



Title	Cs-Beta with an Al-rich composition as a highly active base catalyst for Knoevenagel condensation
Author(s)	Otomo, Ryoichi; Osuga, Ryota; Kondo, Junko N. et al.
Citation	Applied catalysis A-general, 575, 20-24 https://doi.org/10.1016/j.apcata.2019.02.014
Issue Date	2019-04-05
Doc URL	https://hdl.handle.net/2115/80825
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Rights(URL)	https://creativecommons.org/licenses/by-nc-nd/4.0/
Type	journal article
File Information	190206-Alkali-Text-0R.pdf



**Cs-Beta with an Al-rich composition as a highly active base catalyst
for Knoevenagel condensation**

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1 **Abstract**

2 Ion-exchange of an Al-rich zeolite beta, synthesized by organic structure-directing agent-
3 free method (Beta-OF), was studied for application as a base catalyst. While the as-synthesized Beta-
4 OF in Na-form itself had base sites and showed moderate catalytic activity for Knoevenagel
5 condensation, the ion-exchange with Cs^+ improved the catalytic activity. For Knoevenagel
6 condensation of benzaldehyde with ethyl acetoacetate, the catalytic activity of Beta-OF ion-
7 exchanged with Cs^+ largely surpassed that of the conventional zeolite beta with less Al content. CO_2 -
8 TPD and IR observation with chloroform as a probe molecule revealed that the Cs-exchanged Beta-
9 OF had strong base sites comparable to Cs-exchanged Y zeolite. Base strength of Beta-OF was
10 stronger than that expected by Sanderson's theory. A local high density of Al atoms in the framework
11 of Beta-OF resulted in the unexpected base property and high catalytic activity.

12
13 **Keywords:** Beta; Ion exchange; Knoevenagel condensation; OSDA-free; Solid base

1. Introduction

Zeolite beta, with the three-dimensional large pore system, has been well studied and practically used as solid acid catalysts in chemical industries. The conventional synthesis of zeolite beta requires organic structure-directing agent (OSDA), typically tetraethylammonium hydroxide, the use of which unfortunately results in high synthetic cost of the zeolite, CO₂ and NO_x emission, and energy consumption. The recent breakthrough is the successful synthesis of zeolite beta without using any OSDA [1-4]. This sustainable and feasible synthesis method has led us into the extensive research on “OSDA-free” zeolite beta (hereinafter, referred to as “Beta-OF”) relevant to solid acid catalysts for cracking of hydrocarbons [5-8], Friedel-Crafts reactions [9,10], methanol to olefins reaction [11], and conversion of sugars [12].

A unique feature of Beta-OF is a high Al content, which is much higher than the conventional zeolite beta synthesized with OSDAs; a typical Si/Al ratio for Beta-OF ranges from 5 to 8, while that for the conventional beta (Beta-CV) ranges from 10 to 20. Making good use of the high Al content for Beta-OF, ion-exchange with Fe²⁺ or Cu²⁺ has been investigated and the ion-exchanged Beta-OF showed the excellent catalytic performance in decomposition of NO_x and hydrocarbons for purification of automobile exhaust gas [7,13-15].

Generally, zeolites ion-exchanged with alkali metal cations have base properties. In fact, the ion-exchange of faujasite zeolites with high Al contents has been intensively studied because of their high ion-exchange capacities and strong basicity [16-18]. Beta-CV has been studied for the ion-exchange with alkali metal cations and application as a base catalyst for Knoevenagel condensation,

1 Michael addition and so on [19-21]. However, there are only few reports on the ion-exchange with
2 alkali metal cations and base catalysis for Beta-OF.

3 In the present study, taking advantage of its high Al content, Beta-OF was ion-exchanged
4 with various metal cations and used as a solid base catalyst. We found that Cs-exchanged Beta-OF
5 showed an unexpectedly high catalytic performance in Knoevenagel condensation reactions.

