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Insights into the Pyridine-modified MOR Zeolite Catalysts for DME Carbonylation

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ABSTRACT Pyridine-modified MOR zeolite catalyst has attracted great attention in recent years due to its unique shape selectivity within 8-MR side pockets for DME carbonylation to methyl acetate (MA) and syngas conversion to ethylene. Herein, aiming to elucidate the pyridine modification-carbonylation activity relationships and develop high-performance catalyst, we investigated the adsorption/desorption behaviors of pyridine on MOR zeolites with varying Si/Al ratios and their impact on DME carbonylation. Instead of the previously proposed selective adsorption of pyridine in 12-MR channels, pyridine is revealed to penetrate into 8-MR side pockets of MOR zeolites and interact with acidic hydroxyls therein. Upon heating, pyridine in pockets desorbs preferentially, likely arising from the lower stability of pyridine adspecies in constrained spaces. This well explains the observed increment of carbonylation activity following the increase of pretreatment temperature.

Unprecedentedly high MA yield (7.2 mmol/h/g) has been achieved on pyridine-modified MOR (Si/Al=13.8) under controlled pyridine desorption conditions, resulting from the joint contributions of better diffusion properties and larger amount of active acid sites. Moreover, the catalytic activity of Brønsted acid sites within 8-MR pockets is demonstrated to be inhomogeneous, closely associated with their locations.

KEYWORDS MOR, DME carbonylation, FTIR, zeolite, pyridine adsorption

INTRODUCTION

Since the first report of selective carbonylation of dimethyl ether (DME) over zeolite catalysts by Iglesia and his colleagues in 2006, this reaction has been attracting great attention in the field of heterogeneous catalysis¹⁻³, because it offers an effective way to enhance the value of C1 chemicals via the formation of C-C bonds. Methyl acetate (MA), the highly selective product of DME carbonylation, could be further hydrogenated to produce ethanol, which acts as an important chemical and additive for transport fuel⁴. Thus, DME carbonylation indeed opens a novel route for ethanol production from sources such as coal and natural gas. In 2017, a commercial DMTE (DME-to-Ethanol) process with a production capacity of 100 000 tons of ethanol per year, developed by Dalian Institute of Chemical Physics (DICP), has been successfully put into operation in Shaanxi, China⁵.

Mordenite (MOR) and ferrierite (FER) zeolites have been demonstrated to be the most efficient catalysts for the DME carbonylation⁶⁻¹⁰. In particular, MOR exhibits the highest carbonylation activity and selectivity to the desired product MA. MOR framework consists of parallel 12-membered ring (12-MR, 6.5×7.0 Å) and 8-MR channels (2.6×5.7 Å) along the c axis direction, both of which are interconnected by 8-MR side pockets (3.4×4.8 Å) along the b axis direction¹¹⁻¹². As the 8-MR channels along the c axis are too narrow for most molecules to penetrate, MOR practically behaves as

a unidimensional zeolite in catalytic reactions. Previous works have evidenced that the mechanism of DME carbonylation on acidic zeolites involves the adsorption of DME on Brønsted acid sites (BAS) to form the methoxy species and their subsequent reaction with CO to yield acetyl intermediates, which further react with DME to deliver MA¹³; the rate-determining step on MOR zeolite is the formation of acetyl intermediates, which preferentially occurs in the 8-MR side pockets with spatial confinement¹⁴⁻¹⁶. Several research groups have reported that DME carbonylation rates are proportional to the number of BAS in the 8-MR side pockets¹⁷⁻¹⁹. In addition, Corma et al. investigated the carbonylation activities of BAS at different crystallographic positions by quantum-chemical methods¹⁵. They concluded that the T3-O33 position inside 8-MR pockets is the only one selective for carbonylation; both the space-confinement effect of the 8-MR pockets and the unusual orientation of the methoxy groups at T3-O33 positions contribute to the unique carbonylation behavior. The acid sites in the 12-MR main channels, on the other hand, are prone to side reactions (DME to hydrocarbons), resulting in rapid carbon deposition and quick deactivation of the MOR catalysts^{15, 20}. Very recently, based on Monte Carlo and molecular dynamics simulation, Zheng *et al.* also visited the different roles of the 8-MR and 12-MR channels in MOR zeolites, concluding that the CO aggregation properties inside the 8-MR side pockets also contributed to the unique catalytic performance of the 8-MR channels²¹.

To improve the catalytic stability of MOR zeolites in the DME carbonylation, several strategies have been developed via selectively removing/poisoning the acid sites inside the 12-MR channels, including high-temperature steam treatment (dealumination)²², acid/alkaline treatment (dealumination)²³⁻²⁴, pyridine modification²⁵, etc. Among them, pyridine modification strategy represents the most effective one, as the catalytic lifespan of pyridine pre-adsorbed MOR zeolites is evidently superior to those prepared by other methods. Very recently, pyridine-modified MOR zeolite was also reported to be highly selective catalyst for syngas conversion to ethylene and methanol to olefins reaction²⁶⁻²⁷,

1 verifying again the effectiveness of such strategy and the peculiarity of the 8-MR side pockets with
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3 spatial confinement.
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6 Based on carefully prepared H-MOR zeolite ($\text{Si}/\text{Al} \approx 10$) without dealumination, Maache et al. firstly
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8 reported that the BAS inside the 12-MR channels can be selectively titrated by pyridine, whereas the
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10 acid sites located in the 8-MR pockets are inaccessible due to the large molecule diameter of pyridine²⁸.
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12 However, it is very difficult to avoid the occurrence of dealumination during the practical preparation
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14 (such as calcination or pretreatment process) of MOR zeolites²⁸⁻³², which would create silanol or
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16 aluminol defects inside the zeolite framework. This is also the case for other zeolites with lower Si/Al
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18 ratios^{30, 33-34}. The generation of defect sites in MOR zeolite may change the diffusion properties of
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20 reactants/products and the accessibility of BAS in 8-MR side pockets. It is thus important to learn the
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22 adsorption/desorption behaviors of pyridine molecules on the *de facto* imperfect MOR zeolite and
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24 their influence on the catalytic property, which would prompt the improvement of pyridine-modified
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26 MOR catalyst.
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35 In this contribution, the sorption behaviors of pyridine on MOR zeolites with varying Si/Al ratios
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37 ($\text{Si}/\text{Al} = 7-20$) were monitored by FTIR and their impact on the DME carbonylation was explored.
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39 Spectroscopic results evidenced that pyridine could actually interact with the hydroxyl protons in the
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41 8-MR side pockets of these MOR catalysts. However, pyridine desorbs preferentially from the pockets
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43 when heated, which accounts for the good stability and high carbonylation activity of the pyridine-
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45 modified catalysts. The effect of Si/Al ratios on pyridine modification and DME carbonylation activity,
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47 and the inhomogeneity of the active centers inside the 8-MR side pockets were also studied.
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55 EXPERIMENTAL SECTION

