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# Oxidation of cyclohexane with hydrogen peroxide over $\beta\mbox{-}zeolites$ with various Si/Al ratios

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# A R T I C L E I N F O

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# ABSTRACT

Selective oxidation of cyclohexanone to  $\varepsilon$ -caprolactone by H<sub>2</sub>O<sub>2</sub> was investigated on  $\beta$ -zeolites with various Si/Al ratio. The yield of  $\varepsilon$ -caprolactone was increased with decreasing Si/Al ratio. The  $\beta$ -zeolites in which Si/Al ratio was lower than 117 showed the almost constant yield of  $\varepsilon$ -caprolactone with slight decrease of selectivity. The hydrolysis product, 6-hydroxycaproic acid, was observed. The conversion of H<sub>2</sub>O<sub>2</sub> was also increased with decreasing Si/Al ratio, whereas the efficiency of H<sub>2</sub>O<sub>2</sub> was kept constant, ca. 80%. At lower Si/Al ratio, the decrease of efficiency was also observed. These results suggest that Brønsted acid sites play an important role in the selective oxidation of cyclohexanone by H<sub>2</sub>O<sub>2</sub>. Infrared spectra of cyclohexanone and H<sub>2</sub>O<sub>2</sub> were measured in order to elucidate the role of Brønsted acid sites in the oxidation. The IR spectra suggested that cyclohexanone mainly interacted with silanol groups of  $\beta$ -zeolite, whereas H<sub>2</sub>O<sub>2</sub> selectively interacted with Brønsted acid sites. The evacuation of  $\beta$ -zeolite preadsorbed with cyclohexanone and H<sub>2</sub>O<sub>2</sub> at 393 K brought about the formation of the vibration band of  $\varepsilon$ -caprolactone. On Na<sup>+</sup> ion exchanged  $\beta$ -zeolite, no specific peak of  $\varepsilon$ -caprolactone was observed. These results with ketones over  $\beta$ -zeolite with various Si/Al ratios.

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# 1. Introduction

Baeyer-Villiger (BV) oxidation is one of well-established reactions to synthesize esters from ketones and peroxides like carboxylic peroxides in a homogeneous reaction system. A carboxylic peracid plays roles not only as an oxidant but also as Brønsted acidity to activate a carbonyl group of ketones in BV oxidation as shown in Scheme 1. By using the peroxides, stoichiometric amount of carboxylic acids forms. The by-produced carboxylic acids should be neutralized and the obtained salt must be disposed after the reaction. Corma et al. [1] have proposed the BV oxidation process with  $H_2O_2$  as an oxidant over  $Sn^{4+}$ -supported catalysts. By using H<sub>2</sub>O<sub>2</sub> instead of organic peroxide, H<sub>2</sub>O is expected to be coformed as a by-product. This heterogeneous reaction system has a great advantage from the environmental point of view, i.e., the post treatment of both by-product and used homogeneous acid catalyst will be excluded. Since H<sub>2</sub>O<sub>2</sub> is a weak acid not enough to activate carbonyl groups in ketones, the activation of ketones is carried out over Lewis acidity of Sn<sup>4+</sup> instead of protons of organic peroxides. Hydroxyapatite and MgO catalysts also indicated the significant activity for the BV oxidation [2-5] with H<sub>2</sub>O<sub>2</sub> in benzonitrile solvent. Unfortunately, benzamide was co-formed with the corresponding esters over the MgO-containing catalysts. Over the MgO-containing catalysts, carbonyl groups in ketones were activated on Mg<sup>2+</sup> cation sites. Steffen et al. have reported the BV oxidation of cyclohexanone over Al<sub>2</sub>O<sub>3</sub> catalysts [6]. Ketones and H<sub>2</sub>O<sub>2</sub> were separately activated on the different kinds of acid sites on Al<sub>2</sub>O<sub>3</sub>. The authors suggest that the weak Brønsted sites on Al<sub>2</sub>O<sub>3</sub> plays an important role for activation of H<sub>2</sub>O<sub>2</sub> molecules, whereas ketones were activated on the sites with more stronger acidic property.  $\beta$ -Type zeolites have been studied for the BV oxidation of cyclic ketones with H<sub>2</sub>O<sub>2</sub> as an oxidant. The  $\beta$ -zeolite itself without Lewis acidic component like Sn<sup>4+</sup> cations indicated high yield of the corresponding lactones [7]. The Brønsted acidic property of the catalysts would strongly affect the heterogeneous BV oxidation reactions.