6

7 **2. Experimental**

8 *2.1. Synthesis and ion-exchange of Beta-OF*

9 Beta-OF was synthesized following the reported method [1,5]. The obtained Na-form sample
10 is designated as “Na-Beta-OF”. Sodium cation in Na-Beta-OF was exchanged with Zn^{2+} , Ag^+ , Cs^+ ,
11 and La^{3+} using $\text{Zn}(\text{NO}_3)_2$, AgNO_3 , CsCl , and $\text{La}(\text{NO}_3)_3$, respectively. Typically, Na-Beta-OF was
12 soaked into 1 M aqueous solution of metal salts (50 mL/g-zeolite) and the resulting suspension was
13 vigorously stirred at 80 °C for 1 h. The solid sample was recovered by filtration and dried overnight
14 at 80 °C. For the ion-exchange with Zn^{2+} , Cs^+ , and La^{3+} , this operation was repeated two more times
15 in order to increase the ion-exchange degree. Na-Beta-OF was ion-exchanged to ammonium form by
16 stirring the sample powder in 2.5 M NH_4NO_3 aqueous solution and calcined at 550 °C for 5 h to
17 obtain a proton-form sample. The ion-exchanged samples with the metal cations and proton are
18 designated as *i.e.* “M-Beta-OF”, where M is H, Zn, Ag, Cs, and La. As a comparison, the ion-
19 exchange with Cs^+ was conducted on the commercially available conventional H-beta (Si/Al = 11.9,
20 purchased from Zeolyst) and Na-Y (Si/Al = 2.4, purchased from Tosoh). These samples are

1 designated as Cs-Beta-CV and Cs-Y, respectively.

2

3 2.2.Characterization of samples

4 Powder X-ray diffraction (XRD) patterns of the samples were collected on a Rigaku Ultima
5 III diffractometer using a Cu K α radiation (40 kV, 20 mA). The amount of Zn, Ag and La in the
6 samples was analyzed by ICP-AES using a Shimadzu ICPE-9000 spectrometer. The amount of Na
7 and Cs in the samples was estimated by atomic absorption spectroscopy (AAS) on a Shimadzu AA-
8 6200 spectrometer. Since mass of samples changed due to the introduction of heavy metals and
9 sodium contents in mmol/g were unknown, the ion-exchange degree was calculated based on the
10 content of Al atoms, which are the ion-exchange sites.

11 Base properties of samples were examined by temperature-programmed desorption of CO₂
12 (CO₂-TPD). Sample powder (50 mg) was pretreated at 400 °C for 1 h in He flow. The samples was
13 exposed to CO₂ flow (50 ml/min) at 50 °C for 0.5 h and then the gas flow was switched to He for
14 removing weakly adsorbed CO₂. TPD profile was obtained by increasing the temperature of the
15 sample from 50 to 400 °C at the rate of 10 °C/min in He flow (50 ml/min) and effluent gas was
16 analyzed by thermal conductivity detector. Additionally, base properties of Cs-exchanged samples
17 were characterized by FT-IR with chloroform as a probe molecule. Sample powder (50 mg) was
18 pelletized to a self-supporting disk (42 $\pm$ 2 mg) and set in a quartz cell connected to a vacuum line.
19 The sample disk was heated to 400 °C and kept for 1 h *in vacuo* and cooled to 50 °C. Then, the first
20 spectrum was recorded. A pre-determined amount of chloroform was introduced into the cell and after

the pressure became constant a spectrum was recorded. This operation was repeated as the amount of chloroform was changed at 50, 100, and 200 Pa. Here the difference spectra obtained by subtracting the first spectrum from the spectra after a certain amount of chloroform adsorbed were shown.

2.3. Catalytic tests

Catalytic performance of the ion-exchanged samples was assessed in Knoevenagel condensation of benzaldehyde with ethyl cyanoacetate or ethyl acetoacetate (Scheme 1). The sample powder was added to a round-bottom flask and pretreated *in vacuo* at 400 °C for 1 h. Then, dried dimethyl sulfoxide solution containing benzaldehyde and either acetate was poured into the flask. The catalytic reaction was conducted under inert nitrogen atmosphere. Small aliquots of the solution was taken at set time points and analyzed by GC-FID equipped with a DB-5 column (30 m × 0.25 mm × 0.25 μm). Since the corresponding ethyl cinnamate esters were the sole products detected for all the reaction runs, catalytic performance was estimated in terms of product yields.

3. Results and discussion

3.1. Structure and composition of Beta-OF samples

Na-Beta-OF had a highly crystalline *BEA-type structure but the MOR-phase was slightly observed on the XRD pattern (Figure S1). For H- and Zn-Beta-OF samples, the diffraction patterns did not change before and after the ion-exchange. The ion-exchange with Ag⁺, Cs⁺ and La³⁺ resulted in the decrease in the diffraction intensities, while no halo peak was observed. Similar observation

1 has been reported on Cs-exchanged faujasite zeolites [22,23]. With reference to these reports, this
2 decrease would be caused by the strong X-ray scattering on these heavy metals, but not by the
3 destruction of the structure.

