Vapor phase Beckmann rearrangement of cyclohexanone oxime over different ferrierite zeolite catalysts

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Ferrierite zeolite catalysts prepared using different procedures have been tested for their activity for vapor phase Beckmann rearrangement of cyclohexanone oxime to ϵ-caprolactam. We report here the results of a study seeking the influence of temperature, nitrogen feed rate, oxime concentration and solvents on the catalyst performance. At low concentration of oxime (2.5 wt%), using acetonitrile as solvent the maximum in the conversion of oxime and selectivity to ϵ-caprolactam has been obtained. The presence of weak, medium and strong acid sites as indicated by temperature-programmed desorption of NH_3 corroborates well with the catalytic activities of various ferrierites shown here. Solvent polarity is found to significantly affect the conversion of cyclohexanone oxime.

KEY WORDS: ferrierite; cyclohexanone oxime; Beckmann rearrangement; TPD; acetonitrile

1. Introduction

ϵ-caprolactam is used as a monomer for Nylon-6 fibers, engineering plastics and for the preparation of L-lysine, which is an essential ingredient in animal food. Conventional methods of preparation of ϵ-caprolactam involve treating cyclohexanone oxime with concentrated sulfuric acid or phosphoric acid as the catalyst and followed by neutralization with liquid ammonia. The process suffers from a number of disadvantages, such as the requirement of a large quantity of ammonia for the neutralization of sulfuric acid, separation of ϵ-caprolactam from the product mixture, undesirable large quantities of ammonium sulfate or ammonium phosphate rather than the desired ϵ-caprolactam and equipment corrosion due to concentrated acids.

To overcome these problems, a vapor phase Beckmann rearrangement of cyclohexanone oxime using various solid catalysts has been extensively investigated. The solid acid catalysts tested for this reaction include alumina-supported boria [1] ZSM-5 [2], [B]-ZSM-5 [3] silicalite-1 [4] TS-1 [5], FER and LTA [6,7], SAPO-11 [8] and Al_2O_3-supported B_2O_3 [1,9]. It has been reported that the highly siliceous ZSM-5 [10] zeolite and ZSM-5 modified by boron showed high activity and selectivity for this reaction [11,12]. It is also established that relatively strong acid sites are necessary for the Beckmann rearrangement. Recently, Kim *et al.* have studied the vapor phase Beckmann rearrangement for cyclohexanone oxime over a tantalum pillared-ilerite [13]. Butler *et al.* [14] have used the H-Y and H–Pd-Y as catalysts and found that highly-proton-exchanged zeolites were active and selective for this rearrangement. Ko *et al.* [15]

have also studied the vapor phase Beckmann rearrangement of cyclohexanone oxime using an Al-MCM-41 mesoporous molecular sieve. Dahlhoff *et al.* [16] have carried out the reaction over MCM-22. Yashima *et al.* [7] have studied the vapor phase rearrangement of cyclohexanone oxime on the different zeolite catalysts and reported relatively low cyclohexanone conversion (76 mol%) and selectivity (61 mol%) towards ϵ-caprolactam over ferrierite catalyst.

In this study, we synthesized different types of ferrierite catalysts in the presence of nonionic surfactants at low concentration of pyrrolidine template. The purpose of this study is to clarify the influence of various ferrierite zeolite catalysts synthesized under different conditions on the oxime conversion and selectivity for ϵ-caprolactam formation. The application of ferrierite zeolite is expected to give better results due to its acidic nature and stable performance compared with other hydrocarbon conversion reactions.

2. Experimental

2.1. Catalyst preparation

The vapor phase Beckmann rearrangement of cyclohexanone oxime to ϵ-caprolactam was investigated over five different FER zeolite catalysts, *viz.*, (i) H-FER, (ii) St-H-FER, (iii) Si–H-FER, (iv) H-FER-TT and (v) H-FER-TE. The last two were synthesized in the presence of non-ionic surfactants Tween-20 and Tween-80, respectively, according to the procedure reported earlier [19]. In what follows we shall briefly describe the synthesis procedures.

