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Catalytic Behavior of Alkali Treated H-MOR in Selective Synthesis of Ethylenediamine via Condensation Amination of Monoethanolamine

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Abstract: Catalytic behavior of alkali treated mordenite (H-MOR) in selective synthesis of ethylenediamine (EDA) via condensation amination of monoethanolamine (MEA) was investigated. Changes in the structural and acidic properties of alkali treated H-MOR were systematically investigated by N2 adsorption/desorption isotherms, scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD), temperature programmed ammonia desorption (NH3-TPD), pyridine adsorption was followed by infrared spectroscopy (Py-IR), and X-ray fluorescence (XRF) analyses. The results show that alkali treatment produces more opening mesopores on the H-MOR crystal surfaces and leads to an increase in the number of B acid sites and the strength of the acid sites. The mesopores effectively enhance the rate of diffusion in the bulk catalyst. Moreover, the B acid sites are active sites in selective synthesis of EDA. Due to improvements in the diffusion conditions and reactivities, alkali treated H-MOR shows an excellent catalytic performance under mild reaction conditions. The conversion of MEA was 52.8% and selectivity to EDA increased to 93.6%, which is the highest selectivity achieved so far. Furthermore, possible mechanism for the formation of EDA is discussed.

Keywords: alkali treated H-MOR; monoethanolamine; ethylenediamine; condensation amination; mechanism

1. Introduction

Ethylenediamine (EDA) is an important organic intermediate that can be used for the preparation of chelating reagents, surfactants, fabric softeners, lubricating oil additives, fungicides, insecticides, and resinous polymers [1–4]. Conventionally, EDA is synthesized by ammonolysis of ethylene dichloride with ammonia [2]. This process suffers from the co-production of sodium chloride, corrosion associated with chlorides and poor product selectivity to EDA. Alternatively, EDA can be produced via reductive amination of monoethanolamine (MEA) with hydrogen and ammonia over nickel or cobalt catalysts [3]. However, a higher reaction pressure (10–20 MPa) of hydrogen is an essential prerequisite to achieve satisfactory catalytic performance in the above process [1,4], which makes this manufacturing process potentially dangerous for use in industry.
The condensation amination of MEA with ammonia at a lower pressure (0.1–4.0 MPa) over solid acids has been proposed as an alternative method for the selective synthesis of EDA [1,3,4]. Unfortunately, this reaction thermodynamically favors the formation of undesirable by-products, such as cyclic polyamines and alkyl pyrazines [4,5]. To enhance the selectivity to the desired products, a series of shape selective zeolites have been studied as catalysts [6,7]. The micropore system of mordenite (MOR) consists of two pore types: 12-ring channels (6.7 × 7.0 Å) and 8-ring channels (3.4 × 4.8 Å), that are connected via 8-ring channels, which are inaccessible for above C3-molecules [8]. Therefore, MOR was found to be the most promising zeolites used for this reaction [1,4]. Good selectivity to EDA was achieved due to MOR’s narrow tubular structure [1] and by increasing of B acid amount after moderate dealumination by acid leaching [4].

However, one of the major problems associated with the use of microporous H-MOR as a shape selective catalyst is the intra-crystalline diffusion limitations [9,10]. The diffusion limitations cause fewer acid sites to come into contact with the reactant on the internal surfaces of the main channels [11]. This will decrease the intrinsic catalytic performance of the material due to the restricted mass transport [9–11]. The conversion of MEA is often approximately 30% in selective synthesis of EDA over H-MOR [1]. Furthermore, the diffusion limitations of MOR impede the expulsion of products from the acid sites, resulting in a long retention time of the products in the zeolite and an increase in undesirable reactions [12]. To maintain relatively good activity and selectivity to EDA, this reaction requires harsh reaction conditions, such as a high reaction temperature and NH₃/MEA molar ratio [1,4]. The harsh reaction conditions increase the costs associated with energy consumption and restrict the industrial application of the shape selective synthesis of EDA over microporous H-MOR.

Construction of hierarchical zeolite (one that contains both meso- and microporosity) is an effective way to improve the diffusion conditions and catalytic performances [13–22]. Hierarchical zeolites can be prepared by various direct synthesis methods, including using carbon [13,14], organosilane surfactants [15], and cationic polymers [16]. Moreover, it can also be prepared by post treatment with an NaOH solution, which can form mesopores inside zeolite crystallites [17–19]. For Al-rich MOR, it can be prepared by a combination of dealumination and desilication to introduce mesoporosity [20,21]. Hierarchical zeolites have a large external surface area, which allows facile diffusion of reactants and products in and out of the zeolite [12]. This increases the availability of acid sites for reactants and reduces the retention time of the products in the zeolite, resulting in an improvement in the catalytic performance in many reactions, such as alkylation reactions, isomerizations, cracking, and condensation reactions [11,12,17–20]. However, hierarchical MOR has not been used in selective synthesis of EDA via condensation amination of MEA, and the effect of mesopores and acidic properties on the catalytic performances in selective synthesis of EDA are still not clear.

