An approach to prepare nanosized HZSM-22 with enhanced lifetime in the methanol to hydrocarbon (MTH) reaction

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Nanosized HZSM-22 has been successfully prepared using ball milling combined with alkaline and acid leaching treatment. The samples were characterized by XRD, XRF, nitrogen physical adsorption–desorption, SEM and solid state NMR. The results showed that the size of the zeolite crystal was greatly reduced after ball milling treatment, and that the crystallinity of the milled sample can be almost totally restored after further alkaline and acid treatment. The prepared nanosized HZSM-22 exhibited enhanced catalytic stability compared with the parent sample in the MTH reaction. Detailed product analysis implied that the improvement of the diffusion effect and the correspondingly reduced secondary reaction would be the most important factor for the long-term MTH operation over the nanosized catalyst.

1. Introduction

Liquid fuels and olefins are the most important petrochemical products in modern industry and the majority of them are produced from oil resources. The shortage of the resources and the increasing demand for fuels and olefins drive the non-petrochemical route development for the production of these petrochemical commodities. MTH process over acidic zeolites has been developed as the most successfully non-petrochemical route for olefins/gasoline production from the alternative and abundant resources, such as coal, natural gas, biomass or carbon dioxide under proper operation conditions.1–5 Over the past four decades, there have been numerous publications on MTH reaction over a large variety of zeolites and zeotype molecular sieves with different topologies.6,8 SAPO-34 (CHA topology) with small 8-membered ring pore openings and large cages has been employed in the commercialized MTO (methanol-to-olefins) process,7 while ZSM-5 (MFI topology) with 10-membered ring and channel intersections has been used for the industrialized MTP (methanol-to-propene)6 and MTG (methanol-to-gasoline) process.9

ZSM-22, a zeolite with TON topology firstly synthesized by Dwyer, features 1-dimensional 10-membered ring (0.46 × 0.57 nm) channels running parallel to 001 direction.10 ZSM-22 has been utilized as a catalyst for hydroisomerization dewaxing process, exhibiting high mono-branched selectivity due to pore mouth catalysis.11 Besides, its application in the conversion of methanol has been also intensively studied recently.12–19 Cui and coworkers investigated the MTO reaction over ZSM-11 (MEL), ZSM-22 (TON), SAPO-34 (CHA), and SAPO-5 (AFI) and found that ZSM-22 was not reactive for MTO reaction.18 The authors attributed this phenomenon to the absence of large cross-channel or cage structures which could offer large space to accommodate hydrocarbon pool species.12–14 In contrast, other studies indicated that methanol conversion over ZSM-22 presented comparable conversion as that of SAPO-34 and that the products were composed of a majority of branched-chain C5+ hydrocarbons and very little content of aromatics.15–18 However, compared to ZSM-5, methanol conversion over ZSM-22 suffers rapid deactivation due to the diffusion limitation of the reactants and products during the reaction, caused by the narrow 1-dimensional and 10-membered ring microporous structure.20,21 To overcome the mass transfer limitation, the application of molecular sieves with small particle size or hierarchical structure has been one of the potential strategies to prolong the catalyst life span via shortening the diffusion paths of the molecular in the catalysts.22–24 The typical ZSM-22 zeolite prepared by traditional hydrothermal synthesis method exists as needle/rod-shaped submicron particles with the dimension of 1–5 μm in length,16,25–27 Very recently, nanosized ZSM-22...
with length of 100 nm has been firstly synthesized by Oki Muraza and coworkers in hydrothermal system with horizontal rotation.\textsuperscript{39} Besides, mesopore has been introduced into ZSM-22 by desilication with alkaline solution to enhance the capacity of the carbonaceous species accommodation at the expense of the 60% original Brunsted site,\textsuperscript{32} moreover, the desilication efficiency for ZSM-22 was much lower than that of ZSM-5.\textsuperscript{34,35}

Recently, bead milling, as a physical method, was proposed to prepare nanosized zeolites, such as ZSM-5, zeolite A, zeolite X, and SAPO-34.\textsuperscript{36–38} According to these reports, the large zeolite particles could be destroyed by ball milling into fines with crystalline phase and damaged parts, and then the latter could be washed off by the following alkaline leaching process or be remedied by recrystallization in a dilute silicate solution.\textsuperscript{36–40}

In the present work, nanosized ZSM-22 with high crystallinity was successfully prepared using a facile approach, bead milling and following mild basic and acidic treatment. The length of ZSM-22 running parallel to 001 direction was significantly shortened without changing the Si/Al ratio and acidity of the zeolite. The lifetime of MTH reaction over nanosized HZSM-22 was prolonged dramatically as about 8 times as that of the parent HZSM-22, meanwhile the product selectivity was comparable with that before milling treatment.