56 Catalyst preparation

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58 MOR zeolites were prepared through a hydrothermal synthesis method. Sodium hydroxide, sodium
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aluminate, tetraethylammonium hydroxide solution (TEAOH, 35 wt%), and H₂O were first mixed at room temperature and stirred until completely dissolved. Subsequently, under intense stirring, silica sol was added dropwise into the above solution. After aging at the ambient temperature for 1 h, seed crystals (2 wt% relative to SiO₂) were added and the mixture underwent further agitation for another 1 h. The molar compositions of the obtained reaction gels are listed in Table S1. The mixture was further transferred into a 100 mL autoclave and crystallized at 170 °C for 48 hours under static conditions. After crystallization, the solid products were washed with distilled water, recovered by centrifugation and dried at 120 °C for 12 h. To remove the organic amines, the sample was heated (1 °C/min) to 550 °C under dry air and kept at this temperature for 4 h. The resultant sample was further transformed to its proton type by ammonium exchange within 1 mol/L NH₄NO₃ solution (1 h@80 °C, repeated 3 times) and calcination at 550 °C (temperature ramp rate: 1 °C/min) for 4 h under dry air.

Catalyst characterization

The powder X-ray diffraction (XRD) patterns of the as-synthesized samples were recorded using PANalytical X'Pert PRO X-ray diffractometer with Cu K α radiation ($\lambda = 0.154059$ Å) at 40 kV and 40 mA from 5° to 50°. The elemental compositions of the as-synthesized samples were determined on Philips Magix-601 X-ray fluorescence (XRF) spectrometer. The scanning electron microscope (SEM) images of the synthesized samples were recorded on a Hitachi SU8020 SEM equipment. N₂ adsorption and desorption analysis was carried out on a Micromeritics ASAP 2020 analyzer. The total surface area was calculated based on BET method. The micropore volume and area were derived by t-plot method. Temperature programmed desorption of ammonia (NH₃-TPD) analysis was performed using 100 mg powder of the H-MOR zeolites at the temperature range of 100-700 °C after the sample pretreatment at 450 °C for 1 hour under a He flow using Micromeritics Autochem II 2920 equipped with a thermal conductivity detector (TCD). Solid-state NMR spectra were recorded on a Bruker

Avance III 600 MHz spectrometer. Before ^1H MAS NMR measurements, the samples were dehydrated at 420 °C under a vacuum below 10^{-3} Pa for 20 h. ^1H MAS NMR spectra were collected at 600.13 MHz with a 3.2 mm HXY probe using a Hahn-Echo pulse sequence with a $\pi/2$ pulse of 3.2 μs , a 10 s recycle delay, and a spinning speed of 20 kHz. The chemical shifts were referenced to adamantane at 1.74 ppm.

Fourier transform infrared spectra of pyridine (Py-FTIR) analysis were recorded on Bruker Tensor 27 instrument with an MCT detector. The samples (20 mg) were pressed into a self-supporting wafer and placed into a quartz cell. Subsequently, the samples were pretreated at 400 °C for 30 minutes under vacuum. After pretreatment, the samples were cooled down to room temperature. The spectra of MOR samples without pyridine perturbation were subsequently recorded from 4000 to 1000 cm^{-1} . Afterwards, pyridine was introduced into the cell until complete saturation, followed by evacuation of the IR cell for 30 min to remove physisorbed pyridine. The desorption process of pyridine was monitored by heating the sample up to desired temperatures with a heating rate of 5 °C/min under vacuum. Each spectrum was obtained by averaging 64 scans with a resolution of 4 cm^{-1} and all the spectra are recorded at room temperature. Note that the heating rate of the treatment processes was initially set at 1 °C/min in order to avoid the dealumination of the samples. However, the resultant spectra show no obvious difference with those obtained at 5 °C/min, and the experiments are consequently conducted with a heating rate of 5 °C/min (Figure S1).

Catalytic testing

DME carbonylation reactions were performed in a fixed-bed reactor. 0.5 g of the catalyst (40-60 mesh) was loaded into the reactor and pretreated (heating rate 1 °C/min) in Ar at 400 °C for 2 h. Afterwards, the sample was purged with pyridine-Ar mixture (30 mL/min) for 20 min at 200 °C and subsequently flushed with Ar at certain temperature (200, 300, 400, 500 °C), until no obvious pyridine can be detected by gas chromatograph. Finally, the temperature was reduced to 200 °C and a reactant gas mixture (DME: CO: N_2 =5:35:60) was introduced with a GHSV of 3600 mL/g/h. The reaction

pressure was 2.0 MPa. The products were analyzed online by gas chromatograph (Agilent 7890B) equipped with TCD and FID detectors using TDX-1 packed column and Pora PLOT Q capillary column, respectively.

RESULTS AND DISCUSSION

Structural and compositional analysis

Five MOR zeolites with Si/Al ratios between 7 and 20 were synthesized. The elemental compositions of the as-synthesized samples, derived from XRF analysis, are listed in Table 1. To clarify, the samples are denoted MOR(7.0), MOR(9.7), MOR (13.8), MOR(16.5) and MOR(19.4), with the values in the parentheses indicating their Si/Al ratios. The XRD patterns of the as-synthesized samples are presented in Figure S2, all of which could be well-indexed to the MOR structure, indicating their good purity. SEM images (Figure S3) reveal that the MOR samples with lower Si/Al ratios have aggregated morphologies of nano-grains, which is likely owing to the use of seeds for the synthesis. With the increase of Si/Al ratios (samples MOR(13.8), MOR(16.5) and MOR(19.4)), the primary particles become more closely packed and even merge into bulk particles. The change in morphology following the increase of Si/Al ratios is consistent with the increased crystallinity as evidenced by the XRD results. The N₂ physisorption isotherms of the samples are displayed in Figure S4, which can be regarded as type I or composite of type I plus type IV isotherms. For samples MOR (7.0) and MOR(9.7), very small hysteresis loops of H4-type are observed likely resulting from the stacking voids of nano-grains. The corresponding textural properties are listed in Table 1. The micropore surface areas and micropore volumes of the samples are in the range of 371-394 m² g⁻¹ and 0.18-0.19 cm³ g⁻¹ respectively, verifying their good crystallinity.