In the present work, a series of hierarchical H-MOR was prepared by alkali treatment and well characterized by various methods. The main purpose of this work is to determine effect of mesopores and acidic properties on the catalytic performances in selective synthesis of EDA by evaluating the impact of the structures and acidic properties on the catalytic performances.

2. Results and Discussion

2.1. Physico-Chemical Properties of the Catalyst

The N₂ adsorption/desorption isotherm of H-MOR is characteristic of microporous materials and the isotherm for the samples after alkali treatment had shifted from type I to a combination of types I and IV with a pronounced hysteresis loop (Figure 1a), which indicated the formation of intra-crystalline mesopores [23]. The external surface area ($S_{\text{ext}}$) and mesopore volume ($V_{\text{meso}}$) increased with increasing NaOH concentration (Table 1). In contrast, the micropore surface area ($S_{\text{micro}}$) and micropore volume ($V_{\text{micro}}$) decreased with increasing NaOH concentration (Table 1). These results suggest that a higher concentration of NaOH causes the formation of more mesopores, but can cause the zeolite structure to collapses somewhat. The Barret Joyner Halenda (BJH) pore size distributions of
the samples before and after alkali treatment (Figure 1b) show a well-defined distribution of mesopores approximately 4 nm in size and a comparable pattern, and only the volume of the mesopores increased with increasing NaOH concentration (Table 1). This indicated that the formation of mesopores was uniform and increased with increasing NaOH concentration.

![Figure 1](image_url)

**Figure 1.** (a) N\textsubscript{2} adsorption/desorption isotherms of the samples before and after alkali treatment; (b) BJH pore size distributions of the samples before and after alkali treatment.

**Table 1.** Physicochemical properties of the samples before and after alkali treatment.

| Catalyst  | SiO\textsubscript{2}/Al\textsubscript{2}O\textsubscript{3} Molar Ratio | Relative Crystallinity (%) | S\textsubscript{micro} (m\textsuperscript{2}/g) | S\textsubscript{exter} (m\textsuperscript{2}/g) | V\textsubscript{micro} (cm\textsuperscript{3}/g) | V\textsubscript{meso} (cm\textsuperscript{3}/g) | D\textsubscript{ads} × 10\textsuperscript{15} (m\textsuperscript{2}/s) |
|-----------|-------------------------------------------------|-----------------------------|---------------------------------|----------------------------------|--------------------------|--------------------------|--------------------------|
| H-MOR     | 21.6                                            | 100                         | 336                             | 35                               | 0.16                     | 0.11                     | 5.89                     |
| 0.05AT-Cal | 20.1                                            | 111                         | 309                             | 38                               | 0.15                     | 0.12                     | 5.94                     |
| 0.1AT-Cal  | 19.3                                            | 115                         | 305                             | 39                               | 0.14                     | 0.13                     | 6.18                     |
| 0.2AT-Cal  | 18.9                                            | 97                          | 276                             | 42                               | 0.13                     | 0.14                     | 6.24                     |
| 0.4AT-Cal  | 16.4                                            | 89                          | 205                             | 42                               | 0.10                     | 0.15                     | 7.39                     |

The scanning electron microscopy (SEM) image of the sample (Figure 2a) reveals that H-MOR consists of aggregates of thin crystalline 100–200 nm cylinder, which form larger particles, and the external surface of H-MOR particles is clear and smooth, but some amorphous aluminosilicate appeared on the external surface of the H-MOR particles. A quite dramatic change in the morphology of the
H-MOR samples was observed upon alkali treatment; the amorphous aluminosilicate on the external surface of 0.05AT-Cal disappeared (Figure 2b), and the external surface of 0.1AT-Cal (Figure 2c) became rough and rugged, and some cracks and faults appeared on the external surface of 0.1AT-Cal, which was accompanied by visibly enhanced mesoporosity formation. The presence of intra-crystalline mesoporosity in the alkali treated MOR samples was further confirmed by transmission electron microscopy (TEM) investigations (Figure 2d). The etched portions in the inner part of the crystallites consistent with a size of approximately 4 nm, suggesting the formation of intra-crystalline mesopores upon alkali treatment. The formation of mesopores started close to the external surface and progressed toward the center of the crystallites for higher mesoporosities. These mesopores are distributed inside the zeolite crystals and connected to the reaction system through narrow microporous channels [20].

Figure 2. SEM ((a). H-MOR; (b). 0.05AT-MOR; (c). 0.1AT-MOR) and TEM ((d). 0.1AT-MOR) images of samples before and after alkali treatment.

