Catalytic application of mesoporous molecular sieves to vapor-phase Beckmann rearrangement of cyclohexanone oxime

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The vapor-phase Beckmann rearrangement of cyclohexanone oxime to ε-caprolactam catalyzed by mesoporous molecular sieves was studied. The proton-form mesoporous molecular sieves, H-MCM-41 and H-FSM-16, exhibited extremely high activity, selectivity and stability for ε-caprolactam formation when 1-hexanol was used as diluent. The weak acid sites and/or surface silanol groups of mesoporous molecular sieves play an important role in the selective ε-caprolactam formation.

Keywords: Beckmann rearrangement, mesoporous molecular sieves, MCM-41, FSM-16, alcohol diluent effect, 1-hexanol

Recently, the discovery of a new family of mesoporous molecular sieves, named M41S and FSM (folded sheets mesoporous materials), was almost simultaneously reported [1,2]. MCM-41 or FSM-16, one of the members of this family, possesses a hexagonal arrangement of unidimensional mesopore channels varying from 15 to 100 Å. High thermal stability, large sorption capacity, and high surface area render this material very interesting for catalysis. So far, however, despite these very promising properties, the number of studies dealing with the catalytic application of the mesoporous materials is still very limited [3–5].

The vapor-phase Beckmann rearrangement of cyclohexanone oxime to ε-caprolactam has been studied for a wide variety of solid acid zeolites [6–14]. Aucejo et al. reported [6] that the strong Brønsted acidity of the zeolite catalysts is responsible for the formation of ε-caprolactam. However, a majority of researchers suggested that the weak or intermediate-strength acid sites [7–10] or even neutral silanol groups present on the external surface of the zeolites [11] are effective for this rearrangement, while the strong acid sites accelerate the formation of by-products [12,13]. Recently, we have found that, when 1-hexanol was used as diluent, the H-BEA zeolite with medium-strength acidity exhibited excellent catalytic performance in this reaction [14]. Since the mesoporous material MCM-41 or FSM-16 has a large amount of surface SiOH groups [15] and its acidity is considerably weak [16,17], an attempt has been undertaken in the present study to apply mesoporous molecular sieves to the vapor-phase Beckmann rearrangement of cyclohexanone oxime. The alcohol diluent effect was also investigated to improve the catalytic performance of molecular sieves.

Na-form mesoporous materials FSM-16(40) and FSM-16(640) were used in this study. Aluminosilicate MCM-41(38) was synthesized by modifying the method described by Chen et al. [17]. The number in parentheses presents the SiO_2/Al_2O_3 ratio. The proton-forms of mesoporous materials, H-FSM-16(40), H-FSM-16(640) and H-MCM-41(38), were obtained by ion exchange of their Na-form with NH_4Cl aqueous solution followed by calcination at 773 K. As a reference, amorphous silica–alumina, Si–Al(50), was also synthesized. Unless otherwise indicated, all the samples were compressed at 880 kg/cm^2 in a steel die of 20 mm diameter by a pressing apparatus. The rearrangement reaction was carried out using a continuous-flow reactor made of stainless steel operated at ambient pressure. The feed cyclohexanone oxime was dissolved in methanol or 1-hexanol and injected with a syringe pump along with N_2 as a carrier gas. The reaction conditions were as follows: reaction temperature of 623 K, 0.1 MPa, oxime : diluent : N_2 molar ratio of $1:9:5.9$ and W/F of 80 $g_{cat}\,h\,mol_{oxime}^{-1}$. The collected reaction products were analysed by a gas chromatograph equipped with a 4 m long packed column of silicone SE-52 (5%). Acidity measurements were performed by temperature-programmed desorption of ammonia using a Bel Japan Multitask-TPD analyzer. The sample (50 mg) was pretreated in a helium stream (50 ml min^{-1}) at 773 K for 1 h and then exposed to 20 Torr of NH_3 for 15 min at 373 K. Subsequently, the sample was outgassed at the same temperature for 1 h in vacuum. The desorption of NH_3 was measured on mass number 16 by Q-Mass detector from 373 to 873 K at a heating rate of 10 K min^{-1}. Helium was used as carrier gas with a flow rate of 50 ml min^{-1}. The total amount of acidity was calibrated by referring the desorption from the standard sample (JRC-25) with a known amount of strong acid sites. IR spectra were recorded at room temperature on a Perkin-Elmer 1600 FT-IR instrument on self-supported H-FSM-16 pellets, which had been treated for 4 h in refluxing methanol or 1-hexanol at 353 K.

