Vapor phase Beckmann rearrangement of cyclohexanone oxime over MCM-22

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Abstract

A comprehensive study has been made on the Beckmann rearrangement of cyclohexanone oxime (CHO oxime) to $\epsilon$-caprolactam, catalyzed by MCM-22 under various operating conditions. The distinct identities of MCM-22 were characterized by XRD, SEM, and NH\textsubscript{3}-temperature programming desorption (NH\textsubscript{3}-TPD). The acidic strength of MCM-22 is much weaker than those of ZSM-5 and zeolites with similar SiO\textsubscript{2}/Al\textsubscript{2}O\textsubscript{3} ratio. It was found that catalytic active sites with moderate acidic strengths are more favorable for the rearrangement reaction. The carbonaceous residues, which contain mainly functional groups with C≡N bonds, can be effectively removed by purging the H-MCM-22 catalyst with nitrogen gas at higher temperatures in the absence of oxygen. A reaction pathway was proposed which invokes the main rearrangement reaction of CHO oxime accompanied by two side reactions, namely ring opening reaction of $\epsilon$-caprolactam to form 5-hexenenitrile (5-HEN) (coke precursor) and hydrolysis reaction to form cyclohexanone. The effects of the Pt incorporation and operating conditions, viz temperature, carrier gas, space velocity, feed concentration, solvent etc., on related reaction equilibriums of the reactions involved and ultimately on catalyst stability and product selectivity were discussed.

Keywords: Beckmann rearrangement; Cyclohexanone oxime; $\epsilon$-Caprolactam; MCM-22

1. Introduction

$\epsilon$-Caprolactam is an important intermediate for the manufacture of synthetic fibers. The contemporary industrial process for $\epsilon$-caprolactam production invokes Beckmann rearrangement of cyclohexanone oxime (CHO oxime) catalyzed by concentrated sulfuric acid. However, while the process is known to yield $\epsilon$-caprolactam with high selectivity, it is also accompanied by high oleum consumption rate and high ammonium sulfate yield (>1.7 pounds per pound $\epsilon$-caprolactam) as by-product [1,2]. Cost aside, serious environmental and safety concerns (in terms of equipment corrosion) are considered as major drawbacks. To overcome these problems, a more preferable alternative is to use solid acid catalysts. Several potential materials, such as TS-1 [3], SAPO-11 [4], FSM-16 [5,6], Y [7,8], ZSM-5 [9-12], ZSM-11 [13-19], ZSM-11 [20], TiO\textsubscript{2}-ZrO\textsubscript{2} [21], and mordenite [22], have been evaluated. Among them, an extensive study on zeolite ZSM-5 can be found.

Beckmann rearrangement reactions were conducted in the presence of a solvent, which was found to have significant effects on the overall performance of the catalyst used. Interestingly, ethanol and 1-hexanol was found as the favorable solvent for 10-oxygen membered ring (10-MR) and 12-MR zeolites, respectively [1,18,19]. Moreover, it is generally believed that the Beckmann rearrangement reaction occurs mostly on the external surfaces of both 10-MR [23] and 12-MR zeolites [24-28].

The objective of this study is to evaluate the catalytic performance of MCM-22 for Beckmann rearrangement of CHO oxime. The structure of MCM-22 zeolite [26] consists of two independent two-dimensional pore systems: the sinusoidal channels with 10-MR openings and the larger 12-MR supercages (0.71 nm × 0.71 nm × 1.81 nm) interconnected by the 10-MR windows [24]. MCM-22 is known to possess...
unique shape-selective properties in several model catalytic reactions, for examples, during \( m \)-xylene isomerization, toluene alkylation and normal paraffin cracking [27–34]. In particular, owing to its extraordinarily large extracrystalline surface area compared to its zeolite counterparts, MCM-22 is more preferable in catalyzing reactions such as Beckmann rearrangement, which predominately occur on the external surface of the catalyst. In this work, the effects of coking and regeneration on catalytic activity and product shape-selectivity during Beckmann rearrangement of CHO oxime to \( \varepsilon \)-caprolactam over MCM-22 and under various reaction conditions are comprehensively studied. In addition, the roles of solvent and incorporated metal species on the stability of the catalyst are also investigated. A reaction mechanism will be proposed based on the experimental results.

