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FT-IR Study of the Beckmann Rearrangement over Pentasil-type Zeolite

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The temperature dependence of the FT-IR spectra of adsorbed cyclohexanone oxime on pentasil zeolite revealed that the rearrangement to ε-caprolactam takes place at 100 ℃, a higher temperature is necessary for its desorption, and a high selectivity over high silicious zeolite is attributable to its low acidity for both smooth rearrangement and smooth desorption. A neutral silanol is proposed to be an active site.

In the preceding papers,[1,2] we reported that, in the vapor phase Beckmann rearrangement of cyclohexanone oxime, a high lactam selectivity and a long catalytic life (or a low deactivation by coking) were obtained over a high silicious ($Si/Al \geqq 500$) pentasil zeolite having a large external surface area. And we made new proposals that the active site for this rearrangement reaction is not a strong acidic site as has been generally considered,[3,4] but a neutral silanol on the external surface of zeolite. To examine in more detail the influences of Si/Al ratio on the rearrangement reaction, temperature dependencies of the FT-IR spectra of adsorbed cyclohexanone oxime on pentasil zeolite were measured, and several considerations on the reaction mechanism were conducted as follows.

Two types of pentasil zeolite were used; a low silicious one (Z-1) (Si/Al=40)[5] and a high silicious one (Z-2) (Si/Al=1640).[2] The former is acidic, but for the latter, only a trace amount of acid is discernible (Table 1). The results of the rearrangement reaction over each zeolite are also summarized in Table 1. Both the lactam selectivity and the catalytic life are superior for the high silicious Z-2 than for the low silicious Z-1. The FT-IR spectroscopy was measured using a horizontal type in-situ IR cell made of qualtz and equipped with an external heater. A thin zeolite pellet (ca. 10 mg) was first treated at 500 ℃ under evacuation (10^{-4}–10^{-5} Torr) for 3h, and after cooling to room temperature, the FT-IR spectrum was recorded (spectrum A in Fig. 1-(a) and spectrum A in Fig. 2-(a)). Then, under He gas flow, one to two droplets of 1% benzene solution of oxime were added from a microsyringe onto the zeolite pellet held in the

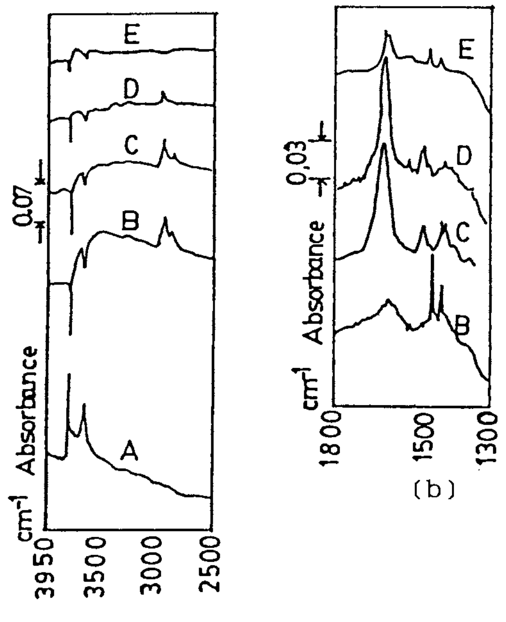
Table 1. Vapor phase Beckmann rearrangement[a] of cyclohexanone oxime over pentasil zeolite catalysts

Catalyst	Si/Al	Acidity[b] (μmol/g)	Conversion/% of cyclohexanone oxime	Selectivity/% to ε -caprolactam
Z-1	40	297	38	45
Z-2	1640	8	100	86

a) Cyclohexanone oxime was fed as a 8% benzene solution. Rearrangement reaction was conducted at 350 ℃ under atmospheric pressure. W/F=137 g-cat. h /mole-oxime. Reaction results were after 10 h time-on-stream.

b) Amount of pyridine adsorbed at 350℃ in GC pulse adsorption method.[6]

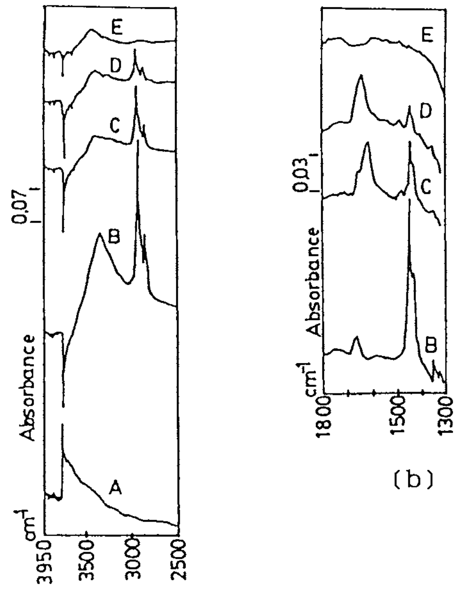
in-situ cell, and after evacuation at the prescribed temperature for 1 h, the FT-IR spectrum was measured at room temperature. The result was recorded as a differential spectrum from a parent spectrum. The results with the low silicious Z-1 are illustrated in Fig. 1-(a) (2500− 3950 cm^{-1}) and Fig. 1-(b) (1300− 1800 cm^{-1}), and those with the high silicious Z-2 are in Fig. 2-(a) (2500− 3950 cm^{-1}) and Fig. 2-(b)(1300− 1800 cm^{-1}).



(b)

(a)

Fig. 1. Temperature dependencies of FT-IR spectra of adsorbed oxime(1); low silicious Z-1 (Si/Al=40)



(b)

(a)

Fig. 2. Temperature dependencies of FT-IR spectra of adsorbed oxime(2); high silicious Z-2 (Si/Al=1640)

A; Z-1, evac. at 500 ℃, B− E; Oxime adsd. then evac. at 35 ℃(B), 100 ℃(C), 250 ℃(D), 400 ℃(E).