Table 1 Elemental compositions and textural properties of the samples

Sample	Si/Al ratio ^a	Surface area ^b (m ² g ⁻¹)			Pore volume ^c (cm ³ g ⁻¹)		
		S _{BET}	S _{micro}	S _{ext}	V _{total}	V _{micro}	V _{meso}
MOR(7.0)	7.0	438	371	67	0.25	0.18	0.07
MOR(9.7)	9.7	461	394	67	0.26	0.19	0.07
MOR(13.8)	13.8	459	390	69	0.25	0.19	0.06
MOR(16.5)	16.5	438	384	54	0.24	0.19	0.06
MOR(19.4)	19.4	447	394	53	0.24	0.19	0.05

^aDerived from XRF analysis. ^bS_{BET}: BET surface area, S_{micro}: t-plot micropore surface area, S_{ext} = S_{BET} - S_{micro}. ^cV_{total}: total volume absorbed at P/P₀=0.99, V_{micro}: t-plot micropore volume, V_{meso}=V_{total} - V_{micro}.

Acid properties

NH₃-TPD was employed to probe the acid properties of the samples, and the corresponding profiles are presented in Figure S5. The existence of two obvious NH₃ desorption peaks could be observed for all the investigated samples. The low-temperature desorption peaks centered around 195 °C are due to NH₃ desorption from weak acid sites and physisorbed NH₃, while the peaks centered at relatively high temperatures are attributed to NH₃ desorption from strong acid sites^{24, 35-39}. The NH₃ desorption temperatures associated with strong acid sites rise in parallel with the increase of Si/Al ratio until 13.8, indicating a gradual increase of acid strength. The reason could be attributed to the decreased number of Al atoms occupying the Next-Nearest-Neighbor (NNN) sites in the MOR framework^{30, 40}. With the further increase of Si/Al ratio to 16.5 and 19.4, the high-temperature desorption peak moves towards lower temperature (from 530 to 500 °C). Given that the chance of Al atoms at the NNN sites is low in the samples with high Si content, this shift should not be interpreted as the decrease of acid strength. Likely, the reduced acid density on the high-Si samples lightens the probability of re-adsorption of desorbed NH₃ and thus leads to the low-temperature shift⁴¹⁻⁴³. The deconvoluted results of the NH₃-TPD profiles are presented in Figure S5 and Table 2. Herein, the NH₃-desorption at higher temperature range is deconvoluted into two peaks, representing the moderate and strong acid sites, respectively.

The total acid amounts of the samples show a decreasing trend with the increase of the Si/Al ratios.

Table 2 Acid properties of the H-MOR samples derived from NH₃-TPD and FTIR of pyridine adsorption

Samples	NH ₃ -TPD (mmol/g)				Py-FTIR ^a (mmol/g)		
	Weak	Moderate	Strong	M+S ^b	BAS ^c	LAS ^c	BAS/LAS
MOR(7.0)	0.83	0.32	0.67	0.98	-	-	-
MOR(9.7)	0.60	0.22	0.66	0.88	-	-	-
MOR(13.8)	0.51	0.18	0.68	0.86	0.76	0.10	7.60
MOR(16.5)	0.44	0.15	0.59	0.75	0.66	0.09	7.33
MOR(19.4)	0.38	0.12	0.52	0.64	0.57	0.07	8.14

^aPy-FTIR was used to evaluate the ratio of Brønsted to Lewis acid sites based on the integrated areas of absorption bands at 1540 and 1450 cm⁻¹.⁴⁴ ^bM+S = Moderate+Strong. All the acid sites of the three high-Si MOR samples can be reached by pyridine (Figure 2). ^cThe amounts of BAS and LAS were derived from the ratio of BAS/LAS and the (M+S) acid amount of NH₃-TPD.

Figure 1 illustrates the FTIR spectra of the hydroxyl vibration region of the H-MOR samples. The absorption at around 3740 cm⁻¹ is due to the terminal silanol groups on external surface of the samples⁴⁵. The signal at 3660 cm⁻¹ is ascribed to the aluminol of extra-framework (EFAl) species⁴⁶⁻⁴⁷, which is more prominent on the samples with low Si/Al ratios (< 10). When the Si/Al ratio increases to 13.8 or even higher, the band at 3660 cm⁻¹ could hardly be discerned, indicating that the low-Si samples are more prone to dealumination. Simultaneously, two new bands at 3690 and 3490 cm⁻¹ emerge in the spectrum of sample MOR(13.8) and their intensities rise with the further increment of the Si/Al ratio. The broad band at around 3490 cm⁻¹ could be unambiguously ascribed to the H-bonded silanol groups inside the silanol nests⁴⁸⁻⁴⁹. However, the assignment of the band at 3690 cm⁻¹ is not straight-forward. There are two possible origins, *i.e.* the silanol groups inside silanol nests with trivial hydrogen bond perturbation⁵⁰ or hydroxyl pairs featuring less hydrogen bonding⁴⁹. Considering the synchronous increase of the two bands in intensity with the Si/Al ratios, it is assumed that they are both closely related to the silanol nests. The appearance of silanol and aluminol on the samples is also confirmed by ¹H MAS NMR spectra (Figure S6). The deconvoluted results confirm that the relative percentage of Al-OH decreases following the increase of sample Si/Al ratios, yet that of Si-OH gives

an opposite trend.