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2.1.1. H-FER [17]

52.5 g of sodium silicate (in 25 ml of distilled water) was stirred with 10 ml pyrrolidine. To this solution, 2.4 g of aluminum sulfate hexadecahydrate (in 25 ml distilled water) and 1.8 g of sulfuric acid (in 10 ml distilled water) was added. Finally, 30 ml of distilled water was added and the gel (pH $= 11.5 \pm 0.2$) was stirred vigorously for 2 h and autoclaved in a 300 ml stainless-steel Parr autoclave (4842, 300 ml) and heated at $160\,^\circ$C for 60 h. The initial gel composition was:

$$20\,Na_2O : Al_2O_3 : 37\,\text{pyrrolidine}:$$
$$66.5\,SiO_2 : 6.3\,H_2SO_4 : 1460\,H_2O.$$
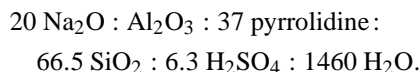
The autoclave was quenched, filtered, and washed and the product was dried at $100\,^\circ$C for 6–8 h. The resulting material was calcined in air at $550\,^\circ$C for 18–20 h. Two more ferrierite samples were prepared using same procedure given above but varying the SiO_2/Al_2O_3 ratio.
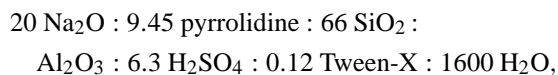
2.1.2. Steaming of H-FER

Dealuminated H-FER was prepared by subjecting it to heating in steam at $550 \pm 10\,^\circ$C for 2–3 h. This steamed sample was then acid treated by making slurry of the powder in 10% oxalic acid solution at 80–$90\,^\circ$C for 2 h. The sample was filtered, repeatedly washed with demineralized water, dried and finally calcined in the presence of air current at a temperature of $550\,^\circ$C for 6–8 h. The sample so prepared exhibits an excellent hydrothermal stability.

2.1.3. Si–H-FER [18]

The organothermal synthesis of siliceous ferrierite was carried out according to the procedure described by Kuperman et al. [18].

2.1.4. H-FER-TE and H-FER-TT [19]

0.00092 moles of Tween-80 or Tween-20 was dissolved in 3 ml pyrrolidine and added to 52.5 g of sodium silicate containing 30 ml of distilled water under vigorous stirring. The gel was stirred for 1 h. To this solution 2.4 g of aluminum sulfate hexadecaanhydrate in 30 ml water and 1.8 g of sulfuric acid (in 10 ml water) was added dropwise resulting in the formation of a thickened gel. Finally, 20 ml of water was added to this thickened gel, stirred for 1 h and transferred to a 300 ml stainless-steel autoclave and put into the preheated oven at $160 \pm 2\,^\circ$C for 35 h. The autoclave was quenched in cool tap water and the precipitate was filtered, washed with distilled water and dried at $100\,^\circ$C. The input gel molar composition was as follows:

$$20\,Na_2O : 9.45\,\text{pyrrolidine} : 66\,SiO_2 :$$
$$Al_2O_3 : 6.3\,H_2SO_4 : 0.12\,\text{Tween-X} : 1600\,H_2O,$$

where X $= 20, 80$. The synthesized sample was then calcined in air at $550\,^\circ$C at the rate of $2\,^\circ$C/min for 15 h. Two more ferrierite samples were prepared using same concentration of Tween-80 but varying the SiO_2/Al_2O_3 molar ratio using a similar procedure.

It is observed that nonionic surfactants play an important role during the crystallization of ferrierite. The use of nonionic surfactant offers the following advantages:

(1) Drastically reduces the requirement of hazardous template (pyrrolidine).

(2) Ferrierite of uniform size can be crystallized in good yield and without impurity of any other phase.

(3) The effect of varying the concentration of nonionic surfactant for the gel having same input SiO_2/Al_2O_3 molar ratio can change (a) the output SiO_2/Al_2O_3 molar ratio of the ferrierite product, (b) particle size of ferrierite crystallites and (c) surface area of the ferrierite product.