2. Experimental

2.1. Material synthesis

MCM-22 zeolite was synthesized using hexamethylenimine (HMI) as the structure directing agent [26]. A gel solution having the following molar ratios of \( \text{SiO}_2/\text{Al}_2\text{O}_3 = 25; \text{OH}^-/\text{SiO}_2 = 0.1; \text{Na}^+ /\text{SiO}_2 = 0.2; \text{HMI}/\text{SiO}_2 = 0.35; \text{H}_2\text{O}/\text{SiO}_2 = 25 \) was prepared from colloidal silica (Nalco, 48.7% \( \text{SiO}_2 \), 0.3% \( \text{Na}_2\text{O} \), 51% \( \text{H}_2\text{O} \)), sodium aluminate (Showa, 46.9% \( \text{Al}_2\text{O}_3 \), 22.8% \( \text{Na}_2\text{O} \)), HMI (Aldrich, 99% purity), and sodium hydroxide (Showa). This solution was first stirred for 30 min and then introduced into a Teflon-lined stainless steel autoclave, which was then maintained at a temperature of 443 K under stirring (550 rpm) for 66 h, and finally cooled to room temperature. Subsequently, the product was recovered from the gel solution by filtration, followed by washing with deionized water till reaching pH 7. The filtered cake was dried at 393 K for 8 h, then calcined at 813 K for 5 h to obtain the as-synthesized sample. The sample was converted to H-form by ion-exchange with ammonium acetate (20 ml of 1N solution per gram of zeolite at 353 K for 12 h, two repeating cycles) then dried at 393 K for 12 h, followed by calcination treatment at 813 K for 5 h. The Pt/H-MCM-22 sample was prepared by impregnation via incipient wetness with Pt(NH\(_3\))\(_4\)(NO\(_3\))\(_2\) for ca. 24 h, calcined, then reduced under flowing hydrogen at 623 K for 4 h.

2.2. Characterization

The structure of the synthesized MCM-22 sample was confirmed by X-ray powder diffractometry (Shimadzu XD-5) using Cu K\( \alpha \) radiation. As shown in Fig. 1, the resultant XRD diffractogram reveals a typical pattern with a main peak at the diffraction angle of 2\( \theta \) = 25.9\(^\circ\). The morphology and mean crystalline size of the MCM-22 sample were determined by scanning electron microscopy (Hitachi S-2300), which shows disc-like platelets with a diameter of less than 1 \( \mu \)m and a thickness of less than 0.1 \( \mu \)m (Fig. 2). The Si/Al ratio of the sample, determined with an inductively coupled plasma-mass spectrometer (Perkin-Elmer SCIEX ELAN 5000), is 13.7. The surface area, measured with a micrometric model instrument (ASAP 2000), is 510 m\(^2\)/g. The acidity of the as-synthesized and H\(^+\) ion-exchanged samples were measured by temperature programming desorption (TPD) of ammonia. Typically, each sample was first calcined at 773 K for 2 h, cooled to 423 K under a nitrogen stream, then exposed to ammonia vapor till saturation adsorption, then subjected to desorption measurement under flowing nitrogen. This was done by first maintaining the sample at 423 K for 5 h; then the temperature was slowly increased at a heating rate of 5 K/min until reaching a final temperature of 950 K. The amount of desorbed ammonia was recorded by a thermal conductive detector (TCD) during various temperature scans.

The coked sample was prepared under the following operating conditions: \( T = 633 \) K; pressure = 1 atm; \( \text{H}_2/\text{feed ratio} = 4 \text{mol/mol}; \text{feed (CHO oxime/CHO)} \) ratio = 0.1 mol/mol; WHSV = 3 h\(^{-1}\); and time-on-stream TOS = 24 h. Then the sample was purged with nitrogen at 633 K for 8 h before unloading. The total content and the nature of the coke powder deposited on the fouled
The catalytic reaction was carried out in a continuous flow, fixed-bed reactor (316 stainless, 19 mm o.d.). A mixture of pelletized MCM-22 (ca. 10–20 mesh) and quartz sands (also 10–20 mesh) was packed into the reactor, then calcined in flowing air at 813 K for 6 h. Subsequently, the reactor was cooled to the desired reaction temperature under a nitrogen flow. CHO oxime dissolved in various solvents, namely benzene, ethanol, and cyclohexanone, was used as the reactor feed. The feed was injected into the reactor by a metering pump along with N₂ or H₂ as the carrier gas. The reaction was carried out under the following conditions: temperature range, 613–673 K; pressure, 1 atm; CHO oxime/CHO mole ratio, 0.10–0.22; WHSV of CHO oxime feed, 3–7 h⁻¹; and gas/feed molar ratio, 0–8. The reactor effluent taken at specified intervals was analyzed using a Hewlett-Packard Chromatograph 5890, equipped with a flame ionization detector and a 30 m RTX-1 capillary column. Regeneration of the catalyst was done by calcination under flowing air at 813 K for 8 h. Accordingly, the conversion and selectivity obtained from the reaction can be derived by the following equations:

\[
\text{Conversion} = \frac{\text{products (mole)}}{\text{(products + oxime residue) (mole)}} \text{in reactor effluent}
\]

\[
\text{Selectivity} = \frac{\text{specific product yield (mole)}}{\text{conversion of oxime (mole)}}
\]

Moreover, to evaluate the stability of the catalyst, the duration over which the catalyst is capable of sustaining 100% CHO oxime conversion is used as an indicator.

### 3. Results and discussion

Fig. 3 displays the NH₃-TPD profiles of Na- and H-form MCM-22 zeolites. Typically, two characteristic peaks were observed at ca. 498 and 649 K; these may be respectively assigned due to NH₃ that desorbs from Brønsted acid sites with weak and medium acidic strengths. Using a pyridine–TPD method, Camblor et al. [35] reported that, for both ZSM-5 and β zeolites with SiO₂/Al₂O₃ ratio of ca. 20, three distinct desorption peaks at 523, 623, and 673 K can be identified. Taking their results as reference, one concludes that the acidic strength of MCM-22 is much weaker than those of ZSM-5 and β zeolites. Nevertheless, a notable increase in the amount of acid sites with medium strength in the H-MCM-22 (obtained after H⁺ ion-exchange) sample compared to the amount in the (Na, H)-MCM-22 (as-synthesized) sample is obvious. Together with the fact that MCM-22 reveals better stability and selectivity of ε-caprolactam after H⁺ ion-exchange (Table 1), these results enable us to conclude that the Brønsted acid sites with medium acid strength are much more favorable for ε-caprolactam yield. This observation is in line with earlier reports, which revealed that the Brønsted acidity of zeolite Y is responsible for the formation of ε-caprolactam [10], and that the selectivity of ε-caprolactam correlates well with the level of exchange of Na⁺ with H⁺ in H-NaY [12]. However, this is seemingly in contrast to the findings of Dai et al. [9], who suggested that a high acid concentration in H-USY is less favorable for selective formation of ε-caprolactam [9]. On the other hand, Sato et al. reported that the conversion and selectivity of ε-caprolactam over ZSM-5 tend to increase with the increasing Si/Al ratio ranging from 8 to 11,000 [36]. Similar study on a highly siliceous ZSM-5 (Si/Al = 147,000), which detected nearly null acidity by NH₃-TPD, also revealed an achievement of nearly 100% conversion with 79.6% selectivity [37]. It has been suggested that the strong acid sites possessed by MFI

### Table 1

The stability and product selectivity for Beckmann rearrangement of CHO oxime over the as-synthesized (Na, H)-form and H-form MCM-22a

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Duration periodb (h)</th>
<th>Selectivity (%)</th>
<th>ε-Caprolactam</th>
<th>Cyclohexanone</th>
<th>Nitriles</th>
<th>Others</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na, H-MCM-22</td>
<td>13</td>
<td>68.2</td>
<td>15.4</td>
<td>4.1</td>
<td>12.3</td>
<td></td>
</tr>
<tr>
<td>H-MCM-22</td>
<td>25</td>
<td>70.8</td>
<td>16.7</td>
<td>11.5</td>
<td>3.0</td>
<td>8.8</td>
</tr>
</tbody>
</table>

a Reaction conditions: pressure = 1 atm; temperature = 633 K; WHSV = 3 h⁻¹; H₂/Feed = 4 mol/mol; feed (CHO oxime/CHO) = 8:1 mol/mol.
b A parameter for evaluation of catalyst stability, representing the time over which the catalyst can sustain a 100% CHO oxime conversion.
zeolites provoke acceleration of the ring opening reaction of \( \varepsilon \)-caprolactam to nitrile as well as the hydrolysis reaction of CHO oxime to cyclohexanone [38]. Furthermore, Heitmann et al. [39,40] proposed that nest silanols are the active sites for the Beckmann rearrangement reaction over MFI zeolites.