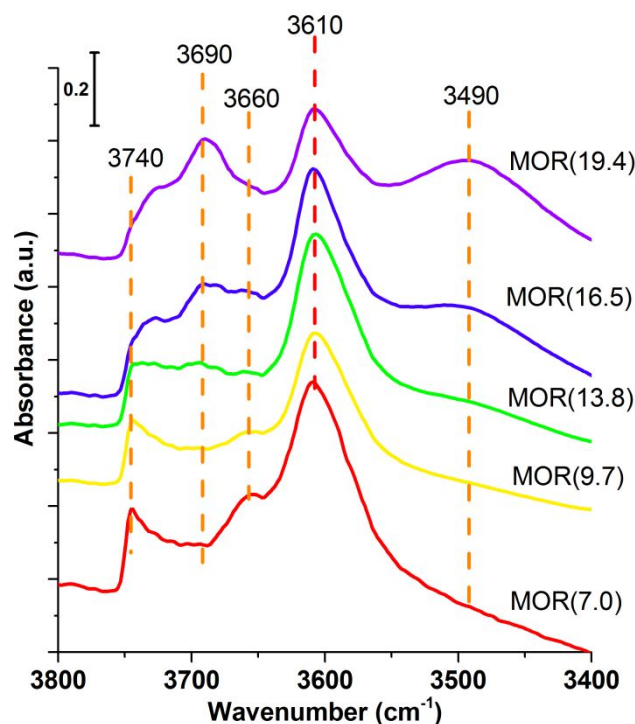


Figure 1 FTIR spectra in the $\nu(\text{OH})$ vibration region of the H-MOR samples.

The most prominent hydroxyl band shown in Figure 1 is located at 3610 cm^{-1} , corresponding to Brønsted hydroxyl groups, which is actually a composite band comprised of high-frequency (HF) and low-frequency (LF) components^{17, 19, 51-52}. It has been demonstrated that the HF band (around 3612 cm^{-1}) and LF band (around 3590 cm^{-1}) are associated with bridging hydroxyls in the 12-MR and 8-MR channels respectively, which behave distinct performances in the DME carbonylation reaction¹⁷. A deconvolution analysis of the Brønsted hydroxyls was thus carried out to determine the acid sites distribution^{17, 19} (Figure S7). To eliminate the interference of the silanol and aluminol groups on the deconvolution, herein NH_3 was employed to selectively titrate the Brønsted hydroxyls at $150\text{ }^\circ\text{C}$. As the bands due to the silanol and aluminol groups were barely perturbed by NH_3 , isolated bands corresponding to the bridging hydroxyls could be derived by subtracting the NH_3 -titrated spectra from the original ones and used for the deconvolution analysis (Figure S8). Based on the assumption that the two hydroxyl groups possess similar molar extinction coefficient, it is calculated that around 50 % of the total BAS locates inside 8-MR side pockets, independent of the Si/Al ratios of the samples

(Figure S7).

Pyridine adsorption

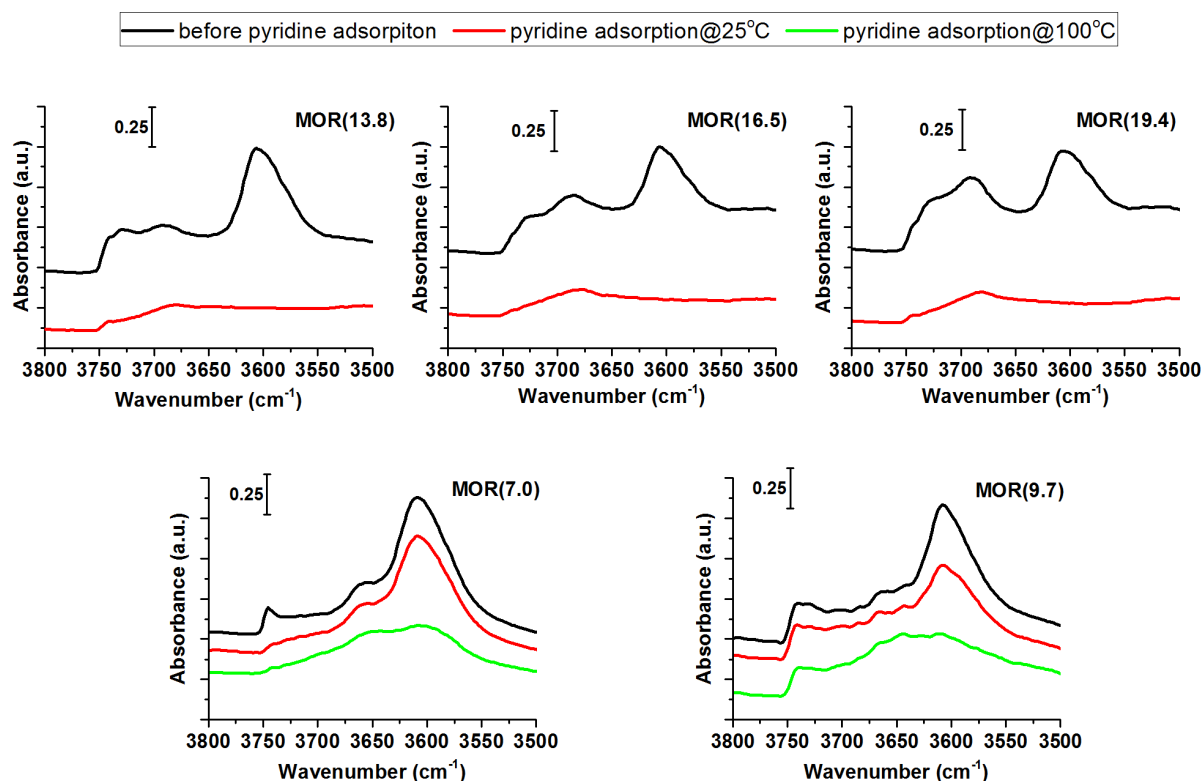


Figure 2 FTIR spectra of the $\nu(\text{OH})$ vibration region of the H-MOR samples before and after pyridine adsorption at different temperatures.

Figure 2 presents the hydroxyl vibration region of the FTIR spectra of the samples before and after pyridine adsorption. Pyridine, as one of the most common probe molecule to assess the acidity of zeolite catalysts, has been reported to be effective to distinguish the acid sites distribution of MOR zeolite, via selective titration of the acid sites inside the 12-MR channels^{7, 23-24, 45, 53}. However, for samples MOR(13.8), MOR(16.5) and MOR(19.4), the bands associated with the Brønsted hydroxyls are completely eroded upon pyridine adsorption at room temperature. It implies that pyridine molecules could actually penetrate into the 8-MR side pockets and capture the protons therein. Such contradiction with the previous findings might result from the existence of defect sites in the samples (Figure 1 and S6), which enlarges the window size of the pockets.