In this study, effect of acidic properties, number of acidic sites and their acidity on the yield and selectivity of  $\varepsilon$ -caprolactone and efficiency of consumed H<sub>2</sub>O<sub>2</sub> was studied for BV oxidation of cyclohexane.

#### 2. Experimental

# 2.1. Catalyst preparation

*Reference catalyst*: H-type of  $\beta$ -zeolite, JRC-Z-HB-150 (Si/Al=75), was purchased from Catalysis Society of Japan. The catalyst was calcined in a flowing air at 773K for 5h. The



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Scheme 1. Reaction mechanism of Baeyer-Villiger oxidation.

catalyst code of the reference catalyst is indicated as HBEA(75)-R. Sodium type  $\beta$ -zeolite was obtained by ion exchanging HBEA(75)-R in 1.0 M of NaNO<sub>3</sub> aqueous solution at 353 K for 1 h followed by rinse with 31 of hot deionized water. The obtained sample was calcined at 773 K for 5 h (NaBEA(75)-R).

Synthesis of  $\beta$ -zeolite: The  $\beta$ -zeolites with various Si/Al ratios were synthesized under hydrothermal condition [8] by using a hydrothermal synthesis reactor KH-02 obtained from Hiro Company, Yokohama, Japan. A hydrogel mixture Al(OH)<sub>3</sub> (Nakarai Tesque, Kyoto, Japan), fumed silica (8.0 g, SIGMA, 0.007 µm of particle size) and tetraethylammonium hydroxide (TEAOH) as a structure directing reagent (30.25g of aqueous solution (35%, Sigma-Aldrich) were stirred at room temperature for 4h. Then the aqueous solution of hydrofluoric acid (4.02 g Nakarai Tesque 46%) was slowly added by drop wise in polyethylene beaker with vigorous stirring. The composition of the hydrogel was  $SiO_2 \cdot yAl_2O_3 \cdot 0.54TEAOH \cdot 0.54HF \cdot 9.3H_2O$  (y = 0, 0.0025, 0.0033, 0.005, 0.0067, 0.01, and 0.02). The obtained gel was transferred to a Teflon-coated stainless steel autoclave and heated at 423 K for 7 days in the synthesis reactor. The obtained white solid was filtrated and rinsed with 31 of hot deionized water and dried at 393 K for 24 h, followed by calcination in atmosphere at 853 K for 5 h to remove the residual structure directing reagent. Sodium ions in the calcined samples were ion-exchanged with  $H^+$  in an aqueous solution of  $NH_4NO_3$  (1.0 mol/l) at 353 K for 6 h. This ion-exchange treatment was repeated twice. Finally, Htype  $\beta$ -zeolites were obtained by drying at 393 K, followed by calcination at 773 K for 5 h. The catalyst code is indicated as HBEA(x) (x = Si/Al).

Ultra stable Y zeolite (HUSY (Si/Al = 15)) was also purchased from ZEOLYST International and HZSM-5 (MFI (Si/Al = 75)) was obtained by the hydrothermal synthesis with the gel mixture of tetraethyl orthosilicate (TEOS), aluminum nitrate, tetrapropyl ammonium bromide, and sodium hydroxide, to compare the activity over some zeolite catalysts.

# 2.2. X-ray fluorescence spectroscopy

The composition of zeolites were analysed by XRF spectrometer, Primini (Rigaku) under 1.7 Pa of vacuum condition. Palladium anode was operated at 40 kV and 1.25 mA.

#### 2.3. X-ray diffraction powder pattern

Structure of zeolites was checked by X-ray diffraction powder pattern. The diffraction patterns were measured by RINT2000 diffract meter (Rigaku). The conventional Cu X-ray tube was operated at 40 kV and 40 mA.