2.2. Characterization

The extent of crystallization and phase purity was evaluated for all the FER samples by recording X-ray diffractograms using Cu Kα radiation (Philips Analytical, PW1710, $\lambda = 1.54056$ Å). The XRD patterns were recorded in the 2θ range at 5°–50°. The degree of crystallinity of the ferrierite samples was estimated by measuring the peak area of the characteristic diffraction peaks at $2\theta = 8.9^\circ$ and between 22° and 25.5°. The framework IR vibration spectra (400–1400 cm^{-1}) of FER samples were recorded using a Perkin–Elmer 221 spectrophotometer. The chemical compositions of ferrierite products were measured using wavelength dispersive XRF (3070, Rigaku). Nitrogen adsorption measurements were performed to estimate BET surface area and pore diameter (Omnisorb 100CX, Coulter, USA) of ferrierite zeolite at room temperature and a relative pressure (P/P_0) range between 0.005 and 0.05. About 200 mg of calcined sample was degassed at a pressure better than 10^{-5} Torr at $450\,^\circ$C before adsorption measurements. The morphology and the habit of the crystalline phase of ferrierite product were examined on a Leica Sterioscan 440 model, manufactured by M/s Cambridge Leica Ltd. The micrographs of the samples were recorded by a 35 mm camera attached to the high-resolution recording unit with a 10 kV EHT and a 50 μA beam current.

2.3. Temperature-programmed desorption of ammonia

The temperature-programmed desorption (TPD) of ammonia was performed in order to determine the distribution of strong acid sites on the catalysts. The analysis was carried out in an Autochem 2910 instrument (Micromeritics, USA). The carrier gas used was He, flowing at a rate of 50 ml/min. The desorption process was monitored by a TCD detector. About 0.4 g of the calcined catalyst was used for each experiment. Prior to the analysis, the catalyst sample was pretreated in situ for 2 h in a He flow (30 ml/min) at $450\,^\circ$C. Adsorption of ammonia was performed by passing a He stream with ammonia vapor over the catalyst for 30 min. The adsorption process was carried out at $80\,^\circ$C. In order to eliminate physically adsorbed ammonia, after the adsorption of ammonia, the sample was flushed with the carrier gas at

105 °C for another 1 h. The TPD profile of ammonia was obtained from 50 to 700 °C at a heating rate of 10 °C/min.

2.4. Reactor and experimental setup

The powdered catalysts are pressed, pelleted, crushed and sieved to obtain 10–20 mesh particles. All the reactions are carried out at atmospheric pressure in a fixed-bed down-flow reactor. About 3 g of catalyst was placed in a cylindrical glass reactor (1.5 cm id; 30 cm length), having a thermowell of 4 mm at the centre. The catalyst was packed in-between inert ceramic beeds in such a way that the thermowell top was at the centre of the catalyst bed. Also the portion above the catalyst bed served as a preheater. The reactor was placed in a constant temperature zone of an electrically heated furnace. The catalyst was activated at 500 °C for 5 h in a flow of dry air. The catalyst was then flushed with dry nitrogen and cooled to the desired temperature. The cyclohexanone oxime was dissolved in acetonitrile (10 wt%) and injected using a high precision feed pump (ISCO, model 500D, USA) at the required rate. Nitrogen was used as a carrier gas. The reactions were carried out at different temperatures between 300 and 450 °C. The liquid products were analyzed by gas chromatography (HP 6890 series, fitted with HP-1 capillary column and FID as detector, the carrier gas being nitrogen) and GCMS (QP 2000A, Shimadzu SE-52 column, non-polar silicon fluid).

3. Results and discussion

The XRD data shows that the samples are fully crystalline and pure phase. Framework IR spectra of various FER zeolites showed two bands around 1220 and 580 cm^{-1}. These two bands can be attributed to the vibrations within the ferrierite framework. Table 1 shows the physico-chemical characteristics of the FER samples.