2. Experiment

2.1. Catalysts preparation

The catalyst of ZSM-22 was calcinated at 600 °C for 10 h to remove the template and marked as ZSM-22(P). 10 g ZSM-22(P) and 25 ml deionized water were mixed and then milled at 500 rpm for 5 h using ball mill instrument of QM-3SP2 planetary. Half of the agate jar was filled with agate balls with diameter of 3, 6 and 10 mm. After milling, the suspension in the jar was gathered and dried at 110 °C overnight. The obtained solid sample was designated as ZSM-22-M.

5 g ZSM-22-M sample was added into a beaker flask containing 100 ml 0.5 M NaOH solution. The mixture was heated with a water bath at 65 °C for 30 min under stirring and then washed three times with deionized water. After being dried overnight, the alkaline treated ZSM-22 was mixed well with 100 ml 0.2 M HCl solution and treated at 65 °C for 6 h under stirring. After being washed and dried, the final sample with alkaline and acid treatment was marked as ZSM-22-M-A-A.

For comparison, 5 g ZSM-22(P) also underwent the same basic and acid treatment as that of ZSM-22-M-A-A without milling. The obtained sample was marked as ZSM-22-A-A.

All the samples were converted into H-form zeolite by 3 times ion exchange at 80 °C for 6 h in 1 M NH₄NO₃ solution, followed by being washed with deionized water, dried at 120 °C for 12 h and calcined at 550 °C for 4 h.

2.2. Catalysts characterization

The crystallinity of the H-form samples were characterized using a PANalytical X’Pert PRO X-ray diffraction (XRD) meter with Cu-Kα radiation (λ = 1.54059 Å) at 40 kV and 40 mA. The chemical composition of the catalysts was determined by Philips Magix-601 X-ray fluorescence (XRF) spectrometer. The morphology and particle size of the catalysts were measured by field emission scanning electron microscopy (FE-SEM, Hitachi, SU8020). The sample crystal size was further determined on a Zetasizer nano laser particle size analyzer. Nitrogen adsorption–desorption isotherms were obtained on a Micrometrics ASAP 2020 system at 77 K. The total surface area was calculated based on the Brunauer–Emmett–Teller (BET) equation. The micropore volume and micropore surface area was evaluated with t-plot method. The mesopore volume was calculated by BJH method. All the solid state NMR experiments were performed on a Bruker AvanceIII 600 spectrometer equipped with a 14.1 T wide-bore magnet. The resonance frequencies were 600.13, 156.4 and 119.2 MHz for ²H, ²⁷Al and ²³Si, respectively. The acidity of the H-ZSM-22 catalyst was determined by temperature programmed desorption of ammonia (NH₃-TPD) on a chemical adsorption instrument (Micromeritics AutoChem 2920). The sample (0.14 g) was loaded in a U-shaped micro-reactor and pretreated at 650 °C for 30 min under helium atmosphere. After cooling to 100 °C, the sample was saturated with ammonia, followed by purging with helium to remove physisorbed ammonia. The ammonia desorption was carried out in helium flow (40 ml min⁻¹) by increasing the temperature from 100 to 600 °C with a heating rate of 10 °C min⁻¹ and monitored by a thermal conductivity detector (TCD).

2.3. Catalytic test

50 mg catalyst was pressed, sieved to 40–60 mesh and loaded in a fixed-bed quartz tubular reactor with inner diameter of 4 mm. Prior to the reaction, the catalyst was activated at 500 °C for 40 min, and then the temperature was adjusted to 400 °C. Methanol was fed by passing the carrier gas (12.4 ml min⁻¹) through a saturator containing methanol at 14 °C, which gave a WHSV of 2.0 g g⁻¹ h⁻¹. Methanol conversion was performed under atmospheric pressure. The effluent products from reactor were kept warm and analyzed by online gas chromatography equipped with a PorapLOT Q-HT capillary column and a FID detector. The conversion and selectivity were calculated on CH₃ basis. Dimethyl ether (DME) was considered as reactant in the reaction.
\[ C = \frac{(1 - \text{wt}_{\text{MeOH\%}} - \text{wt}_{\text{DME\%}})/14}{(1 - \text{wt}_{\text{MeOH\%}} - \text{wt}_{\text{DME\%}})/14 + (\text{wt}_{\text{MeOH\%}}/32) + (\text{wt}_{\text{DME\%}}/23)} \times 100\% \]  