By the same token, we propose a reaction pathway for Beckmann rearrangement over H-MCM-22, as illustrated in Fig. 4. Basically, three main reactions can be envisaged: namely rearrangement reaction of CHO oxime, ring opening reaction of \( \varepsilon \)-caprolactam, and hydrolysis reaction of CHO oxime. Since the CHO oxime molecule has a molecule size of ca. 0.73 nm, it is anticipated that Beckmann rearrangement reaction most likely occurs on the external surface of the 10-MR and 12-MR zeolites [23]. However, several reports [24,25] have indicated that such reactions may also take place within the intracrystalline voids of 12-MR zeolites, which possesses a pore aperture comparable to the size of CHO oxime molecule. Presumably, the rearrangement reaction of CHO oxime for \( \varepsilon \)-caprolactam production should be catalyzed by acid sites with medium acid strength (vide ante). As a result, the \( \varepsilon \)-caprolactam may undergo further reaction processes by re-adsorbing on the acid sites to yield undesired products [43]. Accordingly, the selectivity of \( \varepsilon \)-caprolactam is dictated by the relative rates of rearrangement reaction of CHO oxime versus ring opening reaction of \( \varepsilon \)-caprolactam and hydrolysis reaction of CHO oxime.

Shourot et al. [41] reported that the desorption temperatures of \( \varepsilon \)-caprolactam, cyclohexanone and nitriles in mesoporous FSM-16 molecular sieve are 650, 550, and 550–650 K, respectively. Among them, \( \varepsilon \)-caprolactam has the greatest adsorption strength, such material can be further converted to undesired products before desorbing from the surface of the adsorbent.

As mentioned earlier, the ring opening reaction of \( \varepsilon \)-caprolactam can be catalyzed by the strong acid sites of MFI zeolites [38]. Fig. 5 shows the IR spectra of coked H-MCM-22 sample (TOS = 24 h) after purging by flowing nitrogen. The absorption band at ca. 2300 cm\(^{-1}\) can be assigned due to 5-hexenenitrile (5-HEN), which contains a carbon-nitrogen triple (C≡N) bond. Accordingly, the identity of 5-HEN as the coke precursors can be deduced. This coke precursors may provoke further formation of carbonaceous deposits through a polymerization reaction whose rate should depend not only on the type of catalyst used but also on related reaction conditions, such as temperature, solvent, and carrier gas. It is intriguing to find that the carbonaceous residues so formed can readily be removed by raising the temperature above 773 K, under flow of oxygen-free gas. Presumably, a lower HEN yield would reflect a better catalytic stability.

Takahashi et al. [16] showed that the decay of a catalyst’s life in zeolites follows the trend: HY > Mordenite > MFI. Earlier, Burguet et al. [11] attributed the formation of cokes to polymerization of \( \varepsilon \)-caprolactam over ultrastable Y. In this context, the difference in coke properties between MCM-22 and Y may be due to their difference in framework structure and acidity. In particular, the interconnecting 10-MR windows adjacent to the 12-MR supercages should provoke additional hindrance to the diffusion of \( \varepsilon \)-caprolactam.

The variations of CHO oxime conversion and product selectivity with reaction time-on-stream are shown in Fig. 6. In terms of TOS, the catalytic stability can be divided into two distinct periods: one for stable conversion (period I) and the other for rapid aging (period II). However, one should note that the selectivity observed for various products remains practically unchanged during both periods, I and II. Interestingly, regardless of the level of conversion, the selectivity of CHO is always slightly lower than that of the sum of HEN and other products.

Encouraged by the high \( \varepsilon \)-caprolactam selectivity observed in H-MCM-22, additional experiments were performed in the presence of solvents, which are known to influence the product yields in zeolitic catalysts. Here, since the melting points of \( \varepsilon \)-caprolactam (342 K) and CHO oxime
\[ \text{CHO} \rightarrow \text{Cyclohexanone} \quad \text{100} \]

\[ \text{Ethanol} \quad \text{100} \]

\[ \text{Solvent Conversion} \quad \text{Selectivity} \]