Acid strength distribution can be derived from the rate of desorption of chemisorbed ammonia as temperature is raised. The results of the NH$_3$-TPD measurements are depicted in figure 1. The zeolite releases ammonia over a wide temperature range. It is a reported fact that the difference in the catalytic performance of zeolites is due to the difference in their acidity. Three peaks were observed, in figure 1, peaks were observed around at 225, 432 and 573 °C for both

Table 1
Physico-chemical properties of ferrierite

Catalyst	Gel SiO$_2$/ Al$_2$O$_3$ ratio	Product SiO$_2$/ Al$_2$O$_3$ ratio[a]	BET surface area (m^2/g)	Average particle size (μm)
H-FER	66	34	335.5	[b]
St-H-FER	–	73	262.5	–
Si-FER	–	–	119.2	–
H-FER-TE	66	29	327	1
H-FER-TT	66	31	225.3	3

[a] From XRF.
[b] Irregular polycrystalline mixture of small and large particles [17].

H-FER and St-H-FER corresponding to weak, medium and strong acid sites. For increasing SiO$_2$/Al$_2$O$_3$ ratio (from 34 to 73) the total number of acid sites corresponding to both types, weak as well as strong, decreases as the area under the curve decreases. According to Topsøe *et al.* [20], the TPD peak around 500 °C (550 °C in the case of FER) is due to Brønsted acid sites. An additional observation is the shift in the TPD peak to the lower temperature as the silica to alumina ratio increases. In the case of H-FER-TT (237.7 and 505.8 °C) and H-FER-TE (240 and 533 °C), in the temperature range studied, the figure shows the presence of only two peaks. It can also be seen from the figure that the peaks for Lewis acid sites for H-FER-TE and H-FER-TT have been shifted towards higher temperature, and hence these two samples show better performance at 450 °C.

The vapor phase Beckmann rearrangement of cyclohexanone oxime mainly yielded ε-caprolactam, the by-products being cyclohexanone, cyclohexenone, 1-cyano-pentane and 1-cyanopentene and polymer of ε-caprolactam, which was shown in the tables under "others".

3.1. Effect of reaction time

The oxime conversion and selectivity of ε-caprolactam with time is shown in figure 2. The catalyst activity and product selectivity reached an equilibrium level after 3–4 h and hence all the experimental data were obtained after the stabilization of the activity. The effects of different parameters on the conversion of oxime and selectivities of different products are discussed below.
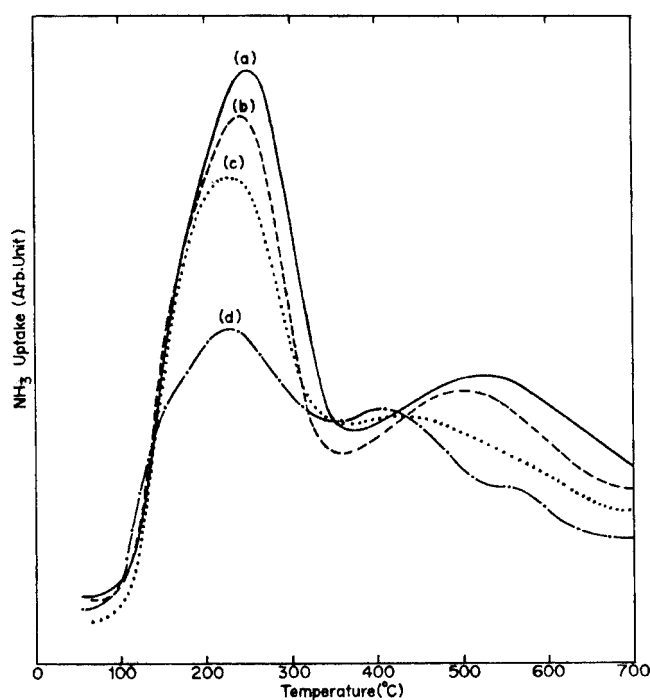