#### 2.4. Specific surface area

BET surface area was evaluated by measuring  $N_2$  adsorption at 77 K with BELSORP-mini (BEL Japan) after calcination at 473 K in 50 ml/min of flowing  $N_2$  for 3 h.

#### 2.5. Temperature programmed desorption

Temperature programmed desorption (TPD) of adsorbed  $NH_3$  was carried out to elucidate the acidity of the zeolites. TPD spectra of adsorbed  $NH_3$  were measured in a static vacuum system. Ammonia was adsorbed on a sample at 373 K and evacuated for 0.5 h. The amount of adsorption was evaluated as the difference of total and reversible adsorption. The heating rate was 10 K/min in the range of 373–773 K. The pressure of desorbed  $NH_3$  (desorption rate) was monitored by an ion gauge vacuum meter. The TPD experiments of adsorbed cyclohexanone were also carried out by a similar procedure. Cyclohexanone was adsorbed on the catalysts at room temperature under vapour pressure of cyclohexanone.

# 2.6. Infrared spectroscopy for the adsorption of cyclohexane and $H_2O_2$ on $\beta$ -zeolites

The infrared spectra of the catalysts were measured by using a Pyrex glass in situ IR cell equipped with KBr single crystal windows under transmission mode. A sample disc (13 mm in diameter) was prepared by pressing 20 mg of  $\beta$ -zeolite. The specimen was evacuated in the IR cell at 523 K for 5 h. After the pre-treatment, the specimen was transferred into a desiccator and the adsorption of cyclohexanone or H<sub>2</sub>O<sub>2</sub> under vapour pressure of each reactant at ambient temperature. After the adsorption, the specimen was transferred back to the IR cell, and then the spectra were accumulated in 200 scans by Nicolet 380 FT-IR spectrometer equipped with MCT highly sensitive detector. The resolution of the spectrometer was 4 cm<sup>-1</sup>.

# 2.7. BV oxidation of cyclohexanone by $H_2O_2$

The oxidation of cyclohexanone with  $H_2O_2$  was carried out in a Pyrex glass Erlenmeyer flask reactor. Cyclohexanone (0.2 mL, 2.0 mmol, Nakarai Tesque), 0.1 mL of 30%  $H_2O_2$  aqueous solution (1.2 mmol, Santoku Kagaku), 4.0 mL of acetonitrile (Nakarai Tesque) and 20 mg of catalyst were charged in the reactor. The reactor was purged by nitrogen gas several times in order to obtain anaerobic atmosphere. The reaction was started by dipping the reactor in a thermostatically controlled oil bath at 303 K. After 20 h of reaction time, the reaction mixture and catalyst were separated by centrifugation and decantation. Products were analyzed by a gas chromatograph equipped with G-300 capillary (40 m  $\times$  1.2 mm). Ethanol was used as an internal standard for quantitative analysis.

Table 1
Catalytic activity of typical zeolite catalysts for BV oxidation of cyclohexane.

Catalyst	$\epsilon$ -Caprolactone yield (%)	H <sub>2</sub> O <sub>2</sub> Conv. (%)	Efficiency (%)
HBEA(12.5)	22.9	71.7	65.4
HBEA(75)	15.0	45.7	66.8
HUSY(15)	5.7	38.0	31.2
MFI(75)	0.5	4.3	25.1

Catalyst: 20 mg; cyclohexanone: 2.0 mmol;  $H_2O_2$ : 1.2 mmol in 30% aqueous solution; solvent: 4.0 ml of acetonitrile; React. Temp.: 303 K; React. time: 20 h.



**Fig. 1.** XRD powder patterns of HBEA catalysts Intensity (a.u.). (a)  $BEA(\infty)$ ; (b) HBEA (176); (c) HBEA (133); (d) HBEA (117); (e) HBEA (106); (f) HBEA (84.3); (g) HBEA (54.6); (h) HBEA (75).

Conversion of cyclohexanone was calculated as the following equation.