For low-Si samples H-MOR(7.0) and H-MOR(9.7), only a small amount of acid sites could be titrated by pyridine at room temperature. Such distinct pyridine adsorption behaviors, as compared to those of high-Si MOR samples, should be owing to their higher acid density, which causes higher local pyridine density and thus larger diffusion resistance. In addition, the relatively high EFAl content in H-MOR(7.0) and H-MOR(9.7) may also aggravate the difficulty in pyridine diffusion. With the adsorption temperature rising to 100 °C, the accessibility of BAS is improved due to the enhanced diffusion, but no preferential location is observed for pyridine molecules.

Pyridine desorption

The temperature-dependent desorption of pyridine is monitored by FTIR (Figure 3 and Figure S9). The desorption behaviors are observed to be qualitatively similar for high-Si samples MOR(13.8), MOR (16.5) and MOR (19.4), showing a gradual recovery of acidic hydroxyls with the temperature ramp until 400 °C. As seen from Figure 3, although the recovery degree at the same temperature differs among the three samples, it is clear that large proportion of BAS is not restored even after desorption at 400 °C, in consistence with the high acid strength of the BAS as revealed by the NH₃-TPD results. More interestingly, pyridine is observed to escape merely from 8-MR side pockets, as evidenced by the gradual grow of the symmetrical band centered below 3592 cm⁻¹. This phenomenon seems contradict to the higher acid strength of the BAS in the 8-MR pockets as revealed previously^{20, 54}. The logic is speculated to be related to the existence of certain steric effect between pyridine and 8-MR pockets. It is acknowledged that strong coulombic field exists in the negative framework of zeolites, and it could disturb the electron clouds of the accommodated guest molecules⁵⁵. This disturbance is especially prominent when the size of guest molecules matches well with the zeolite cages. Under such circumstance, a contraction of the molecular orbitals of guest molecules would occur due to strong electronic confinement effect⁵⁶⁻⁵⁷. Therefore, the enhanced lattice vibration of 8-MR windows

at higher temperature, together with the assistance of the delocalized electron cloud in 8-MR pockets, might help breathe out the adsorbed pyridine in their proximity, leading to preferential recovery of 8-MR hydroxyls. The high recovery proportion on MOR(13.8) shown in Figure 3D possibly relates with its relatively intact framework, which exerts stronger confinement effect on pyridine adspecies in 8-MR pockets and thus reduces their adsorption stability.

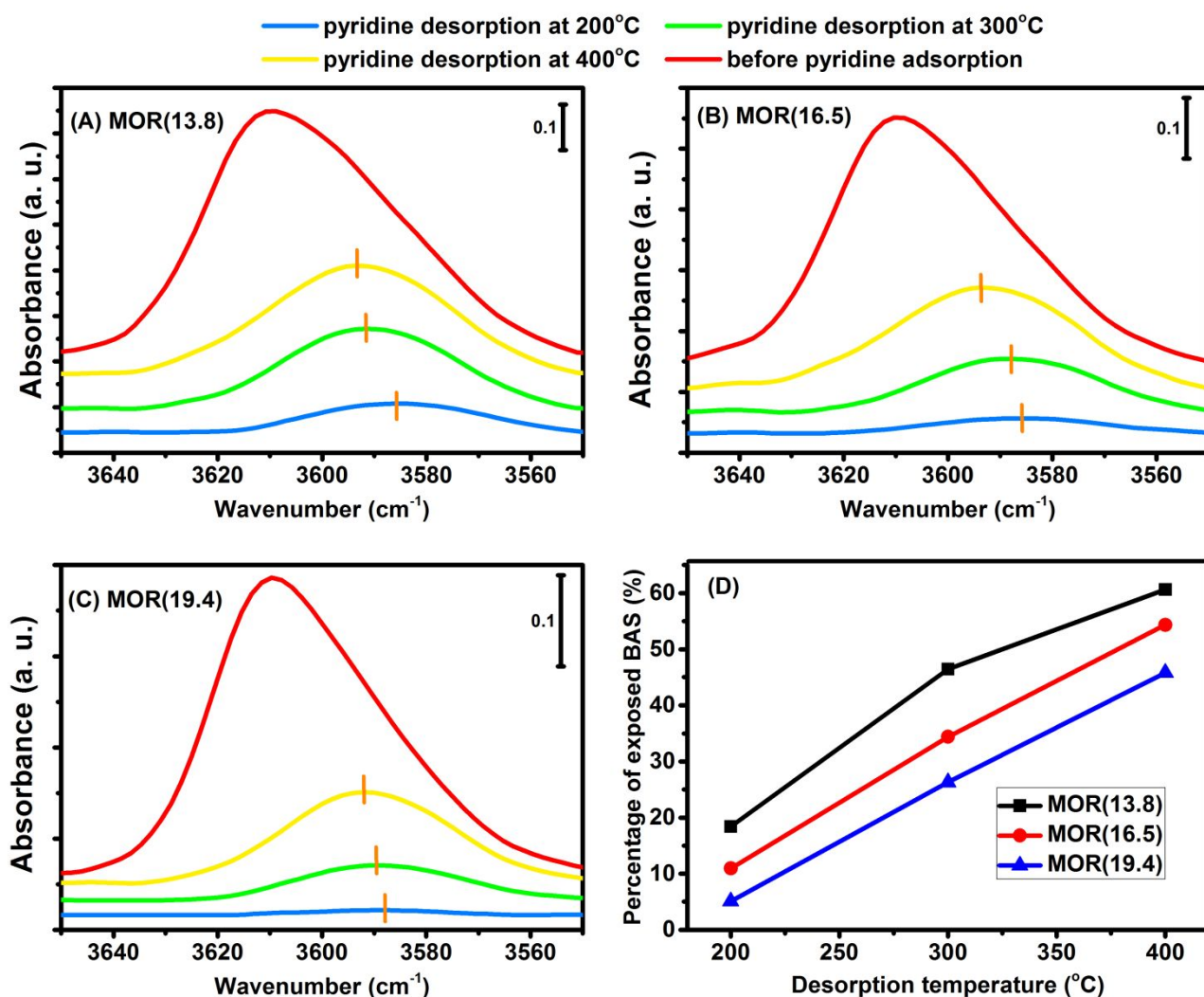


Figure 3 The $\nu(\text{OH})$ bands of the H-MOR samples after pyridine desorption at different temperatures (A, B, C) and the recovery percentage of BAS at different desorption temperatures (D). The calculations in Figure D are based on the variation of the band areas at 1540 cm⁻¹ (Figure S9), because the absorption coefficients of the acidic $\nu(\text{OH})$ bands (3650-3550 cm⁻¹) may vary with the locations of acidic hydroxyls^{13, 17, 58}.