Figure 1. NH$_3$-TPD spectra of ferrierite catalysts: (a) H-FER-TE, (b) H-FER-TT, (c) H-FER and (d) St-H-FER.
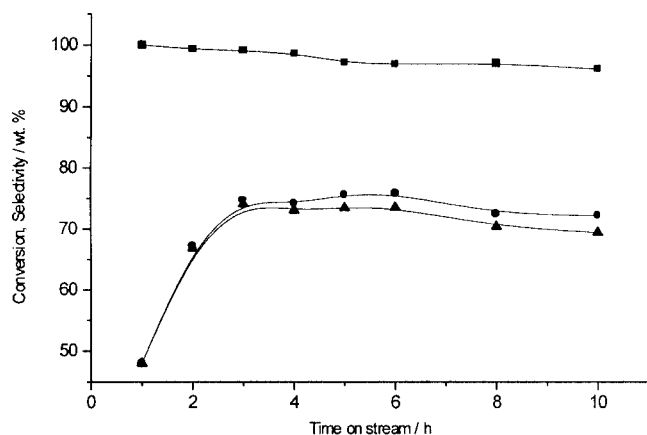
Figure 2. Influence of time on the conversion and selectivity for Beckmann rearrangement of cyclohexanone oxime over H-ferrierite (■) conversion, wt% of oxime; (●) selectivity, wt% of caprolactam; (▲) yield, wt% of caprolactam. Reaction conditions: temperature $= 400\,°C$, pressure $= 1$ atm, WHSV $= 1\ h^{-1}$, oxime concentration in feed $= 10$ wt% in solvent, nitrogen flow rate $= 20\ ml\ min^{-1}$, catalyst weight $= 3$ g.

3.2. Influence of temperature

The conversions of cyclohexanone oxime and caprolactam yield at different temperatures over H-FER, H-FER-TE, H-FER-TT, Si-FER and St-H-FER are shown in table 2.

Table 2

Influence of different temperature on the conversion of oxime and selectivity of ϵ-caprolactam using ferrierite catalyst[a]

Catalyst	Temp. (°C)	Oxime conv. (wt%)	Selectivities[b,c] (wt%)				Yield[d]
			A	B	C	D	
H-FER	300	80.6	77	8.2	13.8	0.9	62.06
	350	91.3	78.3	6.8	12.7	2.2	76.96
	400	99.3	74.8	9	13.4	2.8	74.28
	450	99.9	73.5	9.2	14.1	3.2	73.43
H-FER-TE	300	40	74	0	26	0	29.6
	350	91.4	72.9	3.2	23.8	0	66.63
	400	97	71.5	6.2	22.3	0	69.35
	450	99.9	74.2	5.2	18.9	1.7	74.12
H-FER-TT	300	53.6	77.6	0	19.4	3	41.59
	350	82.2	74.3	2.7	18.3	4.6	61.07
	400	89	72	3.1	17.3	7.5	64.08
	450	97.1	70.5	5	19.5	5	68.45
Si-FER	350	43.3	20.7	29.9	38.4	11	8.96
	400	64.2	42.1	19.9	29.5	8.5	27.03
	450	93.1	24	13.7	25.7	36.5	22.34
St-H-FER	300	71.7	79.3	8.1	9.4	3.2	56.85
	350	82.1	79	7.7	8.6	4.6	64.85
	400	84.2	85.3	6.1	6.5	2.1	71.82
	450	95.4	79.9	4.9	6.5	8.6	76.22

[a] Reaction conditions: pressure $= 1$ atm, WHSV $= 1\ h^{-1}$, oxime concentration in feed $= 10$ wt% in acetonitrile, nitrogen flow rate $= 20\ ml\ min^{-1}$, time on stream of the reaction $= 3$ h, catalyst weight $= 3$ g.
[b] Yield (wt%) of caprolactam $=$ (selectivity wt% X conversion wt%)/100.
[c] Selectivity (wt%) $=$ (wt% of product formed/wt% of cyclohexanone oxime formed) $\times$ 100.
[d] A $= \epsilon$-caprolactam, B $=$ cyclohexanone, C $=$ cyanopentane + cyanopentene, D $=$ others.