(1)

\[ S_x = \frac{\text{wt}_{x\%}/14}{(1 - \text{wt}_{\text{MeOH\%}} - \text{wt}_{\text{DME\%}})/14} \times 100\%. \]  

(2)

3. Results and discussion

3.1. Catalysts characterization

Fig. 1 displays the FE-SEM images of (a) HZSM-22(P), (b) HZSM-22-A-A, (c) HZSM-22-M and (d) HZSM-22-M-A-A. Despite that some crystals align or fuse sideways, the HZSM-22(P) particles display typically rod-like morphology.\(^4^1\) The length of aggregated ZSM-22(P) particles is about 1 \(\mu\)m as shown in Fig. 1(a), which is also confirmed by the particle size distribution in Fig. 2, measured by nano laser particle size analyzer. As presented in SEM image of ZSM-22-A-A in Fig. 1(b), the morphology and particle size of HZSM-22 remain unchanged after alkaline–acid treatment. However, after milling, most of the HZSM-22 particles are well-dispersed and crushed into much shorter and irregular rod-like catalyst particles with length in the range from 50 to 350 nm in Fig. 1(c) and (d). Particle size distribution in Fig. 2 also supported the reduction in crystal size. The average size of HZSM-22-M-A-A is 315 nm, much smaller than that of parent sample (~1000 nm). These results shows that ball milling is a facile and efficient method to prepare nanosized particle catalysts, which is usually difficult to be prepared with conventional one-pot synthesis.\(^1^0,1^6,2^5,3^2\)

Fig. 3 shows the XRD patterns of HZSM-22(P), HZSM-22-A-A, HZSM-22-M, and HZSM-22-M-A-A. All samples displayed the typical diffraction peaks of TON framework.\(^3^0,4^2\) Taking HZSM-22(P) as the reference sample, the relative crystallinity of HZSM-22-A-A, HZSM-22-M and HZSM-22-M-A-A are 102, 59 and 96, respectively, as calculated on basis of the intensity of four typical diffraction peaks in the 2\(\theta\) range of 20° to 27°. Compared to parent sample HZSM-22(P), the relative crystallinity of HZSM-22-M decreased by 41%, indicating the formation of amorphous phase induced by ball milling. While the crystallinity of the milled catalyst can be recovered from 59% (HZSM-22-M) to 96% (HZSM-22-M-A-A) after successive alkaline and acid treatment. The crystallinity of HZSM-22-A-A (102%) was also slightly improved compared with that of HZSM-22(P) (100%) when HZSM-22(P) underwent the same basic and acidic treatment process without milling. Therefore, alkaline and acid post-treatment herein is proved to be an effective approach to remove amorphous debris from the prepared nano catalyst and then restore the crystallinity of the milled sample.
The Si/Al ratios in Table 1, determined by XRF, present very close value among the four samples, indicating that the milling condition and alkaline and acid treatment has little effect on the composition of the HZSM-22 catalysts.

For better understanding of the variation of acidity and element coordination environment of the prepared HZSM-22 catalysts, $^1$H, $^{27}$Al and $^{29}$Si MAS NMR spectra of the calcined HZSM-22[P], HZSM-22-A-A, HZSM-22-M and HZSM-22-M-A-A were recorded and shown in Fig. 4. The signals with chemical shifts at $-112$, $-109$, $-106$, $-102$ and $-96$ ppm in the $^{29}$Si MAS NMR spectra (Fig. 4(c)) are ascribed to two kinds of Si(0Al) ($-112$ and $-109$ ppm), Si(1Al), Si(OH) and Si(OH)$_2$ species, respectively.$^{44}$ The signals with chemical shifts at 55 and 0 ppm in the $^{27}$Al MAS NMR spectrum (Fig. 4(b)) are assigned to framework Al species in tetrahedral coordination state and extra-framework Al species in octahedral coordination state, respectively.$^{44}$ Four peaks with chemical shifts at 1.7, 2.5, 3.9 and 6.0 ppm in the $^1$H MAS NMR (Fig. 4(a)) are attributed to terminal silanol groups (SiOH) on the external surface or at lattice defects, non-acidic extra-framework aluminum hydroxyl groups (EFAl-OH), acidic bridging hydroxyl groups (Si(OH)Al) and disturbed acidic bridging hydroxyl groups (Si(OH)Al) influenced by additional interaction with framework oxygen.$^{45,46}$

