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Article

Spacial hindrance induced recovery of over-poisoned active acid sites in pyridine-modified H-mordenite for dimethyl ether carbonylation

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ABSTRACT

Zeolite catalysts, such as H-mordenite (H-MOR), are readily deactivated by coke deposition in carbonylation reactions. Pyridine modification of H-MOR can improve its stability but can lead to an undesirable loss in catalytic activity. Herein, we report the intrinsic impact of the pyridine adsorption behavior on H-MOR and the spacial hindrance of the zeolite frameworks on dimethyl ether (DME) carbonylation at a molecular level. We discovered that acid sites at O2 positions, located on common walls of eight-membered ring (8-MR) side pockets and 12-MR channels, were active in DME carbonylation, but were unfortunately poisoned during pyridine modification. Density functional theory calculations revealed that the pyridine-poisoned acid sites at the O2 positions could be easily regenerated due to the spacial hindrance of the zeolite frameworks. Accordingly, they can be facily regenerated by proper thermal treatment, which induces 60% promotion in the catalytic activity along with a high stability. Our findings demonstrate the determining role of O2 positions in H-MOR for DME carbonylation and provide a new avenue for the rational design of other efficient zeolite-relevant catalytic systems.

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1. Introduction

Ethanol is becoming an important worldwide clean fuel, fuel-additive, and industrial chemical [1–3]. Hence, it is urgent to explore efficient synthesis routes to meet the significantly increased demands for ethanol [4–6]. Industrially, dimethyl ether (DME) can be easily synthesized from syngas (CO+H₂),

which is produced from coal, natural gas, biomass, and shale gas [7,8]. Moreover, DME can also be directly produced from biomass, and the BioDME project has been industrially built and operated in Sweden [8,9]. A green tandem ethanol synthesis route based on this material, composed of DME carbonylation to methyl acetate (MA) and MA hydrogenation to ethanol, has received extensive attention [10–14] because of its high

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atom efficiency and potential industrial application value [3,15,16]. Currently, the process of MA hydrogenation to ethanol is well-developed, with a high activity and selectivity for ethanol synthesis [17]. However, traditional carbonylation catalysts generally have disadvantages such as environmental pollution, high cost, and short catalyst lifetime, limiting further industrial applications [10,18,19].

Much work has been done to develop green and efficient catalysts for DME carbonylation [3,10–14,20], and zeolites are one of the most excellent candidates among them [21,22]. Particularly, H-mordenite (H-MOR) shows a high catalytic activity for DME carbonylation to MA [23–25]. Researchers believe that Brønsted acid sites located at the eight-membered ring (8-MR) side pockets of H-MOR are active in DME carbonylation [26–30]. Unfortunately, the H-MOR catalyst is readily deactivated by coke deposition in twelve-membered ring (12-MR) channels [10], which blocks mass transfer and limits its commercial application [11].

Pyridine molecules can selectively enter the 12-MR channels of H-MOR due to their specific kinetic size [31]. To inhibit coke deposition during DME carbonylation, pyridine is utilized to modify the acid sites in the 12-MR channels of H-MOR and thereby prolong the catalyst's lifetime [10,11]. However, the improved stability is undesirably accompanied by a decrease of about 40%–50% in the catalytic activity [11,13]. Iglesia et al. [30] supposed that the pyridine modification might perturb a fraction of the active sites for DME carbonylation, inducing a decrease in activity. Nevertheless, the exact reason for these undesired results is still unclear.

Increasing the reaction temperature or adding copper to modify H-MOR promotes DME carbonylation, but still does not overcome the disadvantages of rapid deactivation [10–12]. Therefore, simultaneously achieving a high activity and stability of pyridine-modified H-MOR catalysts becomes a great challenge. Nevertheless, modification of H-MOR with pyridine has many new applications. For example, Bao et al. [32] reported that pyridine modification, interestingly, promoted CO conversion in ethylene synthesis from syngas, but they could not provide any explanation based on the presented results. Therefore, there is a strong need to intrinsically understand the specific mechanisms in pyridine modification of H-MOR at a molecular level.

In this study, we prepared a series of pyridine-modified H-MOR catalysts using various adsorption periods and thermal desorption temperatures. We discovered that some active sites that were pyridine-poisoned during modification could be regenerated by tuning the thermal desorption temperature, which significantly improved the DME carbonylation activity by 60%, and simultaneously supported a high catalytic stability. Using a combination of framework analysis and density functional theory (DFT) calculations, we demonstrate that these recovered active sites are located at O2 positions on common walls of both the 12-MR channels and 8-MR side pockets in H-MOR.

