# Role of Al$^{3+}$ species in beta zeolites for Baeyer–Villiger oxidation of cyclic ketones by using H$_2$O$_2$ as an environmentally friendly oxidant

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## ARTICLE INFO

## ABSTRACT

In this study, the Baeyer–Villiger (BV) oxidation of cyclic ketones to corresponding lactones using proton-type β-zeolite catalysts with various Al contents using an environmentally friendly oxidant (H$_2$O$_2$) was investigated. With respect to the selective oxidation of cyclobutanone to the corresponding γ-butyrolactone, the hydrolysis of which hardly proceeded under the reaction conditions employed, the conversion of cyclobutanone and H$_2$O$_2$ and yield of γ-butyrolactone increased with increasing Al content of up to 418 μmol/g (Si/Al ratio of 39.0), followed by marginal decrease at Al contents greater than 418 μmol/g. These trends were clearly correlated to the amount of Brønsted acid sites as estimated by the combination of temperature programmed desorption of NH$_3$ (NH$_3$-TPD) and Fourier transform infrared spectroscopy (FTIR) measurements for adsorbed pyridine. These results strongly indicated that the Brønsted acid sites in β-zeolite catalysts serve as the active sites for the BV oxidation. On the other hand, for the BV oxidation of cyclohexanone to ε-caprolactone (the corresponding BV product), the selectivity of ε-caprolactone was maintained constant up to an Al content of 418 μmol/g, but it gradually decreased at Al contents greater than 418 μmol/g. An apparent correlation was observed between the amount of Lewis acid sites, attributed to the extra-framework Al species, and the trend of ε-caprolactone selectivity. These results suggested that the extra-framework Al species leads to the acceleration of the successive hydrolysis of ε-caprolactone.

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## 1. Introduction

The Baeyer–Villiger (BV) oxidation involving the conversion of ketones or cyclic ketones to the corresponding esters or lactones, respectively, is an important transformation in synthetic organic chemistry; however, the use of peroxide or organic peroxy acids as the oxidant forms the desired product with the simultaneous generation of a significant amount of harmful waste [1]. For instance, ε-caprolactone is an important intermediate in the synthesis of polyesters, which is industrially produced by the oxidation of cyclohexanone with m-chloroperbenzoic acid, thereby affording a stoichiometric amount of m-chlorobenzoic acid [2]; this co-produced carboxylic acid must be neutralized, and the resultant salt must be disposed. Furthermore, organic peroxy acids are not

only expensive reagents, but also are difficult to transport, store, and handle because of their shock sensitivity and extremely high reactivity [3]. From the viewpoint of environmental considerations, several researchers have focused considerable efforts toward the development of an alternative catalytic process using an environmentally benign oxidant such as hydrogen peroxide (H$_2$O$_2$). By using H$_2$O$_2$ as the oxidant instead of organic peroxy acids, H$_2$O is the expected by-product. However, H$_2$O$_2$ is a weak oxidant for the BV oxidation. Hence, to overcome this drawback, the use of heterogeneous catalysts with H$_2$O$_2$ for the BV oxidation has been extensively investigated to activate the carbonyl group of ketone and/or hydrogen peroxide itself [4–21].

In this context, several heterogeneous catalysts, such as Ti-containing zeolite catalysts [4,5], Sn-containing zeolite catalysts [6–8], mesoporous ordered catalysts [9–11], solid acid catalysts [12–15], cationic clay-based catalysts [16–19], and polymer-anchored metal complex catalysts [20,21], have been reported. Among these catalysts, our group has reported high activity for H-type β-zeolite (HBEA) catalysts for the BV oxidation of cyclohexanone to ε-caprolactone using H$_2$O$_2$ [15]. As has been mentioned

in our previous study, the Brønsted acid sites in these HBEA catalysts possibly activate $H_2O_2$ and facilitate the BV oxidation, as demonstrated by the results obtained from the Fourier transform infrared spectroscopy (FTIR) measurement of $H_2O_2$ adsorbed on the HBEA catalysts and the BV oxidation of cyclohexanone over $Na^+$-exchanged β-zeolites with varying percentages of ion-exchanged $Na^+$ [15]. However, the maximum yield of ε-caprolactone was obtained at a Si/Al ratio of 85 for the HBEA catalyst although the amount of $NH_3$ adsorption over the HBEA catalysts increased with decreasing the Si/Al ratio up to 55. Therefore, the role of Brønsted acid site in the HBEA zeolites for Baeyer–Villiger oxidation of cyclohexanone to ε-caprolactone still remains controversial.

In order to clarify the role of Brønsted acid site, the considerable points seem to be still remained; one is the effect of the successive hydrolysis of ε-caprolactone during BV oxidation of cyclohexanone, and the other is the influence of the amount of Lewis acid sites in HBEA catalysts for BV oxidation of cyclohexanone. As for the former point, the yield of ε-caprolactone is affected by the successive hydrolysis of ε-caprolactone over the HBEA catalysts; these successive reactions make it difficult to elucidate the role of $Al^{3+}$ in HBEA for the BV oxidation. We found that the successive hydrolysis of γ-butyrolactone obtained by the BV oxidation of cyclobutanone barely proceeded. By using cyclobutanone for BV oxidation, the proper activity of HBEA catalysts for BV oxidation itself is expected to be elucidated. With respect to the latter point, it is well known that zeolites possess not only Brønsted acid site, but also Lewis acid site, and both acid sites can chemisorb $NH_3$. By a quantitative determination of both Brønsted and Lewis acid sites, it is expected to elucidate not only the proper relationship between the catalytic activity of HBEA for BV oxidation and Brønsted acid site, but also the effect of Lewis acid site on the catalytic performance of HBEA for BV oxidation.