The X-ray diffraction (XRD) patterns (Figure 3) show that all the samples before and after alkali treatment present the same diffraction peaks as those of the parent H-MOR (9.7, 19.7, 22.4, 25.8, and 26.4° of 2θ). Notably, the intensities of the peaks of these samples confirmed that the crystal structure of H-MOR was maintained after alkali treatment. Compared with that of H-MOR (100%), the relative crystallinity (RC) of 0.05AT-Cal, 0.1AT-Cal, 0.2AT-Cal and 0.4AT-Cal are estimated to be 111%, 115%, 97%, and 87%, respectively (Table 1). The RC of the alkali treated H-MOR initially increased and then...
decreased with increasing NaOH concentration. When NaOH concentration was 0.1 mol/L, the RC of the sample reached its highest value (115%). This is because the amorphous aluminosilicate or zeolites can be removed by the NaOH solution [18] and re-insertion of the aluminum species into the zeolite framework can occur during alkali treatment [20]. However, alkali treatment under certain harsh conditions can extract a large number of Si atoms from the framework to produce mesopores and partially damage the topology of the zeolite [20]. This is in agreement with the results of $S_{\text{micro}}$ and $V_{\text{micro}}$ (Table 1). Thus, the RC of 0.2AT-Cal and 0.4AT-Cal was lower than that of 0.1AT-Cal.

| Catalyst  | SiO$_2$/Al$_2$O$_3$ Molar Ratio | Crystallinity (%) | $S_{\text{micro}}$ (m$^2$/g) | $V_{\text{micro}}$ (cm$^3$/g) | $D_{\text{ads}}$ ($\times 10^{15}$ m$^2$/s) |
|-----------|-------------------------------|------------------|-----------------|-----------------|------------------|
| H-MOR     | 21.6                          | 100%             | 336             | 35              | 5.89             |
| 0.1AT-Cal | 19.3                          | 115%             | 305             | 39              | 6.18             |
| 0.2AT-Cal | 18.9                          | 97%              | 276             | 42              | 7.39             |
| 0.4AT-Cal | 16.4                          | 89%              | 89              | 205             | 15               |
| 0.05AT-Cal| 111%                          |                  |                 |                 |                  |

Figure 3. XRD patterns of the samples before and after alkali treatment.

Compared to H-MOR, the SiO$_2$/Al$_2$O$_3$ molar ratio of the samples before and after alkali treatment noticeably decreased from 21.6 (H-MOR) to 16.4 (0.4AT-Cal) with an increase of NaOH concentration (Table 1). When alkali treatment was applied, the change in the SiO$_2$/Al$_2$O$_3$ molar ratio was accompanied by the cleavage of some Si-O-Al bonds since the Si-O-Si bonds in the absence of neighboring Al ions are easier to hydrolyze and dissolve [23–27]. A substantial amount of Si was dissolved, which decreased the bulk SiO$_2$/Al$_2$O$_3$ molar ratio in the alkali treated MOR [28]. The diffusion coefficient ($D_{\text{ads}}$, m$^2$/s) increased from $5.89 \times 10^{-15}$ m$^2$/s to $7.39 \times 10^{-15}$ m$^2$/s with increasing NaOH concentration (Table 1). This indicates that the diffusion in alkali treated H-MOR improved with increasing mesopore content [26], which will improve its catalytic activity and selectivity to the products in selective synthesis of EDA via condensation amination of MEA.

2.2. Acidic Properties of the Catalyst

NH$_3$-temperature programmed desorption method (NH$_3$-TPD) was utilized to characterize the amount and strength of the acid sites. The NH$_3$-TPD curves (Figure 4) have two NH$_3$ desorption peaks. The lower temperature peak (120–250 °C) corresponds to weak acid sites, and the higher temperature peak (250–600 °C) corresponds to strong acid sites. Compared to the sample of alkali treated H-MOR, both the peak intensities and peak temperatures increased with increasing NaOH concentration (Figure 4). This indicates that the number and strength of the acid sites increased with increasing NaOH concentration. This can be attributed to the fact that few Al atoms were removed, and instead, Si atoms were preferentially removed from the MOR framework during alkali treatment [23–27]. The SiO$_2$/Al$_2$O$_3$ molar ratio of alkali treated H-MOR decreased, thus the acid density of alkali treated H-MOR was higher than that of H-MOR. The NH$_3$-TPD curves of alkali treated H-MOR closely resembled those of others (Figure 4), indicating that structural defects (cracks and faults on the external surface) formed in the bulk phases had a smaller impact on the acid properties, because of the re-insertion of aluminum species into the zeolite framework during alkali treatment [20]. A similar result was also reported by Jin et al. [29].
Pyridine adsorption was followed by infrared spectroscopy (Py-IR) to identify the number and nature of acid sites. Py-IR spectra of the catalysts (Figure 5) exhibit two characteristic bands at approximately 1545 and 1450 cm\(^{-1}\), which are attributed to pyridinium ions chemisorbed on the B acid sites and coordinated to the L acid sites. The number of B acid sites and L acid sites has been quantified according to the integrals of the peaks at 1545 and 1450 cm\(^{-1}\), respectively, and the data are summarized in Table 2. The number of B acid sites in alkali treated H-MOR follows the order of 0.4AT-MOR > 0.2AT-MOR > 0.1AT-MOR > 0.05AT-MOR > H-MOR. The acidity results demonstrate that alkali treatment of H-MOR leads to an increase in the number of B acid sites with increasing NaOH concentration (Table 2). This increase can be attributed to a portion of the four-coordinated Al atoms in the framework being converted into six-coordinated extra-framework species and re-insertion of the extra-framework aluminum into the zeolite framework during alkali treatment [20,29].