2. Experimental

2.1. Catalyst preparation

Na-MOR zeolite with an Si/Al ratio of 6 was synthesized via a facile hydrothermal method [33]. Briefly, the raw materials were mixed together under vigorous stirring to form a gel with a molar composition of 1.0 SiO₂ : 0.07 Al₂O₃ : 0.2 Na₂O : 20 H₂O. The as-prepared Na-MOR was ion-exchanged in 1.0 Mol/L NH₄NO₃ aqueous solution (liquid/sample = 100 mL/g) at 353 K for 3 h. After filtering and washing with deionized water, the obtained powder was dried for 12 h at 383 K and then calcined at 823 K for 2 h to prepare the H-MOR catalyst, which was named as MOR-fresh.

Pyridine-modified catalysts were prepared via pyridine adsorption on H-MOR. Briefly, the MOR-fresh catalyst (500 mg, particle diameter 125–250 μm) was loaded into a fixed-bed micro-reactor and pretreated under N₂ flow (30 mL/min) at 773 K for 2 h. After cooling to 573 K, the H-MOR catalyst was exposed to 2.0% pyridine/N₂ (30 mL/min) for *x* (*x* = 5, 10, and 20) min, and then purged with N₂ flow (30 mL/min) at a temperature of *y* (*y* = 573, 673, and 773) K for 1 h; the resulting catalysts were named as MOR-*x-y* catalysts.

2.2. Catalyst characterization

X-ray diffraction (XRD) patterns were recorded on a Bruker D8 ADVANCE X-ray diffractometer using a Cu-K_α radiation (λ = 1.5418 Å) in a 2 θ range from 5° to 50°.

X-ray fluorescence (XRF) measurements were carried out with a wavelength-dispersive XRF S4 Pioneer (Bruker AXS, Karlsruhe, Germany).

N₂ physical adsorption/desorption isotherms were measured at 77 K using a Quadrasorb gas sorption analyzer (Quantachrome Instruments Co.). The *t*-plot method was used to estimate the micropore specific surface area (*S*_{micro}) and micropore volume (*V*_{micro}). The BET specific surface area (*S*_{BET}) and total pore volume (*V*_{total}) were measured using the BET method.

Ultraviolet-visible (UV-visible) spectra were measured on a PerkinElmer Lambda 750S UV-visible spectrometer equipped with an integrating sphere.

In situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) experiments were performed on a Thermo Scientific Nicolet 7000 connected to a gas-dosing and evacuating system, using pyridine as the probe molecule. The MOR-fresh catalyst (30 mg) was pressed into a 15 mm self-supported wafer and pretreated at 773 K for 0.5 h under He flow (30 mL/min). After pyridine adsorption at 573 K for 10 min, the wafer was evacuated for 0.5 h to eliminate the physically adsorbed pyridine. We recorded the spectra from 573 to 773 K with 50 K intervals, under vacuum. All the spectra were recorded in the range of 4000 to 1100 cm^{−1}, with 32 scans at a resolution of 4 cm^{−1}.

¹H solid-state magic-angle spinning nuclear magnetic resonance (¹H MAS NMR) spectra were measured on a spectrometer (InfinityPlus 300, Varian Technology Co., Ltd.) at 600.1 MHz using a 4 mm MAS probe.

Temperature-programmed desorption (TPD) experiments

were carried out on a TPDRO instrument (TP-5080, Tianjin Xianquan Co., Ltd). The catalyst (100 mg) was loaded into a quartz reactor and heated from 373 to 1073 K (10 K/min) under He flow (30 mL/min). The effluent gas was analyzed using a thermal conductivity detector (TCD).

NH₃-TPD experiments were carried out on the aforementioned TPDRO instrument. The catalyst (100 mg) was loaded into a quartz reactor and exposed to a 10% NH₃/N₂ flow (30 mL/min) at 423 K for 0.5 h, to adsorb ammonia. After cooling to 373 K, the catalyst was heated to 1073 K (10 K/min) under the same flow, and the effluent gas was analyzed using the TCD. The obtained curve was used as the original NH₃ desorption profile. In order to eliminate the influence of desorbed pyridine during the NH₃-TPD experiments, the TPD profile obtained earlier was adopted as the background for each catalyst. The final NH₃-TPD profiles were obtained by subtracting their corresponding backgrounds from the original NH₃ desorption profiles.

2.3. Catalytic performance test

The catalytic activity in DME carbonylation to MA over the catalyst was evaluated on a fixed-bed micro-reactor. The catalyst (500 mg, particle diameter 125–250 μm) was loaded into the reactor and then pretreated under N₂ flow (30 mL/min) at 773 K for 2 h. Thereafter, pyridine modification was carried out as mentioned in the catalyst preparation section. After the modified catalyst was cooled to 463 K, a mixture gas of 3.0% DME-95.5% CO-1.5% N₂ (44 mL/min) was introduced and pressurized to 1.5 MPa. The reaction products were analyzed using an online gas chromatograph (GC 9860, Shanghai Qiyang Information Technology Co., Ltd.).