The data summarized in Table 1 indicated that ball milling gives rise to the decrease of the Bronsted acid density from 0.327 mmol g$^{-1}$ of HZSM-22[P] to 0.199 mmol g$^{-1}$ of HZSM-22-M, and correspondingly the densities of Al–OH and Si–OH increased from 0.122 mmol g$^{-1}$ and 0.134 mmol g$^{-1}$ to 0.206 mmol g$^{-1}$ and 0.322 mmol g$^{-1}$, respectively. Concurrently, the peaks of tetrahedral framework Al were slightly broadened due to the changes of local chemical environment induced by ball milling treatment (Fig. 4(b)). In addition, the amount of extra-framework Al in HZSM-22-M also increased slightly compared with HZSM-22[P] (Fig. 4(b)). Taken together, these results show that the ball milling treatment can mediate the chemical environment of Al and Si and then alter the acidity. However, these changes could be eliminated by the subsequent alkaline–acid treatment. As shown in Table 1 and Fig. 4, the Bronsted acid densities as well as the Al–OH and Si–OH densities can be recovered back to the level close to the parent sample after the alkaline and acid post-treatment. It should be noted that the alkaline and acid post-treatment without ball milling has little effect on the Al and Si chemical environment of the parent sample as shown in Table 1 and Fig. 4. As for the framework Si/

### Table 1 Si/Al ratios and acid density of HZSM-22(P), HZSM-22-A-A, HZSM-22-M and HZSM-22-M-A-A

<table>
<thead>
<tr>
<th>Samples</th>
<th>Si/Al$^a$</th>
<th>Si/Al$^b$</th>
<th>ALOH$^c$, mmol g$^{-1}$</th>
<th>SiOH$^c$, mmol g$^{-1}$</th>
<th>Bronsted acid$^c$, mmol g$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>HZSM-22[P]</td>
<td>34.0</td>
<td>31.8</td>
<td>0.122</td>
<td>0.134</td>
<td>0.327</td>
</tr>
<tr>
<td>HZSM-22-A-A</td>
<td>33.8</td>
<td>31.7</td>
<td>0.119</td>
<td>0.129</td>
<td>0.318</td>
</tr>
<tr>
<td>HZSM-22-M</td>
<td>35.5</td>
<td>32.1</td>
<td>0.206</td>
<td>0.322</td>
<td>0.199</td>
</tr>
<tr>
<td>HZSM-22-M-A-A</td>
<td>36.5</td>
<td>31.4</td>
<td>0.127</td>
<td>0.156</td>
<td>0.304</td>
</tr>
</tbody>
</table>

$^a$ Determined by XRF. $^b$ Determined by $^{29}$Si MAS NMR. $^c$ Determined by $^1$H MAS NMR.

Fig. 4 $^1$H (a), $^{27}$Al (b) and $^{29}$Si (c) MAS NMR spectra of the calcined HZSM-22(P), HZSM-22-A-A, HZSM-22-M and HZSM-22-M-A-A.
Al ratio determined by $^{29}\text{Si} \text{MAS NMR}$ shown in Table 1, the values of the four samples are close to each other in the range of 31–32, indicating that the alkaline and acid treatment condition applied for removing the amorphous phase has little effect on the crystalline phase. These results further confirmed that ball milling treatment could cause the fragmentation of the zeolite, leading to the reduction of crystallinity and Bronsted acid density, while the loss of crystallinity and Bronsted acidity could be restored by the following base and acid treatment to remove the amorphous fractions.