In figure 1, the conversion of cyclohexanone oxime and selectivity to ε-caprolactam, when methanol was used

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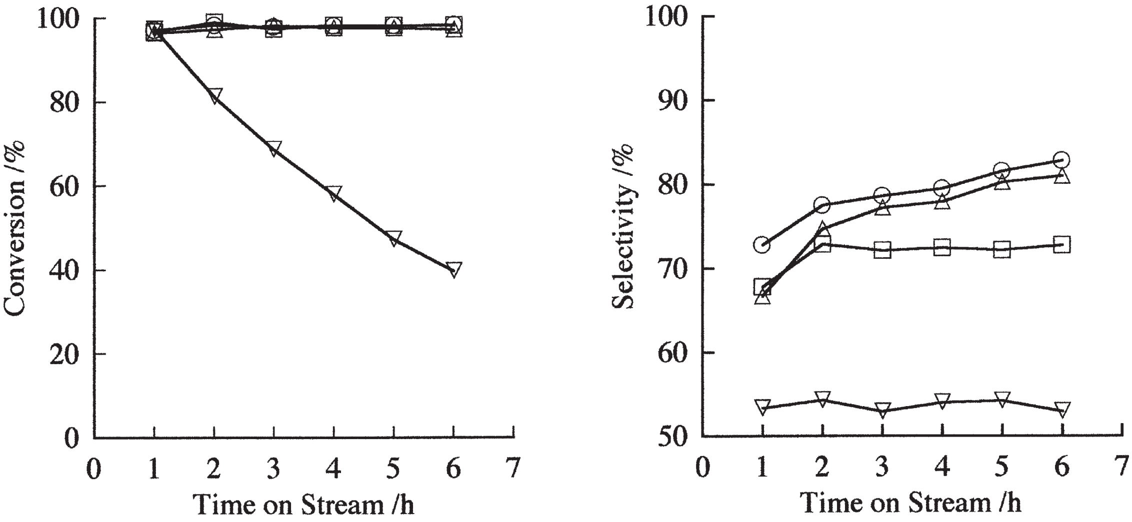
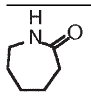
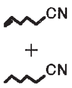
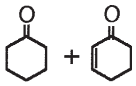


Figure 1. Change in conversion and selectivity with time on stream in the vapor-phase Beckmann rearrangement of cyclohexanone oxime. (○) H-MCM-41(38); (△) H-FSM-16(40); (▽) H-FSM-16(640); (□) Si–Al(50). $T = 623$ K, $P = 0.1$ MPa, oxime : methol : $N_2 = 1:9:5.9$ (molar), $W/F = 80\ g_{cat}\,h\,mol^{-1}_{oxime}$.

Table 1
Products distribution in vapor-phase Beckmann rearrangement reaction.[a]

Catalyst (SiO$_2$/Al$_2$O$_3$)	Acid amount (μmol/g)	Diluent	Conv. (%)	Selectivity (%)			
							Others[b]
H-MCM-41(38)	718	methanol	98.1	82.7	7.0	6.1	4.2
H-FSM-16(40)	532	methanol	97.0	80.9	7.1	6.5	4.5
H-FSM-16(640)	26	methanol	39.6	52.9	22.2	13.6	11.3
Si–Al(50)	257	methanol	98.0	72.7	9.3	10.8	7.2
H-MCM-41(38)	718	1-hexanol	99.8	92.0	2.4	1.7	3.9
H-MCM-41(38)[c]	746	1-hexanol	99.9	93.0	2.4	2.3	2.3
H-FSM-16(40)	532	1-hexanol	99.9	91.1	2.7	1.8	4.4
H-FSM-16(40)[c]	607	1-hexanol	99.9	94.7	2.0	2.3	1.0
H-FSM-16(640)	26	1-hexanol	96.5	90.4	4.4	2.6	2.6
Si–Al(50)	257	1-hexanol	99.8	84.2	4.1	6.7	5.0

[a] Reaction conditions: 623 K, 0.1 MPa, oxime : diluent : $N_2 = 1:9:5.9$ (molar), $W/F = 80\ g_{cat}\,h\,mol^{-1}_{oxime}$ and time on stream = 6 h.