Convesion of cyclohexanone =  $\frac{[initial amount of cyclohexanone] - [residual amount of cyclohexanone]}{[initial amount of cyclohexanone]}$ 

Yield of  $\varepsilon$ -caprolactone =

[formed amount of  $\varepsilon$ -carpolactone] [initial amount of cyclohexanone]

Conversion of  $H_2O_2 =$ 

[initial amount of 
$$H_2O_2$$
] – [residual amount of  $H_2O_2$ ]  
[initial amount of  $H_2O_2$ ]

Efficiency of  $H_2O_2 =$ 

# 3. Results and discussion

H-type  $\beta$ -zeolite catalysts indicated the highest activity and  $H_2O_2$  efficiency among H-Y, HZSM-5 (MFI), and BEA zeolites as shown in Table 1. These results suggest that the acidic property and/or pore structure affects the catalytic activity for BV oxidation reaction.

# 3.1. Texture and acidic properties of the $\beta$ -zeolite catalysts

Table 2 indicates the composition of synthesized  $\beta$ -zeolite catalysts and their BET surface area. The Si/Al ratio of the synthesized catalysts was varied in the range between 54.6 and 176. The Al-free BEA structure silica was also synthesized as shown in Table 2. Aluminium element was not observed in the BEA( $\infty$ ) checked by XRF analysis. The surface area of the  $\beta$ -zeolites was in the range between 430 and 466 m<sup>2</sup>/g. The XRD powder patterns of the catalysts are shown in Fig. 1. Each pattern indicates BEA structure was clearly observed for the catalysts. These



**Fig. 2.** TPD spectra of  $NH_3$  adsorbed on HBEA(x) catalysts.

results suggest that zeolites with BEA structure were properly synthesized.

Fig. 2 indicates the TPD spectra of NH<sub>3</sub> adsorbed on the catalysts. Each desorption spectrum consists of two peaks, low temperature

peak at ca. 400 K and high temperature peak from 530 to 570 K. No high temperature peak was observed on BEA( $\infty$ ) as shown in Fig. 3. The high temperature peaks were ascribable to NH<sub>3</sub> desorption form Brønsted acid sites on zeolite catalysts, whereas the low temperature peaks were assigned to be weakly adsorbed NH<sub>3</sub>

#### Table 2

Synthesized  $\beta$ -zeolite with various Si/Al ratio.

Entry	Si/Al ratio		Surface area (m <sup>2</sup> /g)
	Initial gel	Analysis <sup>a</sup>	
1	50	54.6	456
2	75	84.3	466
3	100	106	451
4	125	117	443
5	150	133	442
6	200	176	442
7	$\infty$	$\infty$	430

<sup>a</sup> Evaluated by XRF analysis.



**Fig. 3.** The relationship between Al content of HBEA(x) catalysts and the amount of adsorbed NH<sub>3</sub>.



**Fig. 4.** (a) Dependence of amount of acid sites on the product yield: ( $\blacklozenge$ )  $\varepsilon$ caprolactone; ( $\blacksquare$ ) 6-hydroxycaproic acid; ( $\blacktriangle$ )  $\delta$ -hexanolactone. (b) Dependence
of amount of acid sites on the conversion and efficiency of H<sub>2</sub>O<sub>2</sub>: ( $\blacklozenge$ ) conversion of
H<sub>2</sub>O<sub>2</sub>; ( $\blacklozenge$ ) efficiency of H<sub>2</sub>O<sub>2</sub>.

on the surface or ammonia molecules interacted with NH4<sup>+</sup> which were NH<sub>3</sub> adsorbed on Brønsted acid sites (not chemisorbed NH<sub>3</sub>) [9]. The amount NH<sub>3</sub> corresponding to the high temperature peak can be evaluated by calculation from the total amount of adsorbed NH<sub>3</sub> and the fraction of the high temperature peak area in the total desorption spectrum. The relationship between the Al content and amount of adsorbed NH<sub>3</sub> corresponding to the high temperature peak is shown in Fig. 3. The dashed line in the figure indicates an equivalent relationship between the Al content and the amount of Brønsted acid sites on HBEA(x) catalysts. The amount of Al in the zeolites was almost equivalent to the amount of adsorbed NH<sub>3</sub>. These results indicate that the Al atoms in the zeolites synthesized here were located in the framework of BEA zeolites and generated Brønsted acid sites. In this paper, the amount of adsorbed NH<sub>3</sub> corresponding to the high temperature peak is indicated as the amount of acid sites.