To further confirm the alteration of acidity of the zeolite resulting from the ball milling and/or the following alkaline and acid treatment, $\text{NH}_3$ adsorption measurement was subsequently performed. The characteristic $\text{NH}_3$ desorption peak centered at 430 °C shown in Fig. 5 represent that the ball milling will lower the acidity of sample, however, the following alkaline and acid treatment can restore the acidity to the level of parent sample. Besides, the acidity of the sample solely subject to the alkaline and acid post-treatment without ball milling is not apparently altered. All these results conform to the acidity change illustrating by the NMR results shown in Fig. 4.

Nitrogen adsorption and desorption isotherms of all the samples are shown in Fig. 6 and the textural properties are summarized in Table 2. The parent HZSM-22(P) exhibits typical microporous properties of ZSM-22 with BET surface area of 217 m$^2$ g$^{-1}$ (microporous surface area 185 m$^2$ g$^{-1}$ and external surface area 32 m$^2$ g$^{-1}$) and the weak hysteresis loop is attributed to inter crystal mesopore. Ball milling greatly reduced the microporous surface. HZSM-22-M has a lowered microporous surface area of 119 m$^2$ g$^{-1}$ and its external surface area increases to 119 m$^2$ g$^{-1}$, and concomitantly the micropore volume of HZSM-22-M decreases from 0.086 cm$^3$ g$^{-1}$ of HZSM-22(P) to 0.054 cm$^3$ g$^{-1}$. This suggests that part of the zeolite framework has been destroyed into amorphous fragments, causing the blockage of the micropore channel of zeolites. It should be noted that, after mild basic and acid treatment, the micropore surface area could be restored from 119 m$^2$ g$^{-1}$ of HZSM-22-M to 176 m$^2$ g$^{-1}$, close to that of the parent sample (217 m$^2$ g$^{-1}$). The same holds true for the micropore volume that was restored from 0.054 cm$^3$ g$^{-1}$ of HZSM-22-M to 0.082 cm$^3$ g$^{-1}$, comparable with the parent sample (0.086 cm$^3$ g$^{-1}$). The recovery of the microporous surface area and volume implicates that the fabricated fragments of the amorphous debris during ball milling process have been effectively cleared up from the zeolite pores, which concurs with the observation with respect to the restoration of the crystallinity of HZSM-22-M sample after successive alkaline and acid treatment shown in Fig. 3. The hysteresis loops of HZSM-22-M and HZSM-22-M-A-A are more obvious than that of HZSM-22(P) in Fig. 6, reflecting the enlarged mesopore volume from 0.212 cm$^3$ g$^{-1}$ of parent sample to 0.258–0.355 cm$^3$ g$^{-1}$ detailed in Table 2. This is probably a consequence of inter crystal mesopore formed with the aggregation of the crushed nano particles during ball milling.

### 3.2. Catalytic performance

The catalytic tests of methanol conversion over the four HZSM-22 catalysts were carried out in a continuous-flow reaction systems and methanol conversions with time-on-stream are shown in Fig. 7. The conversion of MTH reaction over HZSM-

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Table 2  Textual properties of HZSM-22(P), HZSM-22-A-A, HZSM-22-M and HZSM-22-M-A-A

<table>
<thead>
<tr>
<th>Samples</th>
<th>$S_{\text{total}}$ $^a$, m$^2$ g$^{-1}$</th>
<th>$S_{\text{micro}}$ $^b$, m$^2$ g$^{-1}$</th>
<th>$S_{\text{ext}}$ $^b$, m$^2$ g$^{-1}$</th>
<th>$V_{\text{micro}}$ $^b$, cm$^3$ g$^{-1}$</th>
<th>$V_{\text{meso}}$ $^c$, cm$^3$ g$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>HZSM-22(P)</td>
<td>217</td>
<td>185</td>
<td>32</td>
<td>0.086</td>
<td>0.212</td>
</tr>
<tr>
<td>HZSM-22-A-A</td>
<td>215</td>
<td>189</td>
<td>36</td>
<td>0.088</td>
<td>0.258</td>
</tr>
<tr>
<td>HZSM-22-M</td>
<td>238</td>
<td>119</td>
<td>119</td>
<td>0.054</td>
<td>0.297</td>
</tr>
<tr>
<td>HZSM-22-M-A-A</td>
<td>229</td>
<td>176</td>
<td>53</td>
<td>0.082</td>
<td>0.355</td>
</tr>
</tbody>
</table>