[b] Mostly dimers.

[c] The samples were compressed at 1760 kg/am^2.

as diluent, are plotted against time on stream. Stable (>95%) conversion was attained, and no decrease in conversion with time on stream was observed for H-MCM-41(38), H-FSM-16(40) and Si–Al(50) catalysts. Although initially the conversion on H-FSM-16(640) was close to that on H-FSM-16(40), it decayed rapidly to about 40% after 6 h on stream. The selectivity to ε-caprolactam gradually increased for H-MCM-41(38) and H-FSM-16(40) catalysts during 6 h reaction and was practically constant for H-FSM-16(640) and Si–Al(50) samples after 2 h. At 6 h of time on stream, ε-caprolactam selectivity on the catalysts decreased in the order H-MCM-41(38) > H-FSM-16(40) > Si–Al(50) > H-FSM-16(640). Other by-products observed in this study included cyclohexanone, 2-cyclo-1-hexenone, 5-cyanopentane and 5-cyano-1-pentene. The amounts of these by-products observed after 6 h on stream are presented in table 1. The catalysts can be arranged in the following increasing orders for the selectivities for the by-products:

5-cyanopentane plus 5-cyano-1-pentene:

H-MCM-41(38) < H-FSM-16(40) < Si–Al(50) $\ll$ H-FSM-16(640);

cyclohexanone plus 2-cyclo-1-hexenone:

H-MCM-41(38) $\sim$ H-FSM-16(40) < Si–Al(50) < H-FSM-16(640);

others (mostly dimers):

H-MCM-41(38) $\sim$ H-FSM-16(40) < Si–Al(50) < H-FSM-16(640).