The DME conversion (X_{DME}) was calculated using the equation $X_{\text{DME}} = (S_{\text{DME,in}} - S_{\text{DME,out}}) / S_{\text{DME,in}} \times 100\%$, in which $S_{\text{DME,in}}$ represents the integral area of DME in the feeding gas, and $S_{\text{DME,out}}$ represents the integral area of DME in the effluent gas.

2.4. DFT calculations

We applied spin-polarized DFT calculations as implemented in the Vienna Ab initio Simulation Package (VASP) [34]. An energy cutoff of 400 eV was employed for the plane-wave basis sets. To model the system, a p (1 × 1 × 2) MOR was used, with supercell dimensions of 18.09 Å × 20.52 Å × 15.05 Å. We used a proton to compensate the negative charge caused by the replacement of Si with Al, and the models were represented by H-MOR. The Brillouin zone was sampled with a single Γ point. To include the van der Waals interactions, the optB86b-vdW functional was applied [35,36]. During optimization, the total energy converged to less than 1 × 10⁻⁵ eV, and the force on each atom converged to less than 0.05 eV/Å.

We calculated the pyridine adsorption on H-MOR. The pyridine adsorption energy (E_{ads}) was defined as $E_{\text{ads}} = E_{\text{(pyridine/H-MOR)}} - E_{\text{(H-MOR)}} - E_{\text{(pyridine)}}$, where $E_{\text{(pyridine/H-MOR)}}$, $E_{\text{(H-MOR)}}$, and $E_{\text{(pyridine)}}$ represent the energies of the adsorption complex, H-MOR, and pyridine molecules, respectively.

3. Results and discussion

3.1. Structural properties of the catalysts

Fig. 1 shows the XRD patterns of the catalysts. All the diffraction peaks agreed well with those of standard H-MOR (JCPDS 11-0155) [33], and no other impurities were detected. After the catalyst was modified by pyridine, we did not observe any significant change in the diffraction peaks. Fig. S1 (see Supporting Information) shows the SEM images of the catalysts. All the catalysts presented a discoidal shape, which was composed of nanosheet bundles [33]. This indicates that pyridine modification had little influence on the crystallinity and morphology of the H-MOR catalysts. We measured the elemental composition of the MOR-fresh catalyst using XRF, and the Si/Al molar ratio was about 6.

Table 1 lists the detailed textural parameters of the catalysts calculated using the N₂ physical adsorption and desorption isotherms (Fig. S2). As the pyridine adsorption duration increased from 5 to 20 min, both the V_{micro} and S_{micro} of the MOR-x-573 catalysts decreased. Particularly, the V_{micro} and S_{micro} of the MOR-20-573 catalyst significantly decreased by more than 70%, compared with those of the MOR-5-573 and MOR-10-573 catalysts. This indicates that excessive pyridine molecule adsorption seriously blocked the H-MOR channels, even for a small amount of N₂ molecule physical adsorption. After pyridine thermal desorption at 673 K, the V_{micro} and S_{micro} of the MOR-10-673 catalyst increased more than 20%, compared with those of the MOR-10-573. This demonstrated that some pyridine molecules desorbed from the 12-MR channels of

Fig. 1. XRD patterns of (a) MOR-fresh, (b) MOR-5-573, (c) MOR-10-573, (d) MOR-20-573, (e) MOR-10-673, and (f) MOR-10-773.

Table 1
Physical properties of the catalysts.

Catalyst	S_{micro} (m ² /g)	V_{micro} (cm ³ /g)	S_{BET} (m ² /g)	V_{total} (cm ³ /g)
MOR-fresh	313	0.18	481	0.35
MOR-5-573	243	0.12	382	0.27
MOR-10-573	226	0.10	305	0.21
MOR-20-573	51	0.03	178	0.18
MOR-10-673	276	0.13	355	0.24
MOR-10-773	81	0.03	191	0.19

H-MOR through this treatment. After the pyridine desorption temperature was increased to 773 K, the V_{micro} and S_{micro} of the MOR-10-773 catalyst significantly dropped by about 70%, compared with those of the MOR-10-673 catalyst. This might have been due to the blockage of the H-MOR channels by the coke formed by pyridine thermal-polymerization at high temperatures.