4 Table 1 summarizes the composition of the prepared zeolite samples. For all of Beta-OF
5 samples, Si/Al ratio determined by ICP analysis ranged from 5.0 to 5.1, indicating that neither
6 dealumination nor desilication occurred during the ion-exchange procedure. Na-Beta-OF had 2.3
7 mmol/g of Na, which was almost the same as the Al content (2.2 mmol/g), confirming that the
8 negative charge on its framework was compensated by Na^+ . After the ion-exchange to ammonium-
9 form and the following calcination to give H-Beta-OF, the Na content was decreased to a negligible
10 amount. Sodium cation was exchanged with Ag^+ and Cs^+ at 90 and 80% of ion-exchange degree,
11 respectively. Since the total mass of the sample changed and the exact amount of exchangeable Na^+
12 was unclear when heavy metals were introduced, the ion-exchange degree was calculated based on
13 the amount of ion-exchangeable Al. The ion-exchange with Zn^{2+} proceeded at ~70% of the exchange
14 degree, but La^{3+} was introduced at only 55% of the exchange degree. Since ion-exchange with multi-
15 valent cations requires neighboring ion-exchange sites, the exchange degree was not increased for
16 Zn^{2+} and La^{3+} . For Zn- and La-Beta-OF, total positive charges by Na^+ and metal cations (Zn^{2+} or La^{3+})
17 were lower than the Al content. This shortage of the total positive charge would be compensated by
18 proton, because aqueous solution of zinc or lanthanum nitrate was weakly acidic [24].

19 Base properties of Beta-OF samples were examined by CO_2 -TPD (Figure 1). Na-Beta-OF
20 showed a desorption peak at 130 °C with a small peak at 320 °C. The number of base sites was 0.96

1 mmol/g, which was approximately a half of the amount of Na^+ cation, indicating that not all the Na^+
2 cation but particular cation formed such base sites that desorb CO_2 above 50 °C. The ion-exchange
3 of Na^+ for Cs^+ led to enhancement of the basicity; Cs-Beta-OF showed a large desorption peak at
4 280 °C and the number of base sites was estimated to be 1.5 mmol/g. Zn- and La-Beta-OF showed a
5 desorption peak at ~120 °C. These samples had ~0.3 mmol/g of remaining Na^+ , which could form a
6 part of base sites. H- and Ag-Beta-OF had only a small number of base sites. Ag-Beta-OF showed a
7 small peak at 270 °C, implying the presence of strong base sites, while H-Beta-OF did not show any
8 desorption at high temperature.

9

10 3.2. Catalytic properties of ion-exchanged Beta-OF samples

11 Catalytic properties of the ion-exchanged Beta-OF zeolites were studied in Knoevenagel
12 condensation of benzaldehyde with ethyl cyanoacetate (Figure 2). Without a catalyst, only a small
13 amount of ethyl cyanocinnamate was produced. Na-Beta-OF itself acted as a base catalyst promoting
14 the Knoevenagel condensation and gave 39% yield at 3 h. Note that for all the catalysts, ethyl
15 cyanocinnamate was the sole product detected. Cs-Beta-OF showed the best catalytic performance;
16 the yield of ethyl cyanocinnamate reached 52% for 3 h. Ag-Beta-OF showed a catalytic performance
17 similar to Na-Beta-OF regardless of the highest the exchange degree. Zn-Beta-OF exhibited a slight
18 catalytic activity; the yield of ethyl cyanocinnamate was about 9% after 3 h. H-Beta-OF and La-Beta-
19 OF did not show any catalytic activity probably because these zeolites with H^+ and La^{3+} could act as
20 acid catalysts.

1 Cs- and Na-Beta-OF, with a large number of base sites, gave the high yields. However, Ag-
2 Beta-OF showed a catalytic activity similar to that of Na-Beta-OF in spite of the small number of
3 base sites. In terms of the product yield, the catalytic activity was not correlated with the total number
4 of base sites estimated by CO₂-TPD. These three samples commonly showed desorption of CO₂ above
5 200 °C, which implies the presence of strong base sites. Obviously, strong base sites played an
6 important role in promoting the Knoevenagel condensation. On the other hand, weak base sites that
7 were observed in desorption of CO₂ below 200 °C did not contribute to the reaction, probably because
8 they cannot abstract a hydrogen atom at the α -position of ethyl cyanoacetate, which is supposed to be
9 the rate-determining step for Knoevenagel condensation.