Table 3

Conversion of cyclohexanone oxime and selectivity for ϵ-caprolactam over various ferrierite type zeolites[a]

Catalyst	Oxime conv. (wt%)	Selectivities[b,c] (wt%)				Yield[d]
		A	B	C	D	
Na-FER	92.9	41.2	20.6	20.6	14.7	37.94
Na–H-FER-1 (1.3)[e]	94.4	47.2	19.4	22.2	5.6	44.56
Na–H-FER-2 (1.1)[e]	98.3	65	15.1	16.4	1.9	63.90
H-FER (10)[f]	100	76	5.4	10.9	5.4	76.00
H-FER	99.3	74.8	9	13.4	2.8	74.28
H-FER (25)[f]	98.3	77.5	8.5	9.4	4.6	76.18
St-H-FER	84.2	85.3	6.1	6.5	2.1	71.82
Si-FER	64.2	42.1	19.9	29.5	8.5	27.03
H-FER-TE (12)[f]	100	69.4	10.6	14.5	5.5	69.40
H-FER-TE	97	71.5	6.2	22.3	0	69.35
H-FER-TE (29)[f]	96.1	65.8	6.6	13.2	10.5	63.23
H-FER-TT	89	72	3.1	17.3	7.5	64.08

[a] Reaction conditions: temperature $= 400\,°C$, pressure $= 1$ atm, WHSV $= 1\ h^{-1}$, oxime concentration in feed $= 10$ wt% in acetonitrile, nitrogen flow rate $= 20\ ml\ min^{-1}$, time on stream of the reaction $= 3$ h, catalyst weight $= 3$ g.
[b] A $= \epsilon$-caprolactam, B $=$ cyclohexanone, C $=$ cyanopentane + cyanopentene, D $=$ others.
[c,d] See footnotes in table 2.
[e] The value in the parentheses represents the Na weight percent by EDX.
[f] The value in the parentheses represents the Si/Al ratio by EDX.

It can be seen from table 2 that with increase in temperature from 300 to 450 °C, oxime conversion increases and selectivity towards ϵ-caprolactam decreases except for the sample H-FER-TE. At higher temperature (450 °C) the conversion for oxime was 99.9% while the selectivity towards ϵ-caprolactam was 74.2% for the sample H-FER-TE. This low selectivity may be due to decomposition of ϵ-caprolactam at high temperature on the catalyst surface. Table 2 also shows that H-FER at 350 °C gives better performance towards conversion and yield while H-FER-TE and H-FER-TT samples give better performance at 450 °C. This is due to the acidic differences as detailed in the TPD studies.

3.3. Influence of catalyst

The results of the catalytic reactions of the cyclohexanone oxime over different ferrierite catalysts at 400 °C are presented in table 3. The St.-H-FER catalyst shows good selectivity towards caprolactam. (This is due to the high ratio of SiO_2/Al_2O_3 (73). Increase in the SiO_2/Al_2O_3 ratio decreases the total acidity of H-ferrierite zeolites, oxime conversion decreased.) It is known that the catalytic activity for Beckmann rearrangement depends upon the acidity and the nature of the hydroxyl group of catalysts. Corma et al. [21] reported that the strong Brønsted acidity of Y zeolite is responsible for the formation of lactam. However, the majority of previous reports have suggested that the very weak [22–24] or medium-strength acidity [8] or almost neutral hydroxyl groups [25] of zeolites are favorable for Beckmann rearrangement reaction, while the strong acid sites accelerate the formation of by-products [26]. This is in good agreement with the results of our study, since St-H-FER is
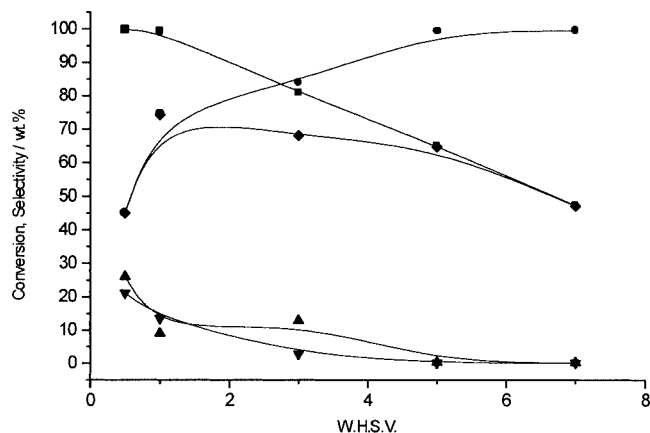
Figure 3. Influence of WHSV data on the conversion and selectivity for Beckmann rearrangement of cyclohexanone oxime over H-ferrierite (■) conversion (wt%) of oxime; (●) selectivity (wt%) of caprolactam, (▲) selectivity (wt%) of cyclohexanone, (▼) selectivity (wt%) of 5-cyano-pent-1-ene and (♦) yield (wt%) of caprolactam. Reaction conditions: temperature = 400 °C, pressure = 1 atm, oxime concentration in feed = 10 wt% in solvent, nitrogen flow rate = 20 ml min^{-1}, time on stream of the reaction = 3 h, catalyst weight = 3 g.