3.2. Pyridine adsorption behavior in the H-MOR catalysts

Fig. 2A shows the photos of the catalysts. The color of the pyridine-modified catalysts, except that of MOR-10-773, changed from the pure white for the MOR-fresh catalyst to light gray. This was attributed to pyridine adsorption in the 12-MR channels of H-MOR. The color of the MOR-10-773 catalyst turned to dark brown, probably owing to the coke deposition in H-MOR.

Fig. 2B shows the UV-visible spectra of the catalysts. For the MOR-fresh catalyst, the bands at about 207 and 275 nm were attributed to H-MOR [37]. For the pyridine-modified catalysts, the newly generated band at about 257 nm was attributed to the pyridine adsorbed on the acid sites in the catalysts [38]. However, the MOR-10-773 catalyst displays strong absorption in the range of 200–1000 nm, similar to activated carbon (Fig. 2B) [39]. This confirms coke formation in the MOR-10-773 catalyst and is in agreement with the analysis of the catalyst photos in Fig. 2A and the N_2 physical adsorption results in Table 1.

Fig. 2. (A) Photos and (B) UV-visible spectra of (a) MOR-fresh, (b) MOR-5-573, (c) MOR-10-573, (d) MOR-20-573, (e) MOR-10-673, (f) MOR-10-773, and (g) activated carbon.

Fig. 3. *In situ* DRIFTS spectra of pyridine-modified MOR-fresh catalyst at different temperatures.

Fig. 3 shows the *in situ* DRIFTS spectra of the pyridine-modified MOR-fresh catalyst at different temperatures. The MOR-fresh catalyst was exposed to pyridine flow at 573 K for 10 min and then evacuated for 0.5 h. The bands at ~ 1540 and ~ 1630 cm^{-1} were attributed to the pyridine adsorbed on the Brønsted acid sites of H-MOR [10]. The band at ~ 1450 cm^{-1} was attributed to the pyridine adsorbed on the Lewis acid sites, and the bands at ~ 1487 and ~ 1610 cm^{-1} were ascribed to the pyridine adsorbed on both the Lewis and Brønsted acid sites of H-MOR [10,40]. The intensities of the IR bands recorded at 573 and 623 K have little difference, indicating that the adsorbed pyridine is hardly removed from the 12-MR channels below 623 K. However, when the pyridine desorption temperature was above 623 K, the intensity of the IR bands began to decrease. This suggests that a fraction of pyridine molecules can be desorbed from the 12-MR channels of the catalyst, which is in agreement with the N_2 physical adsorption results in Table 1. We suspect that increasing the pyridine desorption temperature will regenerate the occupied acid sites in H-MOR and subsequently promote the catalytic activity. In addition, the intensity change of the IR bands between 723 and 773 K was more pronounced than that of the bands between 673 and 723 K. Based on the catalyst photos and UV-visible spectra results in Fig. 2, we attributed this to coke formation at the high temperatures.

Fig. 4 shows the ^1H MAS NMR spectra of the catalysts. For the MOR-fresh catalyst, the strong peak at about 5.1 ppm was attributed to Brønsted acid sites [41]. The weak peaks at 2.5 and 1.7 ppm were assigned to extra-framework $\text{Al}(\text{OH})$ species and nonacidic $\text{Si}(\text{OH})$, respectively [41,42]. As the pyridine adsorption duration increased from 5 to 20 min for the MOR-x-573 catalysts, signals of pyridine, located at 7.8 and 8.7 ppm, gradually emerged and strengthened [11]. Simultaneously, a weak peak at 14.7 ppm was also observed due to the interaction between protons and pyridine molecules in H-MOR [11]. The peak at 6.5 ppm was assigned to adsorbed water molecules on Lewis acid sites [43,44]. Moreover, after the catalysts were modified with pyridine, the signal at 5.1 ppm significantly weakened, indicating pyridine adsorption on the

Fig. 4. ^1H MAS NMR spectra of (a) MOR-fresh, (b) MOR-5-573, (c) MOR-10-573, (d) MOR-20-573, (e) MOR-10-673, and (f) MOR-10-773.

Brønsted acid sites of H-MOR. Compared with that for the MOR-10-573 catalyst, the intensity of the peaks located at 7.8 and 8.7 ppm for the MOR-10-673 catalyst decreased. This suggests that a fraction of pyridine molecules in the H-MOR channels can be desorbed via thermal treatment, thereby regenerating the acid sites of the H-MOR catalyst. As for the MOR-10-773 catalyst, the pyridine signal significantly weakened due to coke formation, as discussed previously.