\begin{tabular}{|c|c|c|c|}
\hline
Solvent & Conversion (%) & \(\epsilon\)-Caprolactam & Cyclohexanone & 5-Hexenitrile \\
\hline
Ethanol & 100 \(\rightarrow\) 97.5 & 82.2 \(\rightarrow\) 81.6 & 8.4 \(\rightarrow\) 8.5 & 9.6 \(\rightarrow\) 10.0 \\
Cyclohexanone & 100 \(\rightarrow\) 88.7 & 80.2 \(\rightarrow\) 78.9 & 8.8 \(\rightarrow\) 9.6 & 2.2 \(\rightarrow\) 1.9 \\
Benzene & 95.7 \(\rightarrow\) 70.4 & 73.5 \(\rightarrow\) 71.1 & 10.6 \(\rightarrow\) 12.1 & 13.5 \(\rightarrow\) 13.9 \\
\hline
\end{tabular}

\(^a\) Reaction conditions: pressure \(\equiv\) 1 atm; temperature \(\equiv\) 633 K; WHSV \(\equiv\) 3h\(^{-1}\); \(\text{H}_2/\text{feed} = 4 \text{ mol/mol}; \text{feed (CHO oxime/CHO)} = 6 \text{ mol/mol}. \)

\(^b\) The saturated nitrile (Hexamethylenitrile) in total nitrile (Hexamethylenitrile + 5-Hexenitrile) is 4.52 \(\rightarrow\) 5.87.

\(\epsilon\)-caprolactam selectivity and HAN product yield is much faster than the rate of CHO oxime and resulting in a better \(\epsilon\)-caprolactam yield. Previous studies have shown that \(\epsilon\)-caprolactam selectivity over ZSM-5 may be enhanced by either modifying the catalyst with chlorotrimethylsilane vapor [42] or in the presence of adsorbing water released from methanol solvent [37]; both of which can be attributed to the increase of nest silanol group concentration. Ethanol is known as the ideal solvent for 10-MR zeolites during Beckmann rearrangement reaction [18], whereas 1-hexanol is more favorable as a solvent for non-MFI zeolites, especially for 12-MR zeolites containing supercages [7,9]. Although Yashima et al. [19] reported that the presence of ethanol solvent tends to suppress \(\epsilon\)-caprolactam yield during Beckmann rearrangement over non-MFI zeolites, the results obtained in the present study show that it is an ideal solvent for MCM-22 zeolite. This may be due to the unique structure of MCM-22, which possesses 12-MR supercages interconnected by 10-MR windows, leading to a solvent effect analogous to 10-MR zeolites. The use of CHO solvent, which has not been reported before, was found to provoke \(\epsilon\)-caprolactam selectivity enhancement during Beckmann rearrangement over MCM-22, deserves further investigation (vide infra).

Although the ethanol solvent exhibits a higher stability than CHO, it is still expendable under the reaction conditions for Beckmann rearrangement. In contrast, CHO, being the major by-product, can be recycled to react with amine hydroxide to form CHO oxime. In view of the applications of a continuous and regenerative fluidized bed, or moving bed reactor to cope with the aging problem, CHO should be a more preferable candidate for solvent.

Most reports in the existing literature used nitrogen as the carrier gas for Beckmann rearrangement. In the present study, the catalytic performance of H-MCM-22 in the presence of nitrogen is also compared with that of hydrogen carrier gas. As shown in Table 3, in the presence of hydrogen, a much higher CHO selectivity and HAN product yield can be achieved at the expense of \(\epsilon\)-caprolactam selectivity. The higher observed HAN yield indicates that hydrogen carrier gas tends to promote hydrogenation reaction with the HEN coke precursor, which is an important intermediate during Beckmann rearrangement reaction of CHO oxime over H-MCM-22 (Fig. 4). Apparently, the surplus HAN will...
shift the equilibrium of ring opening reaction toward excess yields of HEN and water. Consequently, the higher water yield would alter the equilibrium of hydrolysis reaction of CHO oxime, thus resulting in a significant increase in the CHO yield. Upon further increase of reaction temperature to 653 K, a higher HAN and a lower HEN yield are observed, along with enhanced catalytic stability. Nevertheless, only a marginal increase in the observed stability enhancement was found when hydrogen is used as the carrier gas instead of nitrogen. As shown in Table 7, the product distribution is practically invariant with TOS under either hydrogen or nitrogen as the carrier gas. Chen et al. [43] reported that the catalytic activity for cumene disproportionation over β zeolite decreases in the order: of N₂ > H₂ > He > CO₂, while a reversed order was found for catalytic stability. It is anticipated that hydrogen molecules may shift the equilibrium of carbocation ion formation through hydrogenation reactions with reaction intermediates and/or coke precursors.