**Figure 5.** Py-IR spectra of the samples before and after alkali treatment.

**Table 2.** Acid properties of the samples before and after alkali treatment.

| Catalysts | Amount of B (mmol/g) | Amount of L (mmol/g) |
|-----------|----------------------|----------------------|
| H-MOR     | 0.0379               | 0.0175               |
| 0.05AT-Cal| 0.0903               | 0.0395               |
| 0.1AT-Cal | 0.1092               | 0.0373               |
| 0.2AT-Cal | 0.1323               | 0.0521               |
| 0.4AT-Cal | 0.1481               | 0.0722               |
2.3. Catalytic Performance

Catalytic behavior of alkali treated H-MOR in selective synthesis of EDA via condensation amination of MEA was investigated. Preliminary results reveal that the NaOH concentration, reaction temperature, and NH₃/MEA molar ratio are key parameters affecting the catalytic performances. Thus, much attention is paid on these parameters in the following studies.

2.3.1. Effect of Alkali Treatment on Catalytic Performance

The catalytic performance for selective synthesis of EDA over the samples before and after alkali treatment was measured and is summarized in Table 3. It was observed that the conversion of MEA increased to 60.8% (0.4AT-Cal) from a conversion of 11.3% (H-MOR) and the selectivity to EDA increased to 76.8% (0.1AT-Cal) from a selectivity of 43.6% (H-MOR). Obviously, alkali treated H-MOR catalysts exhibited better performances than H-MOR in selective synthesis of EDA via condensation amination of MEA. In addition, the conversion of MEA increased with increasing NaOH concentration; the selectivity to EDA initially increased and then decreased with increasing NaOH concentration, which generated a volcano shaped curve. However, the yield of EDA increased with increasing NaOH concentration. Taking into account the effect of SiO₂/Al₂O₃ molar ratio on the catalytic performances, the selective synthesis of EDA over 0.4AT-Cal and H-MOR* was investigated. H-MOR* has the same SiO₂/Al₂O₃ molar ratio as that of 0.4AT-Cal, whereas the conversion of MEA and selectivity to EDA over 0.4AT-Cal was noticeably higher than that of H-MOR* (Table 3). This result suggests that the effect of SiO₂/Al₂O₃ molar ratio on the catalytic performance is limited, and the enhancement of the reactivity and selectivity to EDA is due to the effect of alkali treatment, which causes positive changes in the structural and acidic properties.

Table 3. Catalytic performances of the samples before and after alkali treatment.

| Catalysts | Conversion (%) | Selectivity (%) | EDA Yield (%) |
|-----------|----------------|-----------------|---------------|
|           | Conversion     | Selectivity     |               |
|           | (Yield)        | EDA | PIP | TEDA | AEP | Others |               |
| H-MOR     | 11.3           | 43.6 | 11.3 | 3.6 | 4.0 | 37.5 | 4.9 |
| 0.05AT-Cal| 26.5           | 57.6 | 8.9 | 2.3 | 2.4 | 28.8 | 15.3 |
| 0.1AT-Cal | 45.3           | 76.8 | 6.3 | 1.6 | 2.0 | 13.3 | 34.8 |
| 0.2AT-Cal | 52.2           | 72.8 | 6.9 | 2.1 | 1.9 | 16.3 | 38.0 |
| 0.4AT-Cal | 60.8           | 70.2 | 7.5 | 2.1 | 2.3 | 17.9 | 42.7 |
| H-MOR *   | 18.5           | 36.4 | 12.1 | 4.3 | 4.4 | 42.8 | 6.7 |
| H-ZSM-5   | 42.6           | 11.6 | 35.3 | 21.3 | 5.3 | 26.5 | 4.9 |

Reaction conditions: temperature = 310 °C; pressure = 4.0 MPa; NH₃/MEA (mol/mol) = 21/1; LHSV = 4.58 h⁻¹; PIP: piperazine; TEDA: triethylenediamine; AEP: aminoethylpiperazine; Others: cyclic polyamines and alkyl pyrazines.