3.3. Acidic properties of the H-MOR catalysts

Fig. 5 shows the TPD profiles of all the catalysts. The MOR-fresh catalyst exhibited no desorption peak below 850 K. The MOR-5-573 and MOR-10-573 catalysts exhibited a similar initial pyridine desorption temperature of about 615 K. This indicates that the pyridine adsorption strength in H-MOR is very strong, in agreement with the *in situ* DRIFTS results in Fig. 3. However, the initial desorption temperature of the MOR-20-573 catalyst was about 550 K, and the intensity of the desorption peak strengthened. This demonstrates the presence

Fig. 5. TPD profiles of (a) MOR-fresh, (b) MOR-5-573, (c) MOR-10-573, (d) MOR-20-573, (e) MOR-10-673, and (f) MOR-10-773.

of excessive pyridine molecules that were weakly adsorbed in the MOR-20-573 catalyst. We speculate that the excess pyridine introduced may interact with other pyridine molecules via hydrogen bonds. The V_{micro} and S_{micro} values of the MOR-20-573 catalyst are much smaller than those of the MOR-10-573 catalyst, as shown in Table 1. Hence, we believe that an excessive pyridine adsorption in the MOR-20-573 catalyst will cause serious blockage in H-MOR, and even inhibit N_2 (a small molecule) transfer and physical adsorption.

For the MOR-10- y catalysts, with an increase in the pyridine desorption temperature from 573 to 773 K, the desorption peaks gradually weakened and shifted to higher temperatures, as shown in Fig. 5. This indicates that a fraction of pyridine can be desorbed from 12-MR channels via thermal treatment. As shown in Table 1, the V_{micro} and S_{micro} of the MOR-10-773 catalyst were quite small; however, it showed the weakest desorption peak among the pyridine-modified catalysts. We attribute these conflicts to coke deposition on it, which blocks the transfer of N_2 molecules in H-MOR.

Fig. 6 shows the NH_3 -TPD profiles of the catalysts. They presented similar ammonia desorption behavior. There were two desorption peaks of NH_3 for each catalyst. The desorption peak below 600 K (peak α) was attributed to NH_3 desorbed from $\text{NH}_4^+ \cdot n\text{NH}_3$ associations [45] or weak acid sites [46]. The peak above 600 K (peak β) was attributed to NH_3 desorption from strong acid sites [47], among which the sites located at the 8-MR side pockets were active in DME carbonylation [33].

Table 2 presents the quantitative analysis results of strong acid sites in the catalysts. The MOR-fresh catalyst has the largest amount of strong acid sites among all the catalysts. For the MOR- x -573 catalysts, as the pyridine adsorption duration increased from 0 to 10 min, the amount of strong acid sites in the catalysts gradually decreased. However, when the pyridine adsorption duration was increased to 20 min, the intensities of the β peak of the MOR-10-573 and MOR-20-573 catalysts had little difference. This indicates that after treating the H-MOR with pyridine for 10 min, the strong acid sites in the 12-MR channels are fully occupied, and NH_3 can only be adsorbed on other strong acid sites of the two catalysts, whereas pyridine cannot be adsorbed due to the size limitation. Nevertheless, the intensity of the ammonia desorption peak of the MOR-20-573

Fig. 6. NH_3 -TPD profiles of (a) MOR-fresh, (b) MOR-5-573, (c) MOR-10-573, (d) MOR-20-573, (e) MOR-10-673, and (f) MOR-10-773.

Table 2Density of acids derived from NH_3 -TPD results above 600 K.

Catalyst	Quantity of acid sites (mmol/g)
MOR-fresh	1.07
MOR-5-573	0.97
MOR-10-573	0.56
MOR-20-573	0.54
MOR-10-673	0.82
MOR-10-773	0.50

catalyst was much weaker than that of the MOR-10-573 catalyst, below 750 K. This reveals that although the strong acid sites in the 12-MR channels of the MOR-10-573 catalyst are fully occupied by pyridine, there is still a passage to allow NH_3 adsorption. However, as shown in Fig. 5, excessive pyridine adsorption occurs on the MOR-20-573 catalyst, inhibiting NH_3 adsorption in H-MOR (shown in Fig. 6). This finding is in agreement with the N_2 physical adsorption results in Table 1.

Compared with that of the MOR-10-573 catalyst, the amount of available strong acid sites in the MOR-10-673 catalyst increased about 46%. This demonstrates that a fraction of pyridine-poisoned acid sites can be regenerated by thermally desorbing the weakly adsorbed pyridine from H-MOR. Surprisingly, the MOR-10-773 catalyst displayed NH_3 adsorption behavior similar to those of the MOR-20-573 catalyst. This indicates that the acid sites in the MOR-10-773 catalyst cannot be effectively regenerated by thermal treatment at 773 K because of the coke deposition.