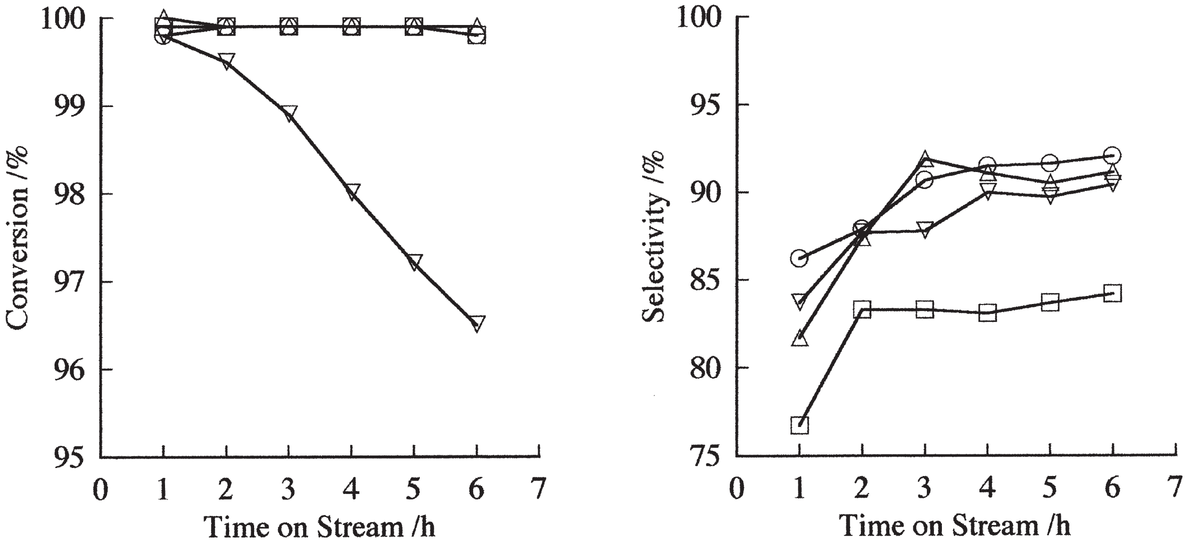


Figure 2. Change in conversion and selectivity with time on stream in the vapor-phase Beckmann rearrangement of cyclohexanone oxime. (○) H-MCM-41(38); (△) H-FSM-16(40); (▽) H-FSM-16(640); (□) Si–Al(50). $T = 623$ K, $P = 0.1$ MPa, oxime : 1-hexanol : $N_2 = 1:9:5.9$ (molar), $W/F = 80\ \mathrm{g_{cat}\,h\,mol_{oxime}^{-1}}$.

When 1-hexanol was fed with cyclohexanone oxime in place of methanol, the performance of the catalysts was greatly improved, as shown in figure 2. Especially, the activity and stability of H-FSM-16(640) remarkably increased. H-FSM-16(640) catalyst exhibited ca. 97% oxime conversion after 6 h, and the other catalysts showed almost 100% conversion for 6 h of time on stream. The selectivity for ε-caprolactam formation on these catalysts increased to a different extent as a result of the use of 1-hexanol diluent; the enhancement of selectivity on H-FSM-16(640) was more remarkable than that on the others. The selectivity for ε-caprolactam decreased in the order H-MCM-41(38) > H-FSM-16(40) > H-FSM-16(640) > Si–Al(50) after 3 h on stream. As shown in table 1, for all the catalysts the formation of three types of by-products were simultaneously retarded by the use of 1-hexanol diluent, resulting in the increase in the activity and selectivity for ε-caprolactam formation. It is noteworthy that both H-MCM-41(38) and H-FSM-16(40) mesoporous molecular sieves exhibited higher selectivity to ε-caprolactam than amorphous Si–Al(50), irrespective of diluents.

The difference in the catalytic performance of mesoporous molecular sieves may be ascribed to the difference in their acidity and hydrophilicity/hydrophobicity. Figure 3 shows NH_3-TPD curves. Inferior performance of the H-FSM-16(640) catalyst should be due to insufficient amount of weakly acidic sites compared to the other samples. The fact that the activity and selectivity to ε-caprolactam on H-MCM-41(38) were slightly higher than those on H-FSM-16(40) might be due to the slightly larger amount of weak acid sites on the former than on the latter. These results confirm the proposition that sufficient amount of weak acid sites are of importance to the vapor-phase Beckmann rearrangement [7,8]. One of the effects of 1-hexanol diluent is to extend the catalyst life (figure 2), especially for H-FSM-16(640) with a small amount of acidity.

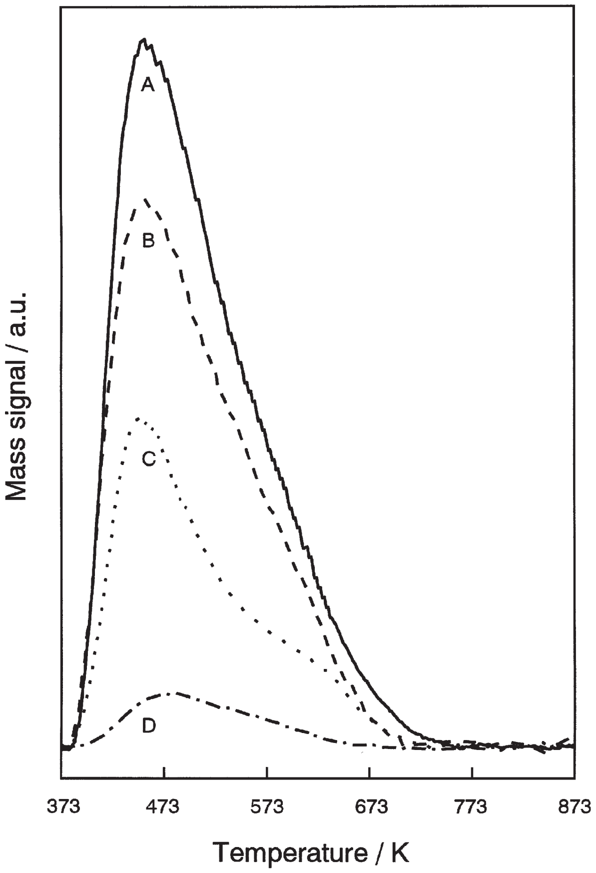


Figure 3. NH_3-TPD profiles of various catalysts. (A) H-MCM-41(38); (B) H-FSM-16(40); (C) Si–Al(50); (D) H-FSM-16(640).