Open mesopores are created on the H-MOR crystal surface by alkali treatment (Figures 1 and 2). This shortens the diffusion paths of the molecules and helps them reach the zeolite acidic sites more easily [30,31]. The D_ads increased from 5.89 × 10⁻¹⁵ m²/s (H-MOR) to 7.39 × 10⁻¹⁵ m²/s (0.4AT-Cal) with increasing NaOH concentration (Table 1). The enhancement of D_ads leads to an increase in the number of acid sites available to reactants [12]. Therefore, the conversion of MEA and selectivity to EDA over alkali treated H-MOR were improved despite the selectivity to EDA showed volcano shaped behavior (Table 3); the yield of EDA is increasing with increasing D_ads (Tables 1 and 3). However, the selectivity to EDA is not always enhanced with an increase in D_ads (Tables 1 and 3). This is in contrast with an increase in D_ads can reduce the retention time of the product in zeolite and the chance of the product undergoing a second reaction, which increases the selectivity to the targeted products [12]. It seems that the presence of more mesopores causes a loss of shape selectivity in selective synthesis of EDA, leading to the formation of bulky by-products outside of the zeolite micropore system.
The catalytic performance of H-ZSM-5 in selective synthesis of EDA was investigated to verify above hypothesis (Table 3). The micropore system of H-ZSM-5 consists of two types of pores: 10-ring straight channels ($5.1 \times 5.5 \, \AA$) and 10-ring zigzag channels ($5.3 \times 5.6 \, \AA$). Both types of H-ZSM-5 channels are smaller than the mesopores (4 nm) of alkali treated H-MOR. However, the reaction results show that the selectivity to EDA over H-ZSM-5 is lower than that of alkali treated H-MOR, and the selectivity to bulky by-products, such as PIP and TEDA, is higher than that over alkali treated H-MOR (Table 3). This result indicates that when using alkali treated H-MOR, the main reaction in selective synthesis of EDA via condensation amination of MEA was still occurring in the MOR’s micropore channels. This can be attributed to the fact that the mesopores are distributed inside the zeolite crystals (Figure 2d) and connected to the reaction system through narrow microporous zeolite channels [20]. The mesopores of alkali treated H-MOR only improve the diffusion conditions and do not destroy the shape selective catalysis of H-MOR in selective synthesis of EDA. The selectivity to EDA is not always enhanced with increasing $D_{ads}$ due to alkali treatment (Tables 1 and 3), which suggests that the acidic properties are another key factor in addition to the structure of mesopores that affects the catalytic performance.

To investigate effect of the acidic sites on catalytic performance, Figure 6 gives relationship between B acid amount and EDA yield. It shows that the yield of EDA is increasing with increasing amount of B acid sites, which proves that EDA is mainly produced on B acid sites. A similar result was also reported by Segawa et al. [4], and suggested that strong B acid sites are active sites in the titled reaction. By comparing the relationship between the strength of acid sites (Figure 4) and the catalytic performance (Table 3), it can be found that the strength of acid sites on 0.1AT-Cal is moderate, but it provided the highest selectivity to EDA. This is likely because the number of strong B acid sites is inversely related to the number of weak acid sites as reported by Segawa et al., which is not sufficiently strong to promote this reaction. The requirement strength of B acid sites in selective synthesis of EDA over alkali treated H-MOR is correlated to the reaction temperature, this will be discussed in Section 2.3.2. At a certain reaction temperature, the B acid sites that are too strong will hinder the desorption of the alkaline reactants and products from the acid sites and greatly increase the chance for further undesirable reactions [32], that is why the selectivity to EDA does not continuously increase with increasing $D_{ads}$ due to alkali treatment (Tables 1 and 3).

![Figure 6](image-url)

**Figure 6.** Relationship between B acid amount and EDA yield of the samples before and after alkali treatment. Reaction conditions: temperature = 310 °C, pressure = 4.0 MPa, NH$_3$/MEA (mol/mol) = 21/1, LHSV = 4.58 h$^{-1}$.

From the above results, it can be concluded that both the structural and acidic properties of alkali treated H-MOR can affect its catalytic behavior in selective synthesis of EDA via condensation amination of MEA. Alkali treatment produces more intra-crystalline mesopores and leads to an increase in the number and strength of B acid sites. The mesopores effectively enhance the rate of diffusion in
From the above results, it can be concluded that both the structural and acidic properties of alkali treated H-MOR in selective synthesis of EDA. Diffusion conditions and reactivities of the catalysts were improved by alkali treatment and resulted in excellent catalytic performance in selective synthesis of EDA.