3.4. DME carbonylation activities of the H-MOR catalysts

Fig. 7 displays the catalytic activities and selectivities of the catalysts for DME carbonylation against the reaction time. All the catalysts showed a high product selectivity to MA. The MOR-fresh catalyst exhibited the highest DME conversion of about 47.5% among the catalysts, but it was quickly deactivated after 3 h. As the pyridine adsorption duration extended from 0 to 10 min at 573 K, the catalytic stability of the catalysts gradually improved, but the catalytic activity decreased. Particularly, the DME conversion of the MOR-10-573 catalyst dropped to 28.0%. As we continued to extend the pyridine adsorption duration to 20 min, the MOR-20-573 catalyst was completely deactivated after 5 h. The TPD results in Fig. 5 demonstrate that excessive pyridine adsorption on MOR-fresh for 20 min causes serious blockage of mass transfer (as indicated in Table 1 and Fig. 6). Accordingly, the MOR-20-573 catalyst showed complete deactivation (Fig. 7a).

As we increased the thermal treatment temperature to 673 K, the DME conversion of the MOR-10-673 catalyst increased about 60% compared with that of the MOR-10-573 catalyst. Notably, a high catalytic stability was simultaneously maintained. The NH_3 -TPD results in Fig. 6 demonstrate that a fraction of pyridine in the 12-MR channels of H-MOR can be desorbed via thermal treatment at 673 K. Hence, these regenerated sites must be located at common walls of both the 8-MR side pockets and 12-MR channels. However, the catalytic activity and stability of the MOR-10-773 catalyst were much lower

Fig. 7. (a) DME conversion and (b) product selectivity in DME carbonylation over MOR-fresh (■), MOR-5-573 (▲), MOR-10-573 (●), MOR-20-573 (★), MOR-10-673 (☆), and MOR-10-773 (○). Reaction conditions: 1.5 MPa, 3.0% DME-95.5% CO -1.5% N_2 , 5280 $\text{mL} \cdot (\text{g} \cdot \text{h})^{-1}$.

than those of the MOR-10-573 catalyst. As discussed previously, the mass transfer is seriously inhibited in both the MOR-10-773 and MOR-20-573 catalysts, but, interestingly, the former showed a much higher activity than the latter (Fig. 7). This indicates that the blockage of H-MOR channels by excessive pyridine adsorption in the MOR-20-573 catalyst is more serious than that by coke deposition in the MOR-10-773 catalyst. Additionally, as shown in Table 1, the V_{micro} and S_{micro} of the MOR-10-773 catalyst increased about 50% compared with those of the MOR-20-573 catalyst, proving the better mass transfer ability of the former.

3.5. Framework analysis and DFT calculation of pyridine adsorption on H-MOR

In order to intrinsically understand the pyridine adsorption positions and behavior, we analyzed the frameworks of H-MOR and calculated the pyridine adsorption energy for the possible acid sites, using DFT.

In this work, the Si/Al molar ratio of the H-MOR catalyst was about 6. For simplification, we assumed that acid sites are isolated in H-MOR for the subsequent simulation. Fig. 8 shows all the possible oxygen positions (O1–O10) and the framework of H-MOR (MOR.cif in IZA-SC) [48]. Table S1 summarizes the categories of the locations of the O atoms in H-MOR. Apparently, the acid sites at O3, O6, O8, and O9 of H-MOR could not contact pyridine molecules in the 12-MR channels. Hence, they are not further discussed herein.

Fig. 8. Schematic drawing of the frameworks of the H-MOR zeolite.

In Fig. 8 and Table S1, the positions of the O atoms on the walls of 12-MR channels can be divided into two categories. The O1 atom is located on the wall of the 12-MR channel instead of on the 8-MR side pocket, whereas the O2, O4, O5, O7, and O10 atoms are located on the common wall of the 12-MR channel and 8-MR side pocket. As discussed previously, the promotion of the catalytic activity of the MOR-10-673 catalyst (Fig. 7) should have resulted from the regeneration of some pyridine-poisoned active sites located on common walls of the 12-MR channels and 8-MR side pockets. Notably, T-O-T has the same direction as that of the OH groups, i.e., the acid sites. It is well-known that DME carbonylation occurs in the 8-MR side pocket [26,30]. However, the direction of T-O-T of O4, O7, and O10 points to the interior of the 12-MR channel instead of the 8-MR side pocket, as shown in Fig. 8 and Fig. S3. Therefore, we propose that the acid sites located at O4, O7, and O10 are not involved in DME carbonylation. In Fig. 9, the direction of T-O-T of O5 points to the center of the 8-MR window on the wall of the 12-MR channel along the tangent direction, whereas that of O2 is almost perpendicular to the wall of the 12-MR channel,

Fig. 9. Pyridine adsorption state on the acid site located at the O5 position of H-MOR along the (A1, A2) "a" axis and (B1, B2) "c" axis.