The present study was undertaken in order to elucidate the role of $Al^{3+}$ species in the HBEA catalysts for BV oxidation of cyclic ketones by using $H_2O_2$. The effect of the Al content on the BV oxidation of both cyclobutanone to γ-butyrolactone, which hardly gives any side reactions, and cyclohexanone to ε-caprolactone was investigated to compare the catalytic performance of the HBEA catalysts. The relationship between the catalytic performance and the amount of each acid site was also discussed.

## 2. Experimental

### 2.1. Catalyst preparation

HBEA catalysts with various Al contents were prepared under hydrothermal conditions [22]. HBEA catalysts were prepared in a hydrothermal synthesis reactor (Model KH-02, Hiro Company, Yokohama, Japan). An aqueous solution of tetraethylammonium hydroxide (TEAOH, 35%) as the structure-directing agent (30.25 g, Sigma–Aldrich), fumed silica (8.0 g, 0.007 μm, Sigma–Aldrich), and $Al(OH)_3$ (Nacalai Tesque) were stirred at room temperature for 4 h in a polyethylene beaker. An aqueous solution of HF (46%, 4.02 g, Nacalai Tesque) was slowly added into the hydrogel mixture prepared in the first step with vigorous agitation. The composition of each compound in the reaction mixture was $SiO_2:yAl_2O_3:0.54TEAOH:0.54HF:9.3H_2O$ ($y = 0.0036$, 0.0050, 0.0063, 0.0100, 0.0125, 0.0185, 0.0250, and 0.0294). The mixture thus obtained was transferred to a Teflon-coated stainless steel autoclave reactor for crystallization at 423 K for 7 days. The obtained white solid was filtered and rinsed with 3 L of hot (ca. 343 K) deionized water. The as-synthesized sample was dried overnight at 393 K, followed by calcination in atmosphere at 853 K for 5 h for removing the structure-directing agent. The calcined sample was converted to its Na form via ion exchange with an

aqueous solution of 1 M $NaNO_3$ at 353 K for 24 h. $Na^+$ was ion-exchanged with $NH_4^+$ from a 1 M aqueous $NH_4NO_3$ solution at 353 K for 24 h. Finally, the sample was dried overnight at 393 K, followed by calcination in air flow at 773 K for 5 h, affording proton-type β-zeolites. Hereafter, the obtained catalysts will be referred to as HBEA$X$, where $X$ represents the Si/Al ratio in the catalysts as estimated by X-ray fluorescence (XRF) analysis.

In addition, β-zeolite (Si/Al ratio of 37.5) was obtained from Zeolyst International (Pennsylvania, USA). This commercial β-zeolite was subjected to the same treatment as the HBEA catalysts described above: ion exchange with $Na^+$ and $NH_4^+$, followed by calcination. Hereafter, the catalyst thus obtained will be referred to as rHBEA37.5.

### 2.2. Characterization

#### 2.2.1. X-ray fluorescence analysis

The contents of Si and Al in the HBEA catalysts were estimated by XRF spectroscopy (Rigaku, Primini) under a vacuum of 1.7 Pa. The HBEA samples were excited using a Pd X-ray tube operated at 40 kV and 1.25 mA.

#### 2.2.2. Powder X-ray diffraction (XRD) patterns

Powder XRD patterns of the HBEA catalysts were recorded on a RINT-2000 (Rigaku) XRD instrument with Cu Kα radiation for confirming the structure of each sample. The X-ray tube was operated at 40 kV and 20 mA.

#### 2.2.3. $N_2$ adsorption measurements

Nitrogen adsorption measurements were performed at 77 K on a BELSORP-mini apparatus (MicrotracBEL Corp.) after pretreatment at 473 K under a $N_2$ flow of 50 mL/min for 2 h.

#### 2.2.4. Temperature-programmed desorption

The temperature-programmed desorption (TPD) of adsorbed $NH_3$ was performed in a static vacuum system for evaluating the amount of acid sites in the HBEA catalysts. The adsorption of $NH_3$ on a sample was conducted at 373 K, followed by evacuation for 0.5 h. The amount of $NH_3$ adsorbed on the sample was estimated by the difference between the total and reversible amounts of adsorbed $NH_3$. The adsorbed samples were heated at 10 K/min at temperatures ranging from 373 to 773 K. The pressure of desorbed ammonia was recorded using an ion gauge vacuum meter.

#### 2.2.5. Infrared spectroscopy for the adsorption of pyridine on the HBEA catalysts

The infrared (IR) spectra of the pyridine adsorbed on each catalyst were recorded using an in situ Pyrex glass cell equipped with KBr single-crystal windows. A sample disk with a diameter of 13 mm was compression-molded from 20 mg of β-zeolite powder. The specimen was evacuated at 723 K for 2 h in the static vacuum system, followed by rapid transfer into the in situ IR cell with subsequent evacuation at 523 K for 2 h in vacuo. After pretreatment, pyridine was adsorbed at room temperature for 30 min, and the sample was evacuated at 523 K for 1 h. A total of 1000 scans for the sample IR spectra were recorded on a Nicolet 380 FTIR spectrometer, equipped with a highly sensitive MCT detector. The resolution of the spectrometer was $4 \, cm^{-1}$.

### 2.3. Catalytic test

#### 2.3.1. Baeyer–Villiger oxidation of cyclic ketones with $H_2O_2$

The BV oxidation of cyclobutanone with $H_2O_2$ was performed in an Erlenmeyer flask fitted with a condenser. Cyclobutanone (0.15 mL, 2.2 mmol, Tokyo Chemical Industry), 30% of a $H_2O_2$ aqueous solution (0.18 mL, 2.2 mmol, Wako), acetonitrile (4 mL, Nacalai