As shown in table 1, H-MCM-41(38) and H-FSM-16 (40) catalysts, pressed at 1760 kg/cm^2, exhibited higher

ε-caprolactam selectivity than those pressed at 880 kg/cm^2, respectively. Since the surface silanol groups of MCM-41 [18] and FSM-16 [19] mesoporous materials are known to increase with increasing compression pressure, this result is in agreement with what has been reported for MFI zeolites [11]: the silanol groups play an important role in the selective ε-caprolactam formation. It is noteworthy that the acid amount slightly increased by compressing the sample at high pressure, as shown in table 1. It should be noted that the sharp distribution of the pore size was kept and the average pore size remained unchanged, while the pore volume decreased with increasing applied pressure [20].

From an FT-IR study of H-FSM-16(40) and H-FSM-16(640) mesoporous materials treated with methanol (not shown), we found that the free Si–OH band at 3740 cm^{-1} decreased in intensity. This was accompanied by appearance of bands at 2997, 2959, 2930 and 2856 cm^{-1}. These bands can be attributed to ν(C–H) bands of the methoxy group Si–OCH$_3$ [21–24], indicating that esterification of the surface hydroxyl groups with methanol molecules took place: $\mathrm{Si{-}OH} + \mathrm{CH_3OH} \rightarrow \mathrm{Si{-}OCH_3} + \mathrm{H_2O}$. Another assignment of the new bands in the range of 3000–2850 cm^{-1} is the presence of an interaction of methanol molecules with the surface OH groups via strong hydrogen bonds [22]. Comparison of the intensities of the bands remaining after outgassing at the same temperature revealed that the adsorption of methanol on H-FSM-16(40) was stronger than that on H-FSM-16(640). Similar FT-IR spectra indicating the esterification by and/or the interaction with 1-hexanol were also obtained for both of the H-FSM-16 samples treated with 1-hexanol. In this case, however, the adsorption of 1-hexanol on H-FSM-16(640) was slightly stronger than that on the H-FSM-16(40) sample.

Since the adsorption of hydrophilic methanol on hydrophilic H-FSM-16(40) or H-MCM-41(38) surface (H-MCM-41(38) should be similar to H-FSM-16(40) in hydrophilicity) was relatively strong as described above, the active sites might be prevented from contacting with the reactant in the presence of methanol, resulting in low selectivity to ε-caprolactam (table 1). These results are consistent with the observation by Landis and Venuto, who reported that such a polar diluent as methanol might block contact of reactant with the zeolite acid sites by competitive adsorption [25]. In contrast, H-FSM-16(640) with a trace amount of Al can be regarded as hydrophobic compared to H-FSM-16(40). The combination of methanol with surface active sites of the H-FSM-16(640) sample seems to be relatively weak, as revealed by change in FT-IR spectra with increasing outgassing temperature; the reactant oxime might adsorb on the surfaces strongly and undergo a series of reactions, resulting in the increase in the selectivity for by-products (including dimers) and a rapid deactivition of the catalyst (even though the initial activity was considerably high). Since the interaction of 1-hexanol on H-FSM-16(40) and H-FSM-16(640) could be appropriate compared to methanol/H-FSM-16(40) and methanol/H-FSM-16(640) systems, the active sites for the formation of by-products would be effectively covered with 1-hexanol, resulting in the increase in the activity, selectivity and stability for ε-caprolactam formation.

The present study has revealed that the proton-form mesoporous molecular sieves, H-MCM-41 and H-FSM-16, exhibited extremely high activity, selectivity and stability for ε-caprolactam formation when 1-hexanol was used as diluent. The weak acid sites and/or surface silanol groups of mesoporous molecular sieves are effective for the vapor-phase Beckmann rearrangement of cyclohexanone oxime.

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