Fig. 10. Pyridine adsorption state on the acid site located at the O2 position of H-MOR along the (A1, A2) "a" axis and (B1, B2) "c" axis.

and points to the 8-MR side pocket (Fig. 10). Accordingly, the acid sites on them should be active in DME carbonylation.

All the H-MOR catalysts investigated in this work were modified by pyridine, except MOR-fresh. According to the directions of T-O-T, pyridine molecules can easily adsorb on the acid sites located at O1, O4, O7, and O10, since their OH groups point to the 12-MR channels (Fig. S3). The acid sites at the O5 position readily contact pyridine as well, because of the sufficient space in the 12-MR channels (Fig. 9). However, for the acid site at the O2 position, the T atoms may inhibit the pyridine adsorption, as shown in the inset in Fig. 10A2. The direction of the acid site must be turned inversely to adsorb pyridine. Therefore, we hypothesize that pyridine may weakly adsorb on the acid site at the O2 position because of the spacial hindrance in the natural frameworks of H-MOR. After pyridine modification, the acid sites at the O2 and O5 positions, i.e., the active sites for DME carbonylation, would be poisoned by pyridine (Fig. 9 and Fig. 10), leading to deactivation (Fig. 7). However, the pyridine-poisoned O2 positions can most probably be regenerated because of the aforementioned spacial hindrance. This might induce a significant promotion of the catalytic activity of the MOR-10-763 catalyst for DME carbonylation, as shown in Fig. 7, via proper thermal treatment at 673 K.

Table 3 provides the pyridine adsorption energies on the acid sites in H-MOR, based on DFT calculations. The results show that the pyridine adsorption energies on the O1, O4, O7, O10, and O5 positions are much larger than that on O2. This finding supports our assumption that pyridine is weakly adsorbed on the acid sites at the O2 positions due to the spacial hindrance in H-MOR. Furthermore, the remaining pyridine

Table 3

Pyridine adsorption energies on H-MOR calculated from DFT.

Position	ΔE_{ads} (eV)
O2	-0.75
O1	-2.09
O4	-2.34
O5	-2.52
O7	-2.22
O10	-2.30

molecules can still be strongly adsorbed by other acid sites in the 12-MR channels to avoid coke deposition. Therefore, the MOR-10-673 catalyst exhibits a highly improved catalytic activity, as well as a high stability.

3.6. Discussion

Compared with the MOR-fresh catalyst, the MOR-5-573 catalyst has less acid sites for NH_3 adsorption (Fig. 6), lower catalytic activity, and higher stability (Fig. 7). However, it is still readily deactivated during the reaction because of the unsaturated pyridine adsorption on acid sites in the 12-MR channels. Compared with the MOR-5-573 catalyst, the MOR-10-573 catalyst exhibits a higher catalytic stability, but a relatively lower initial activity (Fig. 7). Notably, the MOR-10-573 and MOR-20-573 catalysts have a similar amount of strong acid sites (Fig. 6). This indicates that when the pyridine adsorption duration is 10 min, the acid sites in the 12-MR channels are fully occupied. During the pyridine adsorption, the acid sites at the O2 and O5 positions are completely poisoned, lowering the activity of the MOR-10-573 catalyst compared with that of the MOR-5-573 catalyst. For the MOR-20-573 catalyst, an excessive pyridine adsorption seriously inhibits the mass transfer, even for small molecules (Table 1 and Fig. 6). Hence, the blockage of 12-MR channels causes complete deactivation of the MOR-20-573 catalyst (Fig. 7).

Compared with the MOR-5-573 catalyst, the MOR-10-673 catalyst adsorbs a larger amount of pyridine (Fig. 5 and Table S2), i.e., it has a lesser number of available acid sites for NH_3 adsorption (Fig. 6). However, it exhibits a higher activity and stability than those of the MOR-5-573 catalyst (Fig. 7). This indicates that pyridine adsorption is non-selective in 12-MR channels. Hence, even though the interaction is weak, pyridine can still stably adsorb on acid sites at O2 positions, at 573 K. Moreover, this also proves that the regeneration of these sites from pyridine poisoning is essential for improving the catalytic activity of H-MOR.