#### 3.2. BV oxidation of cyclohexanone

The products were  $\varepsilon$ -caprolactone (target molecule),  $\delta$ -hexanolactone (an isomer of  $\varepsilon$ -caprolactone), and 6hydroxycaproic acid (a hydrolyzed product of  $\varepsilon$ -caprolactone) were detected. Some portion of undetectable products (probably be a polymerized product) should be considered. Fig. 4a and b shows the catalytic activity for BV oxidation of cyclohexanone with H<sub>2</sub>O<sub>2</sub> on HBEA(x) catalysts with various Si/Al content. No activity

Table 3

Effect of Na<sup>+</sup> ion exchange on BV oxidation activity.

Entry	Percentage of Na <sup>+</sup> ion exchange (%)	Yield of $\varepsilon$ -CL (%)
1	0	24.9
2	45	22.2
3	77	19.4
4	87	10.7
5	93	7.7
6	98	3.7
7	100	0.5

was observed on the Al-free catalyst,  $BEA(\infty)$ . The conversion of cyclohexanone and yield of  $\varepsilon$ -caprolactone were increased up to 130 µmol/g of the amount of acid sites, whereas the conversion and the yield showed almost constant at the higher amount of acid sites as shown in Fig. 4a. The conversion and efficiency of  $H_2O_2$  were shown in Fig. 4b. The efficiency means percentage of consumed  $H_2O_2$  to form  $\varepsilon$ -caprolactone in the total conversion. The conversion was also increased up to 130 µmol/g of amount of acid sites, whereas the efficiency was maintained in the range of 70-80%. At higher amount of acid sites, the efficiency was slightly decreased as shown in Fig. 4b. These results suggest that the Brønsted acid sites in the  $\beta$ -zeolite in which Al content was less than 130 µmol/g were active sites for the BV oxidation of cyclohexanone. At higher Al content, the excess Al was not effective for BV oxidation and some side reactions, hydration and polymerization, would be accelerated. Sodium ion exchange for HBEA catalysts brought about the decrease of activity for the BV oxidation of cyclohexanone as indicated in Table 3. NaBEA(75)-R zeolite indicated no activity. The sodium ion exchange experiment also support that the Brønsted acid sites in  $\beta$ -zeolites are active sites for the BV oxidation. These reaction experiments strongly indicate that the Brønsted acidic property plays an important role in the BV oxidation of cyclic ketones, especially high silica zeolites.

# 3.3. IR spectra of the catalysts after adsorption of reactants and thermal treatment

In order to elucidate the role of Brønsted acid sites in the BV oxidation of cyclohexanone, i.e., interaction between the Brønsted acid sites and the reactants (cyclohexanone and/or H<sub>2</sub>O<sub>2</sub>). The change of O—H stretching spectrum of the zeolites and the formation of ester group and annihilation of ketone group were investigated. Fig. 5



**Fig. 5.** FT-IR spectra of adsorbed cyclohexanone in wide region. Difference spectra—a: adsorbed cyclohexanone at room temperature; b: evacuated at 393 K after the *spectrum a*; dotted line: background spectrum.



**Fig. 6.** FT-IR spectra of adsorbed cyclohexanone and/or  $H_2O_2$  on HBEA(x) catalysts. a: adsorption of cyclohexanone; b: adsorption of cyclohexanone and  $H_2O_2$  (cyclohexanone  $\rightarrow H_2O_2$ ); c: evacuated at 393 K after the *spectrum b*; d: adsorption of  $\varepsilon$ -caprolactone; dotted line: background spectrum.

