with different sizes.

| Particle size | $\begin{aligned} & \mathbf{S}_{\mathbf{m i c r o}^{[a]}} \\ & {\left[\mathbf{m}^{2} \mathbf{g}^{-1}\right]} \end{aligned}$ | $\begin{gathered} \mathbf{S}_{\mathrm{ext}}^{[\mathrm{a}]} \\ {\left[\mathbf{m}^{2} \mathbf{g}^{-1}\right]} \end{gathered}$ | $\begin{aligned} & \mathbf{S}_{\mathrm{BET}}{ }^{[\mathbf{b}]} \\ & {\left[\mathbf{m}^{2} \mathbf{g}^{-1}\right]} \end{aligned}$ | $\begin{aligned} & \mathbf{V}_{\text {micro }^{[a]}} \\ & {\left[\mathrm{cm}^{3} \mathbf{g}^{-1}\right]} \end{aligned}$ | $\begin{gathered} \mathbf{V}_{\text {pore }}[\mathrm{c}] \\ {\left[\mathrm{cm}^{3} \mathbf{g}^{-1}\right]} \end{gathered}$ |
| :---: | :---: | :---: | :---: | :---: | :---: |
| $14.2 \mu \mathrm{~m}$ | 378 | 24 | 402 | 0.15 | 0.17 |
| 691 nm | 369 | 33 | 402 | 0.15 | 0.21 |
| 536 nm | 367 | 36 | 403 | 0.14 | 0.24 |
| 336 nm | 369 | 44 | 413 | 0.15 | 0.29 |

[a] t-plot method
[b] BET method
[c] $\mathrm{p} / \mathrm{p}_{0}=0.99$


Fig. S5 Particle size distributions of B-ZSM-5 based on measurements of 100 particles by SEM. The amount of seed addition was $0.1,0.5,5$ and $10 \%$, respectively.


Fig. S6 $\mathrm{N}_{2}$ adsorption/desorption isotherms at 77 K of B-ZSM-5 samples with different sizes. The isotherms of each sample in one diagram are offset vertically by $20 \mathrm{~cm}^{3} / \mathrm{g}$.

Table S2 Specific surface areas and porosity characteristics of the samples with different particle

| Particle size [nm] | $\begin{aligned} & \mathbf{S}_{\text {micro }^{[\text {a] }]}} \\ & {\left[\mathbf{m}^{2} \mathbf{g}^{-1}\right]} \end{aligned}$ | $\begin{gathered} \mathbf{S}_{\mathrm{ext}}{ }^{[\mathrm{a}]} \\ {\left[\mathrm{m}^{2} \mathbf{g}^{-1}\right]} \end{gathered}$ | $\begin{aligned} & \mathbf{S}_{\mathrm{BET}}{ }^{[\mathrm{b}]} \\ & {\left[\mathrm{m}^{2} \mathbf{g}^{-1}\right]} \end{aligned}$ | $\begin{aligned} & \mathbf{V}_{\text {micro }}{ }^{[a]} \\ & {\left[\mathrm{cm}^{3} \mathbf{g}^{-1}\right]} \end{aligned}$ | $\begin{gathered} \mathbf{V}_{\text {pore }}{ }^{\text {[c] }]} \\ {\left[\mathrm{cm}^{3} \mathrm{~g}^{-1}\right]} \end{gathered}$ |
| :---: | :---: | :---: | :---: | :---: | :---: |
| $676$ | $378$ | 34 | $412$ | $0.15$ | 0.23 |
| $417$ | $375$ | $38$ | $413$ | $0.15$ | 0.27 |
| $336$ | $369$ | $44$ | $413$ | $0.15$ | 0.29 |
| $195$ | $370$ | $41$ | $411$ | $0.15$ | 0.35 |
| 153 | 375 | 47 | 422 | 0.15 | 0.34 |

[a] t-plot method
[b] BET method
$[\mathrm{c}] \mathrm{p} / \mathrm{p}_{0}=0.99$


Fig. S7 XRD patterns of the B-Al-ZSM-5 samples synthesized with different particle sizes. (a) 676 nm , (b) 417 nm , (c) 336 nm , (d) 195 nm , (e) 153 nm . The seed size was 74 nm and the amount of seed addition was $0.1,0.5,1,5$ and $10 \%$, respectively.


Fig. S8 Particle size distributions of B-ZSM-5 based on measurements of 100 particles by SEM. The seed size was 74 nm and the amount of seed addition was $0,0.1,0.5,1,5$ and $10 \%$, respectively.


Fig. S9 $\mathrm{NH}_{3}$-TPD profiles of the B-ZSM-5 samples with $14.2 \mu \mathrm{~m}, 676 \mathrm{~nm}$ and 336 nm . The seed size was 74 nm and the amount of seed addition was $0,0.1$ and $1 \%$, respectively.

Table S3 Chemical compositions of the B-ZSM-5 samples with $14.2 \mu \mathrm{~m}, 676 \mathrm{~nm}$ and 336 nm . The seed size was 74 nm and the amount of seed addition was $0,0.1$ and $1 \%$, respectively.

| Particle size | $\mathbf{S i} / \mathbf{B}$ | Si/Al |
| :---: | :---: | :---: |
| $\mathbf{1 4 . 2} \mathbf{~ m m}$ | 29 | 375 |
| $\mathbf{6 7 6} \mathbf{~ m m}$ | 24 | 402 |
| $\mathbf{3 3 6} \mathbf{~ m m}$ | 23 | 397 |



Fig. S10 Variations of product selectivity over $14.2 \mu \mathrm{~m}$ (a), 676 nm (b) and 336 nm (c) B-ZSM-5 as a function of the time on stream. Reaction conditions: WHSV $=1 \mathrm{~h}^{-1}, \mathrm{~T}=500^{\circ} \mathrm{C}, \mathrm{n}\left(\mathrm{CH}_{3} \mathrm{OH}\right): \mathrm{n}\left(\mathrm{H}_{2} \mathrm{O}\right)$

$$
=1: 5, \mathrm{P}_{\text {total }}=1 \mathrm{~atm} .
$$



Fig. S11 TG and DTG curves of the coked catalysts with $14.2 \mu \mathrm{~m}$ and 336 nm after 46 and 794 h reaction.