The effects of impregnated platinum on the stability of H-MCM-22 were also examined under a set of optimal operating conditions. As shown in Table 4, the product distribution over Pt/H-MCM-22 varies significantly from that obtained from H-MCM-22. In particular, besides the HEN product, incorporation of Pt tends to promote excess formation of HAN as a by-product through hydrogenation of HEN, and the selectivity of CHO is also increased at the expense of ε-caprolactam. The effect of the hydrogenation activity of Pt is therefore rather similar to that of the hydrogen carrier gas discussed before. That is, HEN hydrogenation and subsequent HAN formation tend to shift equilibria of ring opening and hydrolysis reactions, resulting in a higher CHO yield and a lower ε-caprolactam selectivity.

The optimal operating temperature range for Beckmann rearrangement of CHO oxime over solid acid catalysts was known to be from 573 to 673 K [3–22]. Fig. 8 shows the CHO oxime conversion and selectivity of ε-caprolactam versus operating temperature over H-MCM-22. As expected, the CHO oxime conversion was found to increase slowly with reaction temperature. However, the maximum selectivity of ε-caprolactam was observed at an optimal reaction temperature of ca. 655 K. The observed lower selectivity

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### Table 3

<table>
<thead>
<tr>
<th>Carrier gas</th>
<th>Temperature (K)</th>
<th>Duration period (h)</th>
<th>Selectivity (%)</th>
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</thead>
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<td></td>
<td></td>
<td></td>
<td>CPL</td>
</tr>
<tr>
<td>N₂</td>
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<td></td>
<td>653</td>
<td>45</td>
<td>81.1</td>
</tr>
</tbody>
</table>

* Reaction conditions: pressure = 1 atm; WHSV = 3 h⁻¹; feed (CHO oxime/CHO) = 0.1 mol/mol; carrier gas/feed = 4 mol/mol.

* A parameter for evaluation of catalyst stability, representing the time over which the catalyst can sustain a 100% CHO oxime conversion.

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### Table 4

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Selectivity (%)</th>
</tr>
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<tr>
<td></td>
<td>CPL</td>
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<tr>
<td>H-MCM-22</td>
<td>81.1</td>
</tr>
<tr>
<td>Pt/H-MCM-22</td>
<td>68.9</td>
</tr>
</tbody>
</table>

* Reaction conditions: pressure = 1 atm; temperature = 653 K; WHSV = 3 h⁻¹; H₂/feed = 4 mol/mol; feed (CHO oxime/CHO) = 0.1 mol/mol.

---

### Fig. 7

Effects of N₂ and H₂ carrier gases on variations of CHO oxime conversion and ε-caprolactam selectivity during Beckmann rearrangement reaction over H-MCM-22 zeolite. Reaction conditions: pressure = 1 atm; temperature = 633 K; WHSV = 3 h⁻¹; carrier gas/feed = 4 mol/mol; feed (CHO oxime/CHO) = 0.1 mol/mol.

### Fig. 8

Variations of CHO oxime conversion and product selectivity with reaction temperature during Beckmann rearrangement reaction over H-MCM-22 zeolite. Reaction conditions: pressure = 1 atm; WHSV = 3 h⁻¹; N₂/feed = 4 mol/mol; feed (CHO oxime/CHO) = 0.1 mol/mol.
of ε-caprolactam at higher temperature is attributed to the increasing secondary conversion of ε-caprolactam with the formation of other by-products or coke precursors, as illustrated in Fig. 4. On the other hand, ε-caprolactam, being the strongest adsorbate species, typically requires a desorption temperature of about 650 K. Thus, the lower ε-caprolactam selectivity observed at lower temperature should arise from the strong desorption of ε-caprolactam on the acid sites, and the occurrence of its secondary conversion into other products. The CHO oxime conversions versus TOS over H-MCM-22 at various temperatures are shown in Fig. 9. It is clear that nearly 100% CHO oxime initial conversion is obtained when a reaction temperature exceeding 613 K is reached. Interestingly, the H-MCM-22 catalyst becomes more stable with increasing the temperature up to 653 K.