2.3.2. Effect of the Reaction Condition on the Catalytic Performance

The effect of the reaction temperature on the catalytic performance of alkali treated H-MOR in selective synthesis of EDA was investigated, as shown in Figure 7. The results once again show that alkali treated H-MOR exhibited better catalytic performances than that of H-MOR at different reaction temperatures. The conversion of MEA decreased with decreasing reaction temperature. The selectivity to EDA increased with decreasing reaction temperature. This result implies that a low reaction temperature favors the production of EDA, but disfavors the conversion of MEA. However, as discussed in Section 2.3.1, increasing the number of mesopore and B acid sites is an effective way to improve the catalytic efficiency in selective synthesis of EDA. Alkali treatment with increasing NaOH concentrations produces more open mesopores on the H-MOR crystal surfaces and leads to an increase in the number of B acid sites (Tables 1 and 2). Alkali treatment with increasing concentrations of NaOH mitigated the adverse effects associated with decreasing reaction temperature on the catalytic performance. Moreover, the production of EDA is favored at low reaction temperatures. Therefore, as the reaction temperature decreases, the magnitude of the decrease in the rate of MEA conversion was in the order 0.4AT-Cal < 0.2AT-Cal < 0.1AT-Cal < 0.05AT-Cal < H-MOR, and in contrast, the increase in the selectivity to EDA was in the order 0.4AT-Cal > 0.2AT-Cal > 0.1AT-Cal > 0.05AT-Cal > H-MOR (Figure 7). This is in agreement with that the yield of EDA increases with increase of the mesopore (Tables 1 and 3) and increases with increasing amounts of B acid sites (Figure 6). On the other hand, the increase in the selectivity to EDA over alkali treated H-MOR was in the same order with the increase in the number of acid sites (Figure 4, Figure 7). This result suggests that alkali treated H-MOR with stronger acid sites demands relatively lower reaction temperature to promote the production of EDA, while maintaining high activity.

![Figure 7. Effect of reaction temperature on the catalytic performance. Reaction conditions: pressure = 4.0 MPa, NH₃/MEA (mol/mol) = 21/1, LHSV = 4.58 h⁻¹.](image)

The effect of the NH₃/MEA molar ratio on the catalytic performance of alkali treated H-MOR was investigated, as shown in Figure 8. It shows that alkali treated H-MOR also exhibited better catalytic performances than H-MOR using different NH₃/MEA molar ratios. The conversion of MEA and selectivity to EDA decreased as the NH₃/MEA molar ratio decreased. In a similar reaction, it has been reported that desorption of methyamines assisted by the adsorption of ammonia and/or scavenging of methyl groups with ammonia as the rate-determining step in the selective synthesis of methyamines [32]. That is, the lack of ammonia will suppress the production of amines and
subsequently desorption from the acid sites, resulting in a poor catalytic activity and selectivity to the products. Therefore, conversion of MEA and selectivity to EDA was decreased with decreasing NH$_3$/MEA molar ratio in the titled reaction (Figure 8). It can also be shown that with a decrease in the NH$_3$/MEA molar ratio, the magnitude of the decrease in the rate of MEA conversion and selectivity to EDA was in the order 0.4AT-Cal < 0.2AT-Cal < 0.1AT-Cal < 0.05AT-Cal < H-MOR (Figure 8). This result is similar to the effect of the reaction temperature on the catalytic performance. Alkali treatment produces more open mesopores on the H-MOR crystal surfaces and leads to an increase in the number of B acid sites (Tables 1 and 2). Alkali treatment mitigates the adverse effect of decreasing NH$_3$/MEA molar ratio on the catalytic performance, which is why different trends were observed for alkali treated H-MOR when the NH$_3$/MEA molar ratio was varied.

From the above results, it can be concluded that alkali treated H-MOR catalysts with higher concentrations of NaOH showed excellent catalytic performances under relatively mild reaction conditions. To support this conclusion, 1.0AT-Cal was prepared and measured at 280 °C with an NH$_3$/MEA molar ratio of 12/1. The reaction results showed that the conversion of MEA was 52.8% and selectivity to EDA increased to 93.6%, which is the highest achieved so far (the highest selectivity to EDA in the literature is 86.3%, which was achieved at 330 °C with an NH$_3$/MEA molar ratio of 80/1 [4]). Physico-chemical properties of 1.0AT-Cal show that S$_{exter}$, V$_{meso}$, and B acid amount increased to 45 m$^2$/g, 0.17 cm$^3$/g, and 0.1746 mmol/g, respectively. This further confirmed that increasing the number of mesopores and B acid sites is an effective way to promote the production of EDA, while maintaining high activity under mild reaction conditions.

2.3.3. Catalytic Lifetime of Alkali Treated H-MOR

The catalytic lifetime of H-MOR and 1.0AT-Cal in selective synthesis of EDA was investigated, as shown in Figure 9. The results showed that H-MOR exhibited no catalytic activity at 280 °C with an NH$_3$/MEA molar ratio of 12/1 and showed fast deactivation at 320 °C with an NH$_3$/MEA molar ratio of 21/1. In contrast, 1.0AT-Cal showed excellent catalytic activity, selectivity to EDA and catalytic stability at 280 °C with an NH$_3$/MEA molar ratio of 12/1. After the catalytic reaction was carried out for 1000 h, the conversion of MEA slight decreased from 52.8% to 46.3%, and the selectivity to EDA was maintained at 93.6%. The different trends were observed for the catalytic lifetime of H-MOR and 1.0AT-Cal that is due to the effect of mesopores and acidic properties on the catalytic performances in selective synthesis of EDA. The deactivation of zeolite was attributed to the covering of the active sites by coke deposits [33]. The diffusion limitations of MOR impede the expulsion of products from the acid sites, resulting in an increase in the formation of coke inside the micropore channels, which