In each spectrum, B, C, D and E correspond to the temperatures of 35 ℃, 100 ℃, 250 ℃ and 400 ℃ respectively. The upward peaks correspond to the newly emerged ones by adsorption of oxime and the downward peaks correspond to the disappeared silanol peaks by adsorption of oxime. The height of the downward silanol peak reflects the degree of interaction of silanol with adsorbed species. In the silanol region of Z-1 (spectrum A in Fig. 1-(a)), both the acidic (3615 cm^{-1}) and terminal (neutral; 3740 cm^{-1}) silanols can be recognized, while for Z-2 (spectrum A in Fig. 2-(a)), only the terminal silanol can be recognized and no acidic silanol can be discernible, which corresponds well to the low acidity of Z-2 as shown in Table-1.

By adsorption of oxime on Z-1 at 35 ℃, both the acidic and the terminal silanols decreased in the amount of 48.8 % and 61.9 % respectively, and the characteristic peaks for oxime appeared at 1481 cm^{-1} (δ OHassoc.) and 1450 cm^{-1} (δ CH2). But the characteristic peak for ν C=N around 1662 cm^{-1} could not be observed at all. These results indicate that, on the acidic Z-1, a strong interaction of acidic silanol with N atom of oxime predominates to an interaction with hydroxyl group of oxime. This means that, for the acidic Z-1, the initial step of the rearrangement reaction is N-protonation of oxime by the acidic silanol (Eq. 1).

$$\text{R-C=NOH} + \text{H}^{+}\text{OSi-O-Al}^{-}\text{-O-Si-} \longrightarrow \overset{\text{R-C=N}^{+}\text{OH2}}{^{-}\text{O-Si-O-Al-O-Si-}} \qquad (1)$$

On the contrary, by adsorption of oxime on the non-acidic Z-2, no δ OH peak of oxime was observed around 1480 cm^{-1}, but only δ CH2 peaks at 1441 cm^{-1} and 1450 cm^{-1} were observed (spectrum B in Fig. 2-(b)). And was also observed a weak peak at 1662 cm^{-1}, which is attributable to ν C=N of oxime. As for the silanol peak, the terminal silanol at 3740 cm^{-1} disappeared almost completely (spectrum B in Fig. 2-(a)). These results indicate that, on the non-acidic (or very low acidic) Z-2, a strong interaction exists between the neutral (terminal) silanol and the oxime hydroxyl group, and this strong interaction is regarded as an initial step of the rearrangement reaction over the non-acidic Z-2. As one of the possibilities of this strong interaction, a transient formation of oxime ether by dehydration with terminal silanol might be conceivable (Eq. 2), but this hypothesis must be proved by a well designed experiment.

$$\text{R-CH=NOH + HO-Si-O-Si-} \longrightarrow \text{R-CH=NO-Si-O-Si- + H2O} \qquad (2)$$

By a stepwise rise of evacuation temperature, both low and high silicious zeolites exhibited strong absorption band around 1637 cm^{-1} even at 100 ℃, and this absorbance was almost the same at 250 ℃ (spectra C and D in Figs. 1 and 2). This indicates that the rearrangement reaction takes place even at 100 ℃, and it completes at this temperature. In accordance with this change in the low silicious Z-1, δ OH (1481 cm^{-1}) absorption disappeared, δ CH2 (1456 cm^{-1}) decreased and new several bands around 1437

— 1515 cm^{-1} appeared (spectrum C in Fig. 2-(b)). On the contrary, δ CH2 (1450 cm^{-1}) in the highly silicious Z-2 did not change its position, but slightly changed its absorbance. These data indicate that the rearrangement seems to proceed more smoothly over the non-acidic Z-2 than the acidic Z-1

In the low silicious Z-1, the recoveries of terminal and acidic silanols at 100 ℃ are 45.2 % and 67.8 % respectively. At 250 ℃, the absorbance of carbonyl is the same order with that at 100 ℃, but the absorbances of ν C-H (2930 cm^{-1} and 2850 cm^{-1}) are greatly reduced and the recoveries of terminaland acidic silanols increase to 69 % and 75.8 % respectively. But even at 400 ℃, a trace amount of lactam can be discerned on Z-1 (spectrum E in Fig. 1-(b)). This indicates that the acidity of the low silicious Z-1 prevents the produced lactam from desorption, thus lowering the lactam selectivity.

On the contrary, in the high silicious Z-2, the absorbance of carbonyl (1637 cm^{-1}), which remained largely at 250 ℃, completely disappeared at 400 ℃ (spectra D and E in Fig. 2-(b)), showing the completion of the catalytic cycle. That is, the high lactam selectivity in the non-acidic Z-2 can be explained by the smooth desorption of the product. The above data also coincide with the result that the best choice of the reaction temperature is around 350 ℃.

In conclusion, the rearrangement of cyclohexanone oxime to ε-caprolactam over pentasil zeolite takes place at 100 ℃, but a higher temperatureas (350 ℃), is necessary for the desorption of the produced lactam. The high lactam selectivity over high silicious Z-2 (Si/Al=1640) is attributable to its non-acidity, which eventually facilitates both the smooth rearrangement of oxime and the smooth desorption of lactam. The present FT-IR data, when coupled with our previous results that the ultra-high silicious pentasil zeolite, such as Si/Al≧30000, exhibited the better lactam selectivity than the zeolite with Si/Al=1640,[2)] strongly suggest that the neutral silanol is an active site.

References

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