Another interesting phenomenon is that the absorption bands due to the exposed hydroxyls show a gradual shift towards higher frequencies (from 3585 to 3592 cm⁻¹) with the increase of desorption

temperature, implying the heterogeneity of the BAS on MOR zeolite. Lukyanov *et al.* once carried out FTIR investigation on the BAS in MOR zeolite. By using Fourier Self-Deconvolution method¹³, they identified the existence of six different Brønsted hydroxyl bands arising from different crystallographic positions, among which three HF bands at 3625, 3617 and 3609 cm⁻¹ are located in the 12-MR channels, two LF bands at 3591, 3581 cm⁻¹ are located in the 8-MR pockets, and one band at 3599 cm⁻¹ is at the intersections between the pockets and 12-MR channels. These results are in good congruence with our findings.

For pyridine-modified low-Si samples MOR(7.0) and MOR(9.7), although their acid sites cannot be completely covered after pyridine adsorption at 100 °C, they behave similar desorption behaviors to high-Si samples with preferential recovery of acid sites in 8-MR pockets upon heating (Figure S10). In addition, sample MOR(7.0) shows a more obvious HF shift of the bridging hydroxyl band following the increase of desorption temperature. Its hydroxyl peak moves to 3601 cm⁻¹ after desorption at 400 °C, implying an increased pyridine desorption from the 12-MR channels. This phenomenon might be due to the interference between the adjacent protonated pyridine in 12-MR channels with high acid density.

Catalytic performance for DME carbonylation

The DME carbonylation performances of the pyridine-modified H-MOR zeolites were evaluated under different pyridine desorption conditions, and the corresponding DME conversion and MA selectivity versus time on stream (TOS) are illustrated in Figure 4. All the investigated catalysts exhibit an induction period with lower DME conversion at the beginning of the reaction, which should be due to the interaction of DME with the BAS and the formation of surface methoxyl species¹⁴. As the reaction proceeds, the conversion rises rapidly and reaches a steady plateau. Similar variation trend could be observed for MA selectivity, giving a steady value of around 100%. Moreover, the steady

DME conversions increase in parallel with pyridine desorption temperatures (200–400 °C) for all the samples. The rationale lies in the facts that pyridine actually enters the 8-MR pockets during its pre-adsorption procedure; the carbonylation activity centers inside the pockets are gradually exposed following the increase of desorption temperature. It is noted that further increasing the desorption temperatures to 500 °C would lead to a decreased carbonylation activity and stability (Figure S11). Obvious deactivation trend can be observed within 20 h. This should be caused by the exposure of acid sites in 12-MR channels^{15, 20, 29} and the carbonization of part of pyridine at high temperature¹⁰. These results imply that pyridine desorption temperatures essentially determine the carbonylation activity and stability of the pyridine-modified MOR catalysts.