$^a$ BET method. $^b$ t-plot method. $^c$ BJH method.
22(A) decreases from the beginning of the reaction, indicating the quick deactivation of the catalyst. The fast deactivation of the parent zeolite under the relatively low temperature of 400 °C is attributed to the quick formation of heavier aromatics that covers the acid sites and also blocks the pore mouth. More rapid deactivation also occurs over HZSM-22-M. The sharply reduced methanol conversion of HZSM-22-M can be correlated to the partial amorphization of HZSM-22 catalyst during ball milling, which causes the micropore blockage and Bronsted acid density reduction as indicated in the of XRD pattern (Fig. 3), 1H MAS NMR spectra (Fig. 4(a)) and nitrogen adsorption–desorption (Fig. 6). After the following alkaline and acid treatment, the lifetime of HZSM-22-M-A-A was remarkably improved with only 10% reduction in methanol conversion after reaction for 500 min, presenting more excellent catalyst stability than previous reports.15,18,19 The long catalyst lifetime should be attributed to the enhancement of reactant/product diffusion in the nanosized HZSM-22, which can improve the mass transfer of methanol and avoid the secondary reactions of produced olefin products, such as oligomerization, cyclization and H-transfer, in this way, coke formation can be largely depressed.

For comparison, the parent HZSM-22(P) was also treated with the same alkaline and acid leaching process, but without ball milling. Even some improvement in catalyst stability can be observed (methanol conversion over HZSM-22-A-A decreased to 90% in 150 min), the catalyst lifetime was still much shorter than that of nanosized HZSM-22-M-A-A.

Methanol conversion presented the differences in catalyst life span by the usage of HZSM-22 with varied crystal particle size, while the product distribution at initial 100% conversion was comparable for HZSM-22(P), HZSM-22-A-A, HZSM-22-M and HZSM-22-M-A-A (as shown in Fig. 8). Propene, C4 and C5 hydrocarbons appear as the main products. Ethene and other C2–C4 products are also generated with low selectivity. Compared to HZSM-22(P), the selectivities of C1–C4 light alkanes and xylene products over HZSM-22-M-A-A are very low, indicating the H-transfer reactions are largely depressed over this treated catalyst with reduced particle size. The evolution of the selectivity profiles with time on stream was similar among the four catalysts. C2–C4 alkenes selectivity decreased while C5+ selectivity increased to a maximum value and then declined, indicating that the methanol conversion over the four catalysts follows the same reaction and deactivation mechanism. In this study, it is more reasonable to attribute the enhancement of catalyst lifetime of HZSM-22-M-A-A to the diffusion effect improved by reducing the crystal size.

### 3.3. Analysis of retained coke species in deactivated catalysts

The deposited coke amounts were determined by TGA experiments and the detailed coke species retained within the four deactivated catalysts after the MTH reaction were identified.

**Fig. 7** Methanol conversion variation with time on stream (TOS) over HZSM-22(P), HZSM-22-A-A, HZSM-22-M, and HZSM-22-M-A-A at 400 °C, WHSV = 2 g g⁻¹ h⁻¹, and He/methanol = 10.1.

**Fig. 8** Product selectivities variation with time on stream (TOS) over HZSM-22(P), HZSM-22-A-A, HZSM-22-M and HZSM-22-M-A-A at 400 °C, WHSV = 2 g g⁻¹ h⁻¹, and He/methanol = 10.1.

**Fig. 9** TGA curves of deactivated HZSM-22(P), HZSM-22-A-A, HZSM-22-M and HZSM-22-M-A-A obtained after MTH reaction at 400 °C, WHSV = 2 g g⁻¹ h⁻¹, and He/methanol = 10.1.
4. Conclusions

In summary, nanosized ZSM-22 has been prepared successfully by the combination of ball milling and alkaline and acid post treatment. This method is more advantageous than other strategies because it could effectively shorten the crystal length of HZSM-22 into nanoscale in 001 direction without changing the framework Si/Al ratio and crystallinity. More importantly, the prepared nanosized HZSM-22 exhibited significantly enhanced lifetime in the MTH reactions with similar product selectivity compared with the parent HZSM-22. The shortened diffusion pathway of reactant and products within 1-dimensional and 10-membered ring channel and the resulting depression of H-transfer reactions contribute to the long-term lifetime of nanosized catalyst, HZSM-22-M-A-A.

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Notes and references