shows IR spectra of cyclohexanone adsorbed on the HBEA(75)-R evacuated at 523 K for 5 h in wide wave number range. The dotted line indicates the background spectrum of HBEA(75)-R before adsorption. The sharp peak at ca.  $3730 \,\mathrm{cm}^{-1}$  was assignable to a stretching vibration mode of O-H of silanol group on HBEA(75)-R and the small peak at  $3600 \text{ cm}^{-1}$  can be assigned to the O–H vibration mode of Brønsted acid sites. The spectrum a in the figure indicates the difference spectrum of adsorbed cyclohexanone between before and after adsorption. Significant peaks of adsorbed cyclohexanone were observed in C-H stretching vibration around  $3000 \,\mathrm{cm}^{-1}$  and C=O stretching vibration around  $1700 \,\mathrm{cm}^{-1}$ . It should be noted that the obvious negative peaks were observed at 3730 and 3600 cm<sup>-1</sup>. These results suggest that cyclohexanone interacted with the silanol groups and/or Brønsted acid sites of βzeolite. The adsorbed cyclohexanone was readily desorbed after the evacuation at 393 K as shown in the spectrum b. The interaction of cyclohexanone was not so strong. Successive adsorption of cyclohexanone and H<sub>2</sub>O<sub>2</sub> was carried out. The spectra in the region of O-H stretching and C=O stretching were shown in Fig. 6. The adsorption of cyclohexanone brought about the negative peaks and carbonyl group absorption was observed as shown in the spectrum a. Almost no change was observed after the successive adsorption of H<sub>2</sub>O<sub>2</sub>. After the successive adsorption, the catalyst disc was evacuated at 393 K. A new peak was observed at 1730 cm<sup>-1</sup> after the evacuation at 393 K as shown in spectrum c. The spectrum c was almost identical to the absorption spectrum of adsorbed  $\varepsilon$ -caprolactone as shown in spectrum d. Fig. 7 shows the spectra of the reverse successive adsorption, H<sub>2</sub>O<sub>2</sub> first followed by cyclohexanone. After H<sub>2</sub>O<sub>2</sub> adsorption, the decrease of the peak intensity of the silanol groups was not so obvious, whereas the significant negative peak was observed in the adsorption of cyclohexanone as shown in Fig. 7. The negative peak at  $3600 \,\mathrm{cm}^{-1}$  was clearly observed. These results suggest that H<sub>2</sub>O<sub>2</sub> would selectively interact with Brønsted acid sites of β-zeolite. After the successive cyclohexanone adsorption, the significant negative peak was observed at 3730 cm<sup>-1</sup> and the peak corresponding C=O stretching region at  $1700 \,\mathrm{cm}^{-1}$  appeared as shown in the spectrum b. After the evacuation at 393 K after the cyclohexanone adsorption, the formation of  $\varepsilon$ -caprolactone was also observed as indicated in the *spectrum c*. These results strongly suggest that cyclohexane adsorbed on the silanol groups and H<sub>2</sub>O<sub>2</sub> adsorbed on the Brønsted



**Fig. 7.** FT-IR spectra of adsorbed  $H_2O_2$  and/or cyclohexanone on HBEA(*x*) catalysts. a: adsorption of  $H_2O_2$ ; b: adsorption of  $H_2O_2$  and cyclohexanone ( $H_2O_2 \rightarrow$  cyclohexanone); c: evacuated at 393 K after the *spectrum b*; d: adsorption of  $\varepsilon$ -caprolactone; dotted line: background spectrum.

acid sites will react to form  $\varepsilon$ -caprolactone after the evacuation at 393 K. Infrared spectra of cyclohexanone on NaBEA(75)-R were measured to elucidate the effect of the silanol groups of the zeolite for BV oxidation. The similar absorption bands of cyclohexanone were observed at 1700 cm<sup>-1</sup> of carbonyl group and significant negative peak at 3730 cm<sup>-1</sup> on NaBEA(75)-R as shown in Fig. 8. The shape of the negative peak was slightly different from that on HBEA catalysts, i.e., a broader peak at lower wavenumber accompanying with the sharp silanol band at 3730 cm<sup>-1</sup>. This peak could be ascribed to the absorption band of cyclohexanone on Na<sup>+</sup> cations. The successive H<sub>2</sub>O<sub>2</sub> adsorption did not affect the spectra and the followed evacuation at 393 K did not bring about the formation of  $\varepsilon$ -caprolactone as shown in the spectrum c of Fig. 8. It is considered that H<sub>2</sub>O<sub>2</sub> could not be activated on NaBEA(75)-R because of no Brønsted acid site, and that the BV oxidation reaction did not proceed on NaBEA(75)-R. Fig. 9 shows the spectra of the reverse successive adsorption, H<sub>2</sub>O<sub>2</sub> first followed by cyclohexanone on