weakly acidic as compared to other samples under study. Si-FER showed poor conversion and yield of ϵ-caprolactam towards this reaction and this may be due to large zeolite crystals and the reaction on the surface. Also, this is in contrast with other studies [27]; silanol groups (Si–OH) are not active in the case of FER. The H-FER shows good conversion of cyclohexanone oxime. H-FER-TT shows low conversion of oxime compared to H-FER-TE. This may be due to the difference in particle size and surface area of the catalysts. Also the Si/Al ratio of H-FER and H-FER-TE samples are varied and tested at 400 °C for this reaction. As the Si/Al ratio increases, the conversion decreases but there is not much difference in the selectivity towards ϵ-caprolactum. To know the effect of Na% on activity, Na-FER was exchanged to different levels with NH_4NO_3 and the results are shown in table 3. As the Na% decreases, increase in conversion and selectivity is noticed. The following studies were done with H-FER as catalyst.

3.4. Influence of space velocity (WHSV)

The increase in WHSV of the feed on the conversion of oxime and selectivity of the products is shown in figure 3 over H-FER catalyst. It can be seen from figure 3 that as the WHSV increases there is a decrease in oxime conversion and an increase in caprolactam selectivity. The formation of cyclohexanone and 5-cyanopentane and 5-cyanopent-1-ene is reduced at higher WHSV because the reactants are in contact for less time and hence secondary product formation is suppressed. The maximum yield of caprolactam is at WHSV = 1.

3.5. Influence of solvent

Table 4 shows the influences of various solvents for cyclohexanone oxime on the catalytic performance of H-FER.

Table 4
Influence of various solvents for cyclohexanone oxime on the catalytic performance of H-FER[a]

Solvent	Oxime conv. (wt%)	Selectivities[b,c] (wt%)				Yield[d]
		A	B	C	D	
EtOH	99.5	70.7	7.8	20.3	1.2	70.35
Acetonitrile	99.3	74.8	9	13.4	2.8	74.28
Benzene	95.7	69.4	9.5	12.2	8.9	66.41

[a] Reaction conditions: temperature = 400 °C, pressure = 1 atm, WHSV = 1 h^{-1}, oxime concentration in feed = 10 wt% in solvent, nitrogen flow rate = 20 ml min^{-1}, time on stream of the reaction = 3 h, catalyst weight = 3 g.
[b] A = ϵ-caprolactam, B = cyclohexanone, C = cyanopentane + cyanopentene, D = others.
[c,d] See footnotes in table 2.