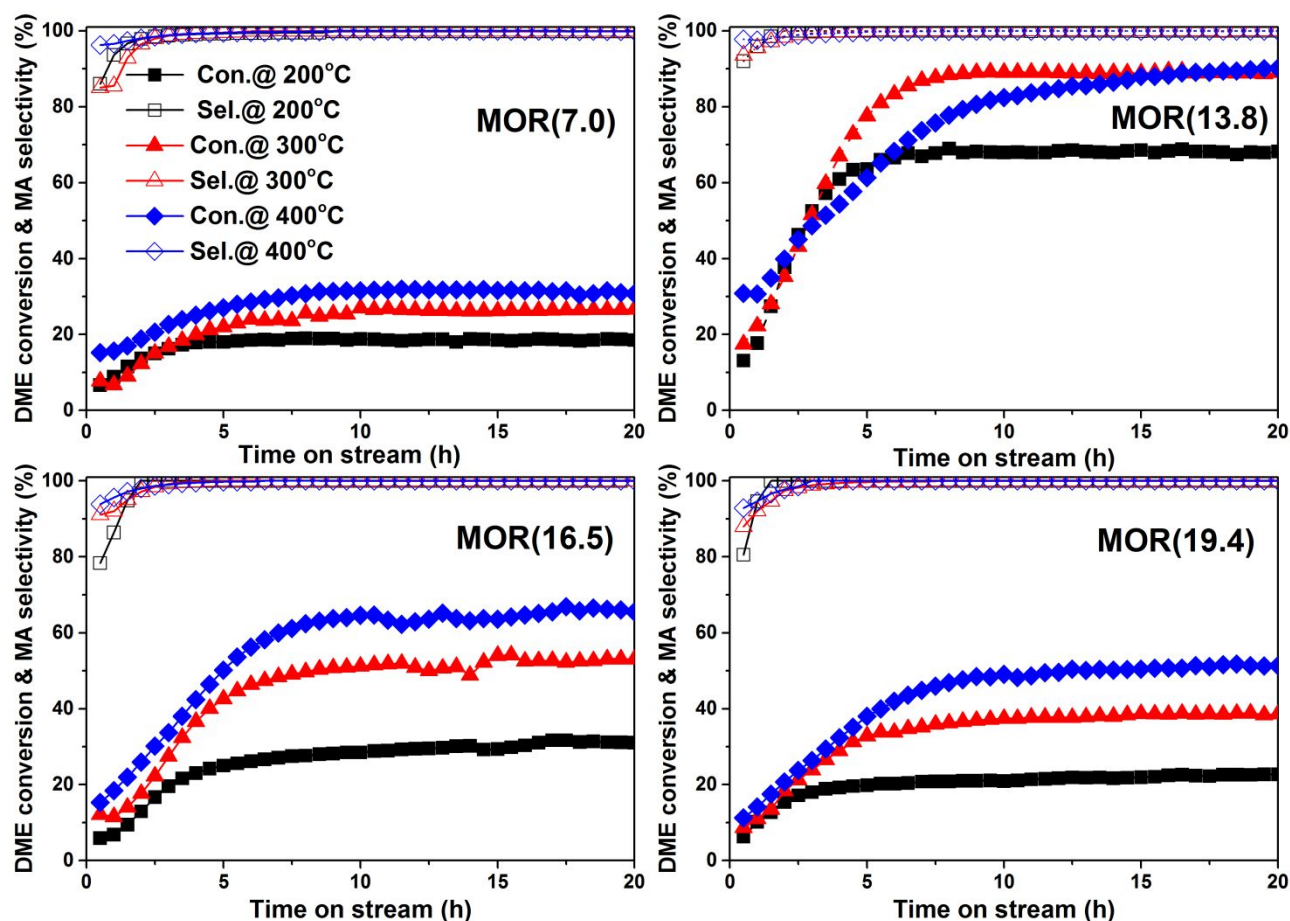


Figure 4 DME conversion and MA selectivity over pyridine-modified H-MOR catalysts after pretreatment at different pyridine desorption temperatures. Reaction conditions: 200°C, 2 MPa, DME/CO/N₂ = 5/35/60, GHSV=3600 mL/g/h.

The DME conversion activity follows a volcanic trend as a function of the Si/Al ratios. MOR(13.8)

1 exhibits the best DME carbonylation activity, independent of the pyridine desorption temperatures.
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4 The reason behind this should be multifold. Firstly, MOR(13.8) possesses relatively strong acidity, as
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6 revealed by NH₃-TPD analysis. Besides, for sample MOR(7.0) with lower Si/Al ratio, the excessive
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8 acid density causes an over-crowdedness of pyridine molecules within the 12-MR channels (see
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10 pyridine-FTIR section), and consequently exerts negative effect on the diffusion of reactants and
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12 products. For high-Si samples MOR(13.8), MOR(16.5) and MOR(19.4), the relatively low acid
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14 densities are beneficial to the improvement of mass transfer. Compared to MOR(13.8), the inferior
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16 catalytic performances of MOR(16.5) and MOR(19.4) should result from their fewer active sites. In
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18 consequence, sample MOR(13.8) with higher acid strength and optimal acid density, exhibits the best
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20 DME carbonylation performance. In addition, the existence of defects such as silanol nests or
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22 aluminols is less obvious for sample MOR(13.8). The negative effect of these defects on the DME
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24 carbonylation could not be excluded and deserves further study.
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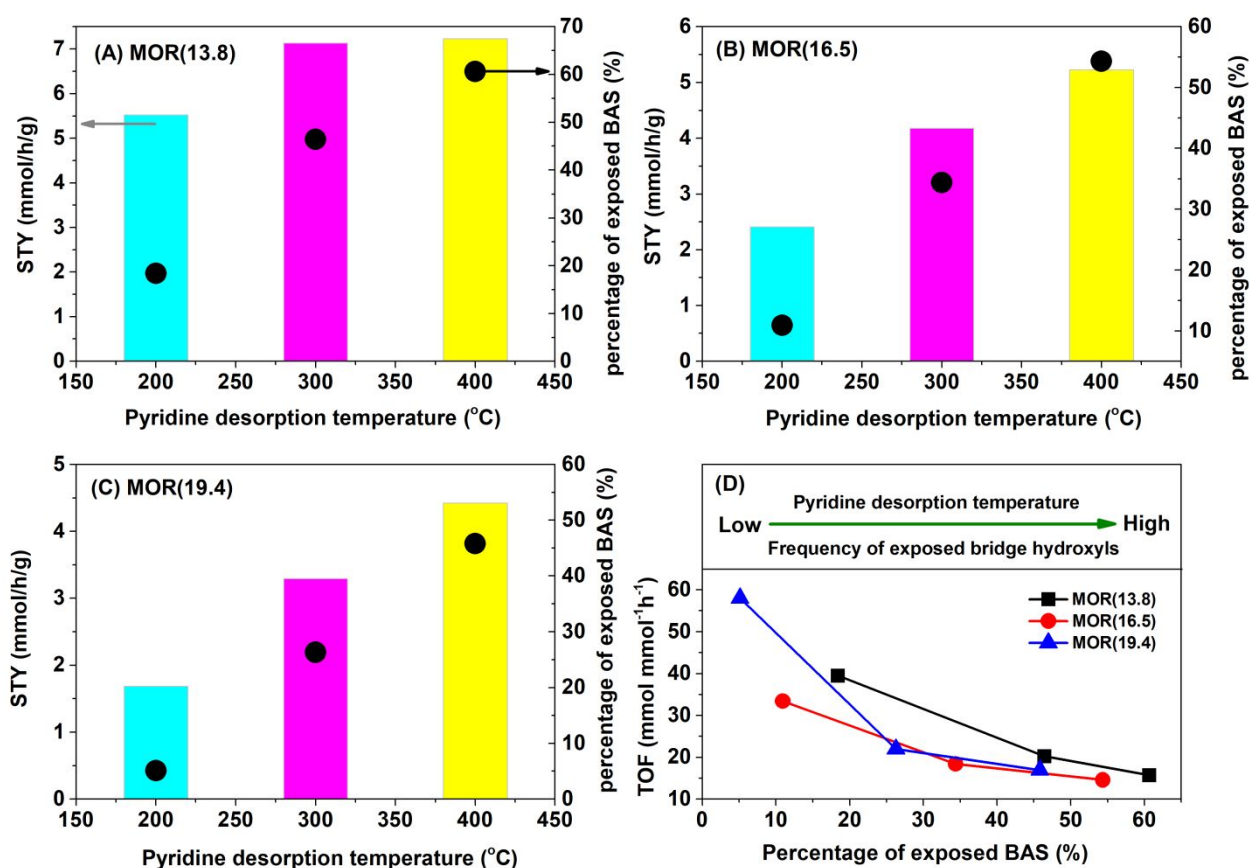


Figure 5 The MA space-time yield (bar chart, TOS = 20 h) and the percentage of exposed BAS (black circles) at different pyridine desorption temperatures on the H-MOR zeolites (A, B and C). Figure D presents the variation of the TOF of the catalysts following the BAS exposure. The percentage of exposed BAS is from Figure 3D. The exposed BAS amount for TOF calculation is evaluated based on the total BAS in Table 2 and its exposed percentage. They are mainly from the 8-MR pockets when desorption temperature is less than 400 °C.