**Fig. 8.** FT-IR spectra of adsorbed cyclohexanone and/or  $H_2O_2$  on NaBEA(75)-R. a: adsorption of  $H_2O_2$ ; b: adsorption of  $H_2O_2$  and cyclohexanone (cyclohexanone  $\rightarrow H_2O_2$ ); c: evacuated at 393 K after b; dotted line: background spectrum.



**Fig. 9.** FT-IR spectra of adsorbed  $H_2O_2$  and/or cyclohexanone on NaBEA(75)-R. a: adsorption of  $H_2O_2$ ; b: adsorption of  $H_2O_2$  and cyclohexanone ( $H_2O_2 \rightarrow$  cyclohexanone); c: evacuated at 393 K after b; dotted line: background spectrum.



**Fig. 10.** TPD spectra of adsorbed cyclohexanone on HBEA(*x*) catalysts.

NaBEA(75)-R. The adsorption of  $H_2O_2$ , however, indicated a slight decrease of the silanol group, the successive adsorption followed by the evacuation at 393 K did not provide  $\varepsilon$ -caprolactone. These results indicate that the silanol groups on  $\beta$ -zeolites play a role of activation or only adsorption which means weakly electronic interaction between the silanol groups and cyclohexanone, and that the Brønsted acid sites on  $\beta$ -zeolite may activate  $H_2O_2$  and accelerate

the BV oxidation reaction of cyclohexanone. Bellussi et al. [10] have reported the role of tetrahedral-coordinated Ti<sup>4+</sup> in the titanium silicate. The site, Ti–O–Si, was hydrolyzed by water and formed TiOH and SiOH in the titanium silicate. These TiOH sites were considered to activate the protic substrates for selective oxidation reactions. In our system, protons play an important role in the reaction because sodium ion exchange completely suppress the activity, and the IR spectra clearly showed H<sub>2</sub>O<sub>2</sub> molecules can interact with Brønsted acidic sites. It should be noted that the role of active sites seems to be different from the sites in titanium silicate catalysts for epoxidation with H<sub>2</sub>O<sub>2</sub>. Steffen et al. have also proposed that the hydroxyl groups of tetrahedrally coordinated Al<sup>3+</sup> cations activate H<sub>2</sub>O<sub>2</sub> [6]. Fig. 10 shows TPD spectra of cyclohexanone adsorbed on β-zeolites. There is no specific relationship between the amount of acid sites and both desorption peak position and intensity. The zeolites which Si/Al ratio was larger than 117, on which the linear relationship was observed between the amount of acid sites and the BV oxidation activity as shown in Fig. 4a, the desorption peak position was almost identical and the peak intensity did not depend on Si/Al ratio. The Al-free  $\beta$ -zeolite, BEA( $\infty$ ) showed only small peak at a low temperature. The amount and chemical properties of silanol groups on BEA( $\infty$ ) might not be different from those on  $\beta$ -zeolites. The details of the behavior are still under investigation.

## 4. Conclusions

- (1) The BV oxidation activity strongly depended on the amount of Brønsted acid sites and the linear relationship was observed between the yield of  $\varepsilon$ -caprolactone and the Al content up to 117 of Si/Al atomic ratio (the amount of adsorbed NH<sub>3</sub>: 130 µmol/g).
- (2) NaBEA(75)-R shows no activity for the BV oxidation of cyclohexanone with H<sub>2</sub>O<sub>2</sub>.
- (3) The Brønsted acid sites play an important role for H<sub>2</sub>O<sub>2</sub> activation.
- (4) The silanol groups are adsorption sites for cyclohexanone.

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