Compared with the MOR-10-573 catalyst, the robust MOR-10-673 catalyst has a larger number of available acid sites (Fig. 6 and Table S2), and it exhibits a higher activity (Fig. 7). This demonstrates that the poisoned acid sites at O2 positions (Fig. 10) are regenerated upon thermally desorbing pyridine at 673 K, without affecting other adsorbed pyridine molecules in H-MOR (Fig. 11). However, compared with the MOR-10-573 catalyst, the MOR-10-773 catalyst exhibits a lower activity and stability (Fig. 7), indicating that coke deposition blocks the H-MOR channels (Table 1, Fig. 2, and Fig. 6). This inhibits the mass transfer and causes catalyst deactivation. In addition, the MOR-10-773 and MOR-20-573 catalysts have a similar number of strong acid sites (Fig. 6), but the former's catalytic activity is much higher than the latter's (Fig. 7). This demonstrates that the blockage of H-MOR channels by excessive pyridine adsorption is more serious than that by coke deposition.

Fig. 11 describes the process of regenerating the pyridine-poisoned O2 atoms in H-MOR, based on the above analysis results. In Fig. 11, the direction of mass transfer of reactants and products is along the "a" axis, whereas pyridine poisons the

Fig. 11. Schematic drawing for O₂ regeneration from pyridine-modified H-MOR.

acid sites on the O2 atoms along the "b" axis direction. Our findings demonstrate that the thermal treatment at 673 K can only regenerate the pyridine-poisoned acid sites on O2 atoms and has little influence on those on other O atoms such as O1, O4, O5, O7, and O10.

4. Conclusions

In summary, by combining experimental and theoretical results, we report the intrinsic impact of the pyridine adsorption location and behavior in H-MOR on DME carbonylation at a molecular level. Our results show that the acid sites at the O2 positions, located on common walls of 8-MR side pockets and 12-MR channels, play a key role in DME carbonylation. Unfortunately, they are readily poisoned during pyridine modification. Interestingly, we discovered that the pyridine-poisoned acid sites at the O2 positions could be successfully regenerated via thermal treatment at 673 K, while other pyridine molecules in the 12-MR channels still remained. Hence, the MOR-10-673 catalyst exhibits a highly improved catalytic activity and maintains a high stability. Furthermore, our work illuminates the importance of the mass transfer in 12-MR channels for DME carbonylation. Both the excessive pyridine adsorption in the MOR-20-573 catalyst and the coke deposition in the MOR-10-773 catalyst inhibit the mass transfer. However, the former causes a much more serious catalytic deactivation than the latter. Our achievement is an approach to develop efficient and green ethanol synthesis systems.

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Graphical Abstract

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Spatial hindrance induced recovery of over-poisoned active acid sites in pyridine-modified H-mordenite for dimethyl ether carbonylation

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We newly discovered that acid sites at O2 positions, located on common walls of 8-MR side pockets and 12-MR channels, play a key role in promoting an efficient and robust catalytic activity for DME carbonylation.

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空间位阻对吡啶过度修饰导致丝光沸石二甲醚羰基化酸性位中毒后再生的诱导作用

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摘要: 当今世界环境与能源问题日益加剧, 乙醇作为一种重要的清洁燃料和化学品受到广泛关注, 迫切需要探索高效的乙醇合成方法, 以满足日益增长的市场需求. 其中, 将煤炭、生物质、页岩气等为原料合成的二甲醚通过羰基化反应制乙酸甲酯、乙酸甲酯加氢制乙醇的串联式绿色乙醇合成路线具有重要的工业应用前景. 然而, 在二甲醚羰基化过程中, 丝光沸石分子筛易积碳失活, 阻碍了其工业应用. 吡啶改性可以毒化丝光沸石12元环孔道中的酸性位, 抑制积碳的形成, 进而大幅度提高该催化剂的稳定性, 但同时会使其催化活性降低约40%–50%.

为了解决这一难题, 本文从分子水平上研究了吡啶吸附行为以及分子筛骨架空间位阻对丝光沸石催化剂上二甲醚羰基化反应的影响. 通过解析丝光沸石的骨架结构, 我们发现位于8元环侧袋和12元环孔道共用孔壁处O2位置上的酸性位是二甲醚羰基化反应的活性位, 但它们在吡啶修饰过程中易被毒化而使催化剂活性下降. 密度泛函理论计算结果表明, 吡啶分子因受分子筛骨架空间位阻的影响, 在O2处酸性位上的吸附较弱. 而实验结果也表明, 通过673 K热处理可以再生被吡啶毒化的O2活性位, 而并不影响12元环孔道中其它吡啶分子的吸附. 因此, 该热处理方法可以使丝光沸石催化剂保持高稳定性的同时, 将二甲醚羰基化反应催化活性提高约60%. 本文从分子水平证明了丝光沸石中O2活性位对二甲醚羰基化反应的重要作用, 为绿色乙醇合成技术研究提供了新的思路, 也为其它高效分子筛催化体系设计提供了有益的参考.

关键词: 丝光沸石; 吡啶修饰; 二甲醚; 羰基化; 再生; 空间位阻; 稳定性

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