Figure 5 presents the space-time yield (STY) of MA and the percentage of exposed BAS at different desorption temperatures over the high-Si H-MOR catalysts. It can be seen that the STY of MA on MOR(13.8) reaches as high as 7.2 mmol/h/g when the pyridine desorption temperatures are higher than 300 °C. This value is the highest ever reported for MOR-catalyzed DME carbonylation reaction (Table S2). However, it is noted that the increase of STY is not linearly proportional to the increased BAS exposure, despite the fact that the majority of these BAS is from the 8-MR pockets (see Figure 3). The turnover frequency (TOF) of the samples at different desorption temperatures is further

1 calculated and plotted against the percentage of exposed BAS. As shown in Figure 5D, the TOF value
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3 drops significantly following the exposure of BAS for all the samples, which reveals that the catalytic
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5 activity of the BAS inside the 8-MR pockets is inhomogeneous; the BAS exposed at lower desorption
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7 temperatures possess superior catalytic activity. As the above Py-FTIR results have demonstrated that
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9 the LF acidic hydroxyls of the 8-MR pockets are preferentially exposed upon pyridine desorption, it
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11 is concluded that these sites with LF vibrations have the highest carbonylation activity.
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16 To explore the location of the LF hydroxyls in the pockets, we tried to prepare pyridine-exchanged
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18 MOR(13.8) by ion-exchanging the calcined Na-form sample with pyridine aqueous solution and found
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20 that the Na/Al ratio of the sample decreased from 0.76 to 0.13 after the ion exchange. Previous work
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22 reported that there are three positions for Na⁺ cations in the structure of MOR⁵⁹; the ratio of Na⁺ in
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24 unconstrained and constrained environments is 1:2²⁸. Herein, such a low Na content implies the
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26 incorporation of pyridine into the pockets. We suppose that the residual Na⁺ cations are located at the
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28 bottom of the pockets, where the constrained environment limits the exchange with bulky hydrated
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30 pyridine ions. As shown in Figure S12, extremely low activity is observed for the pyridine-exchanged
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32 MOR(13.8). This suggests that the BAS at the bottom of the 8-MR pockets should be the most active
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34 sites for DME carbonylation, which correspond to the LF acidic hydroxyls in the FTIR spectra.
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45 CONCLUSIONS

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47 The adsorption/desorption behaviors of pyridine on a series of MOR zeolites and their impact on
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49 DME carbonylation have been investigated in order to elucidate the pyridine modification-catalytic
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51 property relationships and to improve the catalyst performance. It is demonstrated that pyridine
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53 molecules could penetrate into 8-MR pockets and interact with the Brønsted hydroxyls therein. This
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55 is likely owing to the existence of defect sites in the MOR framework, which enlarges the window
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57 size of the pockets. The Si/Al ratios of MOR zeolites influence the pyridine adsorption process. Low
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Si/Al ratios, corresponding to high acid density and relatively large amount of EFAL species, would cause increased diffusion limitation and incomplete acidity coverage. However, for MOR with higher Si/Al ratio (> 10), all the acid sites can be easily reached by pyridine molecules. With the ramp of pyridine desorption temperature (≤ 400 °C), the BAS in 8-MR side pockets are preferentially recovered, leading to incremental conversion. Pyridine desorption temperature essentially determines the carbonylation activity and stability of the catalysts. The DME carbonylation activity follows a volcanic trend with the increase of Si/Al ratios. The optimal Si/Al ratio is around 13.8, over which high MA yield of 7.2 mmol/g/h can be achieved under controlled pyridine desorption temperature (300 ~ 400 °C). The higher acid density, stronger acidity and better diffusion properties corporately contribute to the excellent catalytic performance. The catalytic activity of the BAS in the 8-MR pockets is rather inhomogeneous, and the LF bridging hydroxyls siting at the bottom of the side pockets have superior carbonylation activities.

AUTHOR INFORMATION

Author contributions

Δ(Kaipeng Cao, Dong Fan) These authors contributed equally.

Notes

The authors declare no competing financial interest.

ASSOCIATED CONTENT

Supporting Information

The initial gel compositions, the $\nu(\text{OH})$ bands of the H-MOR pretreated with different heating rates, XRD, SEM, N_2 physisorption isotherms, NH_3 -TPD, ^1H MAS NMR spectra, the deconvoluted $\nu(\text{OH})$ bands of FTIR spectra, the derivation of the isolated Brønsted $\nu(\text{OH})$ band for deconvolution, the FTIR spectra of pyridine ring-related vibration regions, the $\nu(\text{OH})$ bands of the low-Si H-MOR samples after pyridine desorption at different temperatures, the DME carbonylation activities of the samples after pyridine desorption at 500°C, the detailed procedure for pyridine exchange and the DME

1 carbonylation activities of the pyridine-exchanged sample, the summary of the product STY in the
2 zeolite-catalyzed DME carbonylation reaction.
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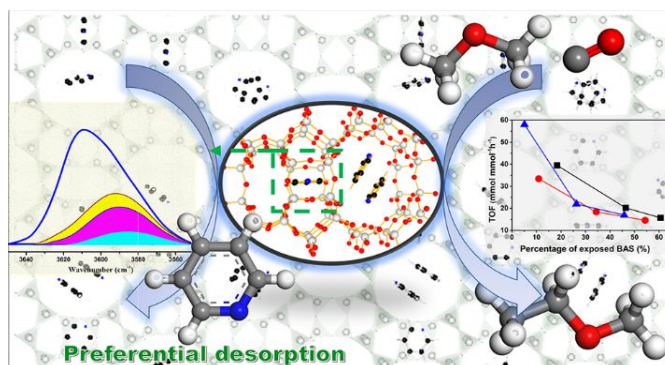
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