10 The order of catalytic activity was opposite to that of electronegativity of hydrogen and metal
11 atoms except for lanthanum. The electronegativity is in the order of Cs (2.2) < Na (2.9) < La (3.1) <
12 Ag (4.4) < Zn (4.5) < H (7.2) < O (7.5), where the figures in the parentheses are electronegativity
13 values in eV [25,26]. It can be considered that a metal species with a low electronegativity could
14 donate electron on the zeolite framework to a high degree and consequently the resulting
15 electronegative framework oxygen atoms would act as base sites promoting the Knoevenagel
16 condensation. The lower electronegativity a metal species has, the stronger base site the neighboring
17 framework oxygen atom forms. This tendency supports the assumption that the catalytic activity was
18 governed by the strength of base sites.

19 Catalytic properties of Cs-Beta-OF was compared with Cs-exchanged Beta-CV, and Y
20 zeolites (Figure 3). Cs-Beta-OF gave a higher yield of ethyl cyanocinnamate than Cs-Beta-CV and

1 Cs-Y (Figure 3A). The catalytic activity of these samples was further compared for the reaction with
2 ethyl acetoacetate instead of cyanoacetate (Figure 3B). Since the acidity of active methylene for ethyl
3 acetoacetate is lower than that for ethyl cyanoacetate ($pK_a = 14.1$ and 13.1 , respectively), the
4 reactivity of ethyl acetoacetate was much lower, resulting in the low production rate of ethyl
5 acetylcinnamate [27]. Cs-Beta-OF also showed the highest yield of ethyl acetylcinnamate, being
6 comparable to Cs-Y, which has been well known as a highly active base catalyst [16-18]. Cs-Beta-
7 CV showed poor catalytic activity, resulting in only a slight yield of the product, though it showed
8 moderate catalytic activity for the reaction with ethyl cyanoacetate.

9 The catalytic activity of these three samples were compared in terms of turnover frequency
10 (TOF) for the production of the cinnamate esters over Cs^+ cation (Table 2). Cs-Beta-OF showed
11 higher TOF than Cs-Y for both of cinnamate esters, suggesting the advantage of Cs-Beta-OF over the
12 conventional zeolite-based base catalyst. Cs-Beta-CV showed high TOF for the production of ethyl
13 cyanocinnamate, while it showed much lower TOF for that of ethyl acetocinnamate. Because the
14 formation of ethyl cyanocinnamate could occur over all the base sites formed by Cs^+ cation, TOF for
15 Cs-Beta-OF and Cs-Y was estimated to be low due to their large number of base sites. On the other
16 hand, the formation of ethyl acetocinnamate requires specifically strong base sites. The high TOF for
17 Cs-Beta-OF suggest the presence of such strong base sites on it. Cs-Beta-OF showed much higher
18 catalytic activity than Cs-Beta-CV for ethyl acetocinnamate, indicating the advantage of OSDA-free
19 beta over the conventional one in terms of not only the synthesis cost and simplicity but also the
20 catalytic performance.

1

2 3.3. Base properties of Cs-exchanged zeolites

3 In order to obtain information on base properties in detail, the Cs-exchanged zeolites were
4 examined by FT-IR using chloroform as a probe molecule (Figure 4). Cs-Beta-OF showed a broad
5 band at around 3000 cm^{-1} , which is assigned to C-H stretching vibration of chloroform on base sites
6 [28]. The asymmetric shape of the band indicates the overlap of at least two bands centering at around
7 3000 and 2970 cm^{-1} . The former band is assigned to chloroform simply adsorbed on top of a basic
8 framework oxygen atom, and the latter is assigned to chloroform that adsorbed at two points of the
9 oxygen atom and neighboring Cs^+ (Figure S2) [29,30]. The redshift of the bands compared to gaseous
10 chloroform (3034 cm^{-1}) was due to the elongation of the C-H bond by the interaction with base sites
11 on the zeolite [31]. The intensities of these bands were increased along with the dosing pressure
12 (Figure S3). Cs-Beta-CV gave an absorption band at around 3017 cm^{-1} in a low intensity. Cs-Y
13 showed an absorption band similar to that of Cs-Beta-OF centering at 3000 cm^{-1} . Table 2 shows of
14 the band shift to gaseous chloroform and integrated peak area of the IR bands for Cs-exchanged
15 zeolites. Since the degree of red shift and the peak area are indicative of the strength and the number
16 of base sites on the zeolites, respectively, Cs-Beta-OF and Cs-Y had the similar number of base sites
17 with similar strength. Cs-Beta-CV had only a small number of weak base sites. Obviously, the
18 catalytic activity in TOF is governed by both the number and the strength of base sites, but scarcely
19 affected by the microporous structures. In particular, there is a threshold strength of base sites that
20 can promote the deprotonation of ethyl acetoacetate; Cs-Beta-OF had enough base strength to