Table 5 shows the catalyst stability and product distribution under various N₂ carrier gas to feed molar ratios (0–8) at a reaction temperature of 633 K. While the CHO oxime conversion is less than 100% in the absence of carrier gas (N₂/feed ratio = 0), the catalytic stability and selectivity of ε-caprolactam are found to increase with increasing N₂/feed molar ratio or at a lower partial pressure of CHO oxime. Furthermore, as shown in Table 6, upon increasing the CHO oxime/CHO molar ratio from 0.10 to 0.22, a lower catalytic stability was evident. As a result, the duration period decreases markedly from 16 to 4 h, and the selectivity of ε-caprolactam also degrades from 85.3 to 75.6%. Finally, the effect of space velocity (WHSV) on the conversion of CHO oxime and product selectivity was also examined. As shown in Fig. 10, while the stability of the catalyst degrades sharply with increasing WHSV, only a slight decrease in selectivity of ε-caprolactam was observed.

### Table 5: Effects of N₂/feed molar ratio catalyst stability and product selectivity over H-MCM-22

<table>
<thead>
<tr>
<th>N₂/feed ratio (mol/mol)</th>
<th>Duration period (h)</th>
<th>Selectivity (%)</th>
<th>CPL</th>
<th>CHO</th>
<th>HEN</th>
<th>Others</th>
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<tr>
<td>0</td>
<td>–</td>
<td>71.6</td>
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<td>12.6</td>
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<td>1</td>
<td>11</td>
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<td>2</td>
<td>26</td>
<td>85.3</td>
<td>6.0</td>
<td>1.7</td>
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<tr>
<td>4</td>
<td>28</td>
<td>92.2</td>
<td>3.8</td>
<td>1.5</td>
<td>2.5</td>
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</tr>
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</table>

* Reaction conditions: pressure = 1 atm; temperature = 633 K; WHSV = 3 h⁻¹; N₂/feed = 4 mol/mol; feed (CHO oxime/CHO) = 0.1 mol/mol.

### Table 6: Effect of CHO oxime concentration on catalyst stability and product selectivity over H-MCM-22

<table>
<thead>
<tr>
<th>CHO oxime concentration (mol/mol)</th>
<th>Duration period (h)</th>
<th>Selectivity (%)</th>
<th>CPL</th>
<th>CHO</th>
<th>HEN</th>
<th>Others</th>
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</thead>
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<tr>
<td>0.10</td>
<td>16</td>
<td>85.3</td>
<td>6.0</td>
<td>1.7</td>
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<tr>
<td>0.22</td>
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<td>75.6</td>
<td>12.0</td>
<td>5.1</td>
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</table>

* Reaction conditions: pressure = 1 atm; temperature = 633 K; WHSV = 3 h⁻¹; N₂/feed = 4 mol/mol; feed (CHO oxime/CHO) = 0.1 mol/mol.

* Represents CHO oxime/CHO molar ratio.

* A parameter for evaluation of catalyst stability, representing the time over which the catalyst can sustain a 100% CHO oxime conversion.

4. Conclusions

A comprehensive study has been made of the effects of operating conditions, viz reaction temperature, carrier gas, reactant concentration, solvent, and WHSV, on catalytic stability and performance of MCM-22 zeolite during Beckmann rearrangement reaction over H-MCM-22 zeolite. Reaction conditions: pressure = 1 atm; temperature = 633 K; WHSV = 3 h⁻¹; N₂/feed = 4 mol/mol; feed (CHO oxime/CHO) = 0.1 mol/mol.
For H-MCM-22 zeolite, optimal performances can be obtained under ambient pressure, reaction temperature ranging from 633 to 653 K, and WHSV = 3 h⁻¹ in the presence of CHO solvent (CHO oxide/CHO ratio = 0.1 mol/mol) and hydrogen carrier gas (H₂/feeding > 4 mol/mol). As the result, the achievable stability of H-MCM-22 was about two days. Both the incorporation of platinum and the use of hydrogen as the carrier gas tend to catalyze the hydrogenation of 5-hexenenitrile and favor ring opening and hydrolysis reactions, resulting in higher cyclohexanone yield and ε-caprolactam selectivity. It is also concluded that the selectivity of ε-caprolactam and the catalytic stability of H-MCM-22 may be improved by operating at a specified reaction temperature of ca. 653 K and particularly by using cyclohexanone or ethanol as the solvent of CHOoxime feed. By comparing with existing reports for 12-MR zeolites, we conclude that the effect of ethanol solvent over H-MCM-22 is different from that of 10-MR zeolites.

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References