![Figure 8. Effect of NH$_3$/MEA molar ratio on the catalytic performance. Reaction conditions: temperature = 310 °C, pressure = 4.0 MPa, LHSV = 4.58 h$^{-1}$.](image)
is one of the main reasons for the fast deactivation of H-MOR. However, 1.0AT-Cal has a relatively large S_{exter}, which facilitates the coke precursors desorption, and therefore, leading to a lower carbon deposition and weaker carbon formation intensity [12,34]. Furthermore, as discussed in Section 2.3.1, the main reaction was occurring in the MOR’s micropore channels, whereas the coke is preferential formed in the mesopores [35]. On the other hand, 1.0AT-Cal has large number of B acid sites, which are the active sites in the titled reaction; that is another possible reason for the long catalytic lifetime of 1.0AT-Cal. Therefore, 1.0AT-Cal showed excellent catalytic stability than H-MOR in selective synthesis of EDA via condensation amination of MEA.

![Graph of Conversion and Selectivity](image)

**Figure 9.** Catalytic lifetime of alkali treated H-MOR in selective synthesis of EDA. Reaction conditions: H-MOR: temperature = 320 °C, pressure = 4.0 MPa, NH₃/MEA (mol/mol) = 21/1, LHSV = 4.58 h⁻¹; 1.0AT-Cal: temperature = 280 °C, pressure = 4.0 MPa, NH₃/MEA (mol/mol) = 12/1, LHSV = 4.58 h⁻¹.

### 2.4. Possible Mechanism for Selective Synthesis of EDA

The adsorption energy was investigated using Our-own-N-layered Integrated molecular Orbital molecular Mechanics (ONIOM) method (B3LYP/6-31G (d, p): HF/3-21G) and the Gaussian 09 program [36]. The results show that the adsorption energy of MEA–N–H–MOR (178.38 kJ/mol) is higher than that of MEA–O–H–MOR (98.13 kJ/mol) and NH₃–H–MOR (140.21 kJ/mol) (Figure 10), this indicates that the –NH₂ of MEA is priority to –OH of MEA and NH₃ in the adsorption over H-MOR. Moreover, the adsorption energy of the reactants is very high, which indicates that the reactants were chemisorbed on the acid sites and that desorption was difficulty [32]. As discussed in Section 2.3.2, desorption of reactants and products was only aided by the adsorption of ammonia and/or the scavenging of alkyl groups with ammonia. This step is the rate determining step. Thus, the reaction occurs via an SN₂ attacking by NH₃ to produce EDA followed by desorption from the acid sites.

From these results, we can propose the possible reaction mechanism as described in Scheme 1. The –NH₂ group of MEA is adsorbed on the surface of H-MOR to form an adsorbed species and then is converted to a protonated surface species via an electron transfer. The protonated surface species is SN₂ attacking by NH₃ and produces EDA by adsorption assisted desorption or scavenging of a hydroxyl from adsorbed MEA. This step is the potentially rate determining step. That is why excess NH₃ was required to improve the catalytic performance, especially the selectivity to EDA (Figure 8). The excess NH₃ not only removes protonated surface species from the acid sites but also reduces the S_N2 attacking of the protonated surface species by MEA or EDA to produce by-products.
was denoted as xAT-Cal (where x represents the concentration of NaOH). For example, 0.1AT-Cal

Catalysts

Figure 10. Adsorption model of NH\textsubscript{3} and different groups of MEA over H-MOR. (a) MEA–N–H–MOR (178.38 kJ/mol); (b) MEA–O–H–MOR (98.13 kJ/mol); (c) NH\textsubscript{3}–H–MOR (140.21 kJ/mol).

Scheme 1. Possible mechanism for selective synthesis of EDA via condensation amination of MEA.

3. Materials and Methods

3.1. Preparation of the Catalysts

The commercially available dealuminated H-MOR with a small crystal size (SiO\textsubscript{2}/Al\textsubscript{2}O\textsubscript{3} molar ratio = 21) and other zeolites used in the present work were supplied by Nan Kai Catalyst Manufactory (Tianjin, China). H-MOR was stirred for 2 h at 100 °C (conventional heating plate) in NaOH solutions [m (zeolite)/V (solution) = 1/8 g/mL] of concentrations ranging from 0.05 to 0.4 mol/L. Subsequently, the slurry was cooled by adding cool distilled water, filtered, washed carefully with distilled water until the filtrate reached pH = 7, and then dried overnight at 120 °C. The alkali treated solid was converted into the corresponding H-form by two consecutive exchanges in 1 mol/L of NH\textsubscript{4}Cl solution [m (zeolite)/V (solution) = 1/4 g/mL] at 100 °C for 2 h each times. The solid was carefully washed until the filtrate reached pH = 7, and then the material calcined at 450 °C for 4 h. The alkali treated H-MOR was denoted as xAT-Cal (where x represents the concentration of NaOH). For example, 0.1AT-Cal represents H-form sample treated in 0.1 mol/L NaOH solution. All the samples were pressed into pellets and calcined at 530 °C for 4 h prior to use.