1 promote the deprotonation, while Cs-Beta-CV did not have such strong base sites, as observed in the
2 red shift at 17 cm^{-1} . These results clearly demonstrated that Cs-Beta-OF had a large number of strong
3 base sites owing to the high aluminum content of OSDA-free beta, leading to a high catalytic
4 performance.

5 According to Sanderson's theory [32], electronegativity (S) of a multi-component material
6 can be estimated as a function of electronegativity of each element (see *Supporting Information*). The
7 partial charge of oxygen atom (δ_{O}) can be estimated by using Sanderson's electronegativity [33]. The
8 composition, electronegativity, and partial charge on oxygen atoms calculated by using the reported
9 electronegativity of each element for the Cs-exchanged zeolites are listed in Table 3 [33]. The partial
10 charge on oxygen atoms for Cs-Beta-OF and Cs-Y were estimated to be -0.32 and -0.37, respectively.
11 Since an electronegative framework oxygen atom can act as a base site, the δ_{O} is a good index for
12 strength of base sites [29,33,34]. It is noteworthy that Cs-Beta-OF showed a similar IR band shift to
13 Cs-Y in the adsorption of chloroform and showed similar or slightly better catalytic activity than Cs-
14 Y, though Cs-Beta-OF was estimated to have less basic oxygen atoms by Sanderson's theory.
15 Following Sanderson's theory that hypothesize the delocalized electronic properties of each oxygen
16 atom in a material, the negative charge on oxygen atoms becomes larger along with the Al content
17 (Figure S4). However, physicochemical properties of framework oxygen atoms differ depending on
18 a coordination state and a framework type. Al atoms do not equally occupy T-sites of the framework
19 but preferentially occupy particular T-sites. In a ^{27}Al MAS NMR spectrum, Cs-Beta-OF showed an
20 intense peak at 57 ppm with a small shoulder peak at 54 ppm, whereas Cs-Beta-CV showed a main

1 peak at 54 ppm (Figure 5). These two peaks are assigned to Al atoms at different T-sites, indicating
2 different distributions of Al atoms between these beta zeolites. In ion-exchange with Co^{2+} , Beta-OF
3 showed a higher Co/Al ratio than Beta-CV (Table S2), demonstrating that Beta-OF had a large
4 number of Al atoms located close to each other, so called “paired Al atoms” [11,35]. It is conceivable
5 that the negative charge on oxygen atoms in such structures with locally a high density of Al atoms
6 would be higher than that predicted by Sanderson’s theory and that such highly electronegative
7 oxygen atoms could act as strong base sites, promoting Knoevenagel condensation reactions.

8

9 **4. Conclusions**

10 The Na-form Beta-OF exhibited remarkable ion-exchange capability due to its high Al
11 content. The Na^+ cation was able to be exchanged with various cations including multi-valent cations.
12 For the ion-exchanged Beta-OF, the order of catalytic activity in Knoevenagel condensation was
13 opposite to that of electronegativity. Cs-Beta-OF had strong base sites comparable to Cs-Y and
14 showed a remarkable catalytic activity. The strong base properties and high catalytic activity of Cs-
15 Beta-OF was attributed to a local high density of Al atoms, which was particular to OSDA-free zeolite
16 beta. Our findings in this work will contribute to the expansion of the application of various OSDA-
17 free zeolites with high Al contents as well as the improvement of the base catalytic and ion-exchange
18 properties of metal cation-exchanged zeolites.

19

20 **Acknowledgement**

1 This work was performed under the Cooperative Research Program of “Network Joint Research Center for Materials
2 and Devices”. This work was supported by JSPS KAKENHI Grant Number JP16H06596.

3

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1

Table 1 Composition of ion-exchanged beta and Y zeolites.