There is not much appreciable change in the conversion but the selectivity of caprolactam was strongly influenced by the type of solvent used. The selectivity increases by increasing the dipole moment of the solvent. The selectivity in presence of benzene (0 D) was low (69.4 wt%), selectivity in presence of ethanol (1.44 D) was 70.7 wt% while selectivity in presence of acetonitrile (3.92 D) was high (74.8 wt%). Roseler *et al.* [17] have reported the deactivation of MFI borosilicate in the Beckmann rearrangement of cyclohexanone oxime using different organic solvents and found that the degree of deactivation depends on the kind of solvent used. Komatsu *et al.* [4] have reported that the solvent with medium polarity was preferable for the Beckmann rearrangement on silicalite-1. But for ferrierite it is observed that the solvent with high polarity is preferable for this reaction.

3.6. Influence of concentration of cyclohexanone oxime

It can be seen from table 5 that the dilution of the cyclohexanone oxime in acetonitrile improves the conversion and the selectivity of caprolactam. At low oxime concentration (2.5 wt%) the yield of caprolactam was high. At high oxime concentration (20 wt%) in acetonitrile the formation of by-products cyclohexanone, cyanopentane and cyanopentene was high. Also with higher concentration of oxime deactivation of the catalyst is rather faster.

Table 5
Influence of oxime concentration on oxime conversion and caprolactam selectivity using H-FER as a catalyst[a]

Oxime concentration (wt%)	Oxime conv. (wt%)	Selectivities[b,c] (wt%)				Yield[d]
		A	B	C	D	
2.5	99.8	95.5	3.2	0.9	0.4	95.31
5	99.6	87.7	6.7	4.4	1.2	87.35
10	99.3	74.8	9	13.4	2.8	74.28
20	90.1	49	20.3	18.1	12.6	44.15

[a] Reaction conditions: temperature = 400 °C, pressure = 1 atm, WHSV = 1 h^{-1}, solvent = acetonitrile, nitrogen flow rate = 20 ml min^{-1}, time on stream of the reaction = 3 h, catalyst weight = 3 g.
[b] A = ϵ-caprolactam, B = cyclohexanone, C = cyanopentane + cyanopentene, D = others.
[c,d] See footnotes in table 2.

Table 6
Influence of nitrogen feed on the oxime conversion and caprolactam selectivity using H-FER as a catalyst[a]

N_2 feed	Oxime conv.	Selectivities[b,c] (wt%)				Yield[d]
	(wt%)	A	B	C	D	
140	94.3	70.4	25.9	1.2	2.5	66.39
90	96.6	70.1	22.4	3.4	4.1	67.72
60	98.6	71.4	17	7.7	3.9	70.40
20	99.3	74.8	9	13.4	2.8	74.28

[a] Reaction conditions: temperature = 400 °C, pressure = 1 atm, WHSV = 1 h^{-1}, oxime concentration in feed = 10 wt% in acetonitrile, time on stream of the reaction = 3 h, catalyst weight = 3 g.

[b] A = ϵ-caprolactam, B = cyclohexanone, C = cyanopentane + cyanopentene, D = others.

[c,d] See footnotes in table 2.

3.7. Influence of N_2 feed

Table 6 shows the influence of nitrogen flow on the conversion of oxime and selectivity of ϵ-caprolactam. Increase in flow rate of N_2 reduces the residence time of reactants over the catalyst leading to increase in selectivity and decrease in conversion of oxime. The yield of ϵ-caprolactam is maximum when the carrier gas flow rate was 20 ml/min. At higher nitrogen flow rate the selectivity of cyclohexanone is seen to increase.

4. Conclusions

In conclusion, using an appropriate Si/Al ratio or highly dealuminated H-ferrierite and an appropriate diluent can increase catalytic performance of H-ferrierite zeolite catalysts for the vapor phase Beckmann rearrangement of cyclohexanone oxime. H-FER and St-H-FER catalysts show good activity at 350 °C while H-FER-TE and H-FER-TT show good activity at 450 °C. This is in agreement with NH$_3$-TPD results. It is also seen that the type of solvent used for this rearrangement strongly affects the conversion of cyclohexanone oxime and selectivity of ϵ-caprolactam. Acetonitrile has been found to be the best solvent for cyclohexanone oxime to improve the selectivity for ϵ-caprolactam formation.

Acknowledgment

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