3.2. Characterization

N\textsubscript{2} adsorption/desorption isotherms were measured at −196 °C (Micromeritics, ASAP 2020, GA, USA). Prior to analysis, the samples were degassed at 350 °C under a 10\textsuperscript{−3} Pa vacuum for 10 h. The Brunauer-Emmett-Teller (BET) equation was used to calculate the apparent surface area from the
adsorption data. The size distribution of the mesopores was calculated using the BJH model. The t-plot method was used to discriminate between the micro- and mesoporosity. The morphology of the sample was investigated by SEM (Philips, XL30E scanning electron microscope, Netherlands) at 15 kV and TEM (Hitachi, H-600 microscope, Tokyo, Japan) at 200 kV. Prior to observation, the samples were dispersed in anhydrous alcohol using ultrasonication, and the resulting suspension was transferred drop wise to a copper grid and dried in air. The RC of the sample was determined by XRD (Bruker, D8 Advance diffractometer, Billerica MA, USA) at 30 kV and using Cu Kα radiation (λ = 0.1541 nm). The RC of the sample was estimated by comparing the total areas of the characteristic peaks (9.7, 19.7, 22.4, 25.8, and 26.4° of 2θ) of the samples, and the RC of H-MOR was regarded as 100%. In a typical NH3-TPD (Micromeritics, AutoChem II 2950 instrument, GA, USA) experiment, the sample (100 mg) was pre-treated at 350 °C for 2 h under an He flow rate of 25 mL/min to remove any adsorbed organic species and moisture, and then the sample was cooled to 120 °C and saturated with NH3. After the baseline leveled off, the sample was heated at a rate of 10 °C/min from 120 to 600 °C. Py-IR to identify the number and nature of acid sites (Bruker, Tensor 27 IR spectrometer, Billerica MA, USA) at a resolution of 4 cm−1. The sample was pre-treated at 500 °C for 3 h under 10−2 Pa in an IR cell with CaF2 windows. Subsequently, the wafer was exposed to pyridine vapor for 30 min at 25 °C and then degassed at 150 °C for 30 min. Finally, the Py-IR spectra of the sample were collected at room temperature. The B and L acid amounts were calculated based on the intensity of 1545 and 1450 cm−1, and the molar extinction coefficient used was 2.2 cm µmol−1. The 95% confidence limits were estimated at ± 15%. The SiO2/Al2O3 molar ratio of the sample was determined by XRF spectrometer (Philips, Magix 601X, Eindhoven, Netherlands). The diffusion coefficient (Dads, m2/s) at P/P0 = 0.2 was calculated by a chemical diffusion coefficient calculator from the sorption-time data recorded during an isothermal measurement.

3.3. Catalyst Evaluation

The catalytic experiments were performed in a continuous flow fixed-bed reactor. The reactants were fed into the reactor by means of a piston pump. The feed composition was NH3/MEA = 21/1 (molar ratio). The reaction temperature was maintained at 310 °C and the reaction pressure was kept under 4.0 MPa. The liquid hourly space velocity (LHSV) was 4.58 mL reactant/mL cat h−1. The reaction products were trapped out of the reaction system as liquids, and analyzed by gas chromatography (FID, GC-930, Haixin, Shanghai, China) on a system equipped with a 30 m capillary column (DB-35). The by-products were analyzed by GC-MS (GC-17A, Shimadzu, Kyoto, Japan).

4. Conclusions

Hierarchical H-MOR was prepared by alkali treatment and was used in selective synthesis of EDA via condensation amination of MEA for the first time. Alkali treatment produces more intra-crystalline mesopores and leads to an increase in the number and strength of B acid sites. The mesopores effectively enhance the rate of diffusion in the bulk catalyst. Moreover, the B acid sites are active sites in selective synthesis of EDA. Diffusion conditions and reactivities of the catalysts were improved by alkali treatment and resulted in excellent catalytic performance under relatively mild reaction conditions. The conversion of MEA was 52.8% and selectivity to EDA increased to 93.6%, which is the highest achieved so far. Furthermore, alkali treated H-MOR also exhibited excellent catalytic stability in selective synthesis of EDA. In the future, the investigators can use alkali treated H-MOR as a support and further modify the structural and acidic properties of the catalyst. This will be one of the most promising methods for overcoming the disadvantages of conventional methods in selective synthesis of EDA.

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