Sample	Si/Al (-)	Al content ^a (mmol/g)	Cation ^{a,b} (mmol/g)		Ion-exchange ^c (%)	Base site ^d (mmol/g)
			Metal	Sodium		
Na-Beta-OF	5.1	2.2	-	2.3	-	0.96
H-Beta-OF	5.0	2.3	-	0.03	-	0.04
Zn-Beta-OF	5.1	2.2	0.73	0.27	66	0.55
Ag-Beta-OF	5.1	2.1	1.9	0.08	90	0.06
Cs-Beta-OF	5.0	2.0	1.6	0.27	80	1.53
La-Beta-OF	5.1	1.9	0.35	0.28	55	0.61
Cs-Beta-CV	11.9	1.0	0.26	trace	26	0.19
Cs-Y	2.8	3.0	1.6	1.5	53	0.44

2 ^a Determined by ICP-AES.3 ^b Determined by AAS.4 ^c Ion-exchange degree for Mⁿ⁺ is defined as (n × Metal content) / (Al content) × 100.5 ^d The amount of base site determined by CO₂-TPD.

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Table 2 Base and catalytic properties of Cs-exchanged zeolites.

Sample	Composition ^a	Peak shift ^b (cm ⁻¹)	Peak area ^c (cm ⁻¹)	S ^d	δ_{O} ^e	Turnover frequency ^{f, g} (h ⁻¹)	
						ECA ^h	EAA ^h
Cs-Beta-OF	Na _{0.13} Cs _{0.81} Al _{1.0} Si _{5.0} O _{12.0}	-34	9.6	3.69	-0.32	13.8	3.0
Cs-Beta-CV	H _{0.74} Cs _{0.26} Al _{1.0} Si _{11.9} O _{25.8}	-17	1.5	4.14	-0.23	20.0	< 0.1
Cs-Y	Na _{0.46} Cs _{0.54} Al _{1.0} Si _{2.8} O _{7.6}	-34	9.8	3.47	-0.37	9.1	2.0

^a Determined by ICP-AES and AAS.^b IR peak shift in C-H stretching vibration of adsorbed chloroform relative to gaseous molecule.^c Integrated peak area of IR band for C-H stretching vibration.^d Sanderson's electronegativity.^e Partial charge on oxygen atoms.^f Turnover frequency was calculated as (mmol of product at 0.5 h) / (mmol of cesium in a catalyst) / 0.5 h.^g Reaction conditions were identical to those for Figure 3.^h TOF for Knoevenagel condensation of benzaldehyde with ethyl cyanoacetate (ECA) and ethyl acetoacetate (EAA).

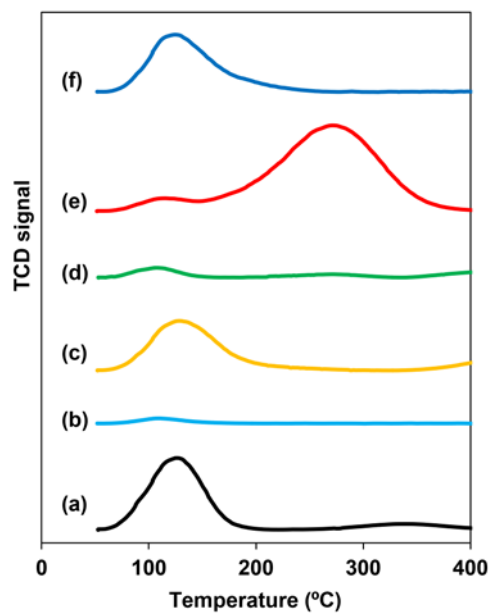


Figure 1 CO₂-TPD profiles of (a) Na-Beta-OF, (b) H-Beta-OF, (c) Zn -Beta-OF, (d) Ag-Beta-OF, (e) Cs-Beta-OF, and (f) La-Beta-OF.

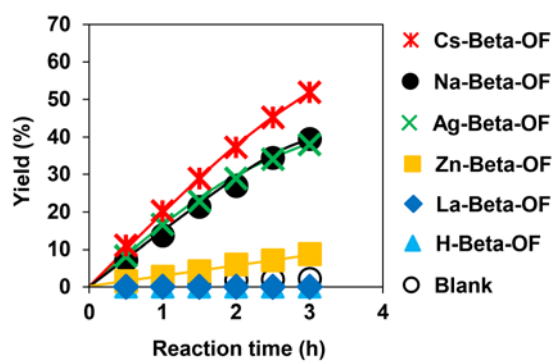


Figure 2 Catalytic performance of ion-exchanged zeolites for in Knoevenagel condensation of benzaldehyde with ethyl cyanoacetate. Reaction conditions, catalyst, 50 mg; benzaldehyde, 5 mmol; ethyl cyanoacetate, 5 mmol; DMSO 25 ml; temperature, 60 °C.

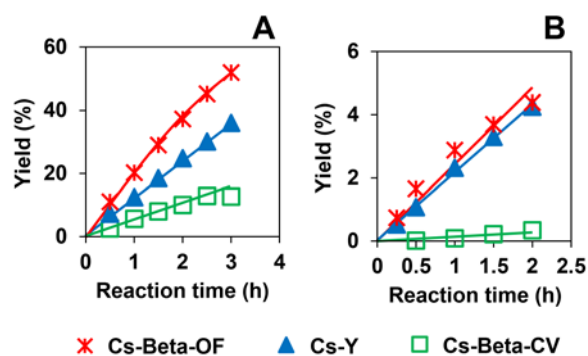


Figure 3 Catalytic performance of Cs-exchanged zeolites in Knoevenagel condensation of benzaldehyde with (A) ethyl cyanoacetate and (B) ethyl acetoacetate. Reaction conditions, catalyst, 50 mg; benzaldehyde, 5 mmol; ethyl cyanoacetate or acetoacetate, 5 mmol; DMSO 25 ml; temperature, 60 and 100 °C for ethyl cyanoacetate and acetoacetate, respectively.

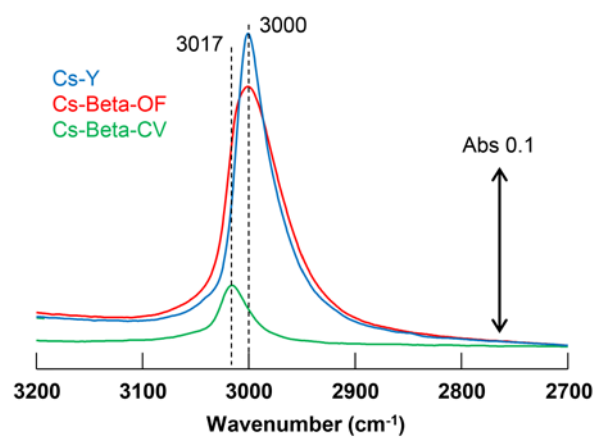


Figure 4 IR spectra of chloroform adsorbed on Cs-exchanged zeolites at the dosing pressure of 50 Pa.

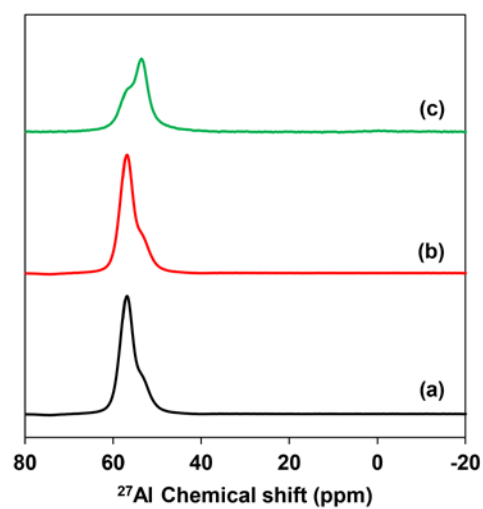
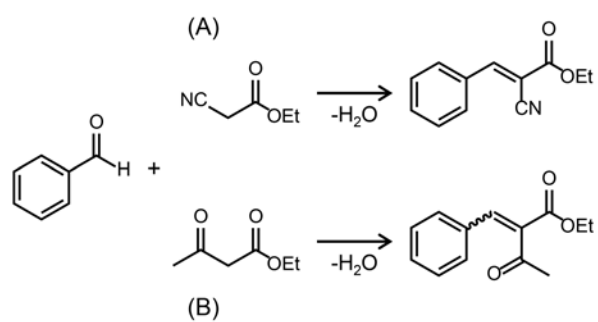


Figure 5 Solid-state ^{27}Al MAS NMR spectra of (a) Na-Beta-OF, (b) Cs-Beta-OF, and (c) Cs-Beta-CV.



Scheme 1 Knoevenagel condensation of benzaldehyde with (A) ethyl cyanoacetate or (B) ethyl acetoacetate.