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Sustainable production of acrylic acid: Rb^+- and Cs^+-exchanged Beta zeolite catalysts for catalytic gas-phase dehydration of lactic acid

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ABSTRACT

Rb^+- and Cs^+-exchanged Beta zeolites ($Rb_xNa_{1-x}\beta$ and $Cs_xNa_{1-x}\beta$) of varying exchange degrees ($x = 0$–1.00) were employed to catalyze the gas-phase dehydration of lactic acid (LA) for sustainable production of acrylic acid (AA) in a flow fixed-bed reactor at 360 °C, using an aqueous solution of LA (10 mol% or 35.7%) as the reaction feed at a weight hourly space velocity by LA of 2.1 h^{-1}. An appropriate window of the ion exchange degrees for highly selective AA production ($\geq$60 mol%) was determined for either series of the samples, i.e., $x = 0.85$–0.98 for the $Rb_xNa_{1-x}\beta$ and $x = 0.71$–0.90 for the $Cs_xNa_{1-x}\beta$ samples. The best performing catalysts $Rb_{0.95}Na_{0.05}\beta$, and $Cs_{0.81-0.90}Na_{0.19-0.10}\beta$ offered the highest AA selectivity (ca. 70 mol%) and yield (ca. 60–65 mol%) for reaction periods of longer than 10 h. Measurements of the surface acidity and basicity of the catalyst samples by temperature-programmed desorption of NH_3 and CO_2 showed that the highly selective catalysts in such widows should have both weakly acidic and weakly basic surface sites with suitably balanced acidity and basicity. The acid-catalyzed decarbonylation/decarboxylation and base-catalyzed condensation of LA, which lead respectively to formation of acetaldehyde and 2,3-pentanedione, always occurred as the competing reactions over the investigated catalysts. Observations on the catalyst selectivity changes for these competing reactions clearly demonstrate that the suitably balanced acidity and basicity at the catalyst surface is the key to the high selectivity for the desired dehydration reaction.

1. Introduction

Acrylic acid (AA) is an important intermediate for a number of key molecules and materials such as acrylate polymers [1], whose production by gas-phase dehydration of bio-derivative lactic acid (LA) has been recommended as a promising green and sustainable alternative to current commercial AA production technology based on a two-step selective catalytic oxidation technology using petroleum-derivative propylene as the feed [2–5]. A number of heterogeneous catalysis studies on this LA-to-AA (LTA) reaction seem to indicate that a suitable acidity and basicity at the catalyst surface should be essential for enabling highly selective AA production chemistry [6–9].

Zeolite beta (β) in different forms has been widely used as solid catalyst in fine chemicals synthesis and petrochemical industries [10,11], due to its three-dimensional 12-membered ring channel system [12–14] and easily adjustable acid–base and redox properties according to the nature and exchange degree of the extra framework cations [15–17]. For instance, the exchange with alkali ions of β zeolites has frequently been used to increase their basicity and correspondingly decrease their acidity [18–23]. Thus, the alkali-ion exchanged forms of β zeolites were used to serve as base or acid–base bifunctional catalysts for a number of reactions, including the side-chain alkylation of toluene [24–26], Knoevenagel reactions [27,28], and Michael addition reactions [27,29]. Alkali-ion exchanged β zeolites ($M_xNa_{1-x}\beta$, M = Li^+, Na^+, K^+, Rb^+ or Cs^+) were prepared and employed recently to catalyze the LTA reaction under different conditions in our laboratory. When the ion-exchange degrees were made higher than 80% or $x \geq 0.80$, the less acidic and more basic K^+-, Rb^+- and Cs^+-exchanged samples appeared to be more selective for AA production than their Li^+- and Na^+-exchanged counterparts at nearly complete LA conversion (97–100%) [30]. By systematic investigation of the effect of K^+-exchange degree on the catalytic performance of the $K_xNa_{1-x}\beta$ ($x = 0$–1.00) catalyst, a window for the K^+-exchange degrees (i.e., $x = 0.92$–0.98) was uncovered for offering suitably balanced surface acidity and basicity to enable a high AA selectivity ($\geq$50 mol%) [30]. These previous data imply that a further investigation of

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RbNaβ and CsNaβ catalysts with respectively widely varied Rb^+- and Cs^+-exchange degrees would be deserving as the appropriate ion-exchange windows of Rb^+ and Cs^+ ions for the LTA reaction remained unexplored in the earlier report.

We report herein the surface acid–base property of these $Rb_xNa_{1-x}\beta$ and $Cs_xNa_{1-x}\beta$ catalysts and their performance in catalyzing the LTA reaction. The data obtained in this study are discussed by comparison with those obtained previously on the $K_xNa_{1-x}\beta$ samples, which confirm that suitably balanced acidity and basicity at the catalyst surface is the key to the high efficiency of the LTA reaction. Besides, the present $Rb_xNa_{1-x}\beta$ and $Cs_xNa_{1-x}\beta$ catalysts are found superior to the previous $K_xNa_{1-x}\beta$ catalysts in catalyzing the LTA reaction in terms of AA selectivity and yield.

2. Experimental

Raw powders of as-synthesized Beta zeolite (SiO_2/Al_2O_3 = ca. 40, Nankai University Catalyst Co., Ltd.) were calcined in ambient air at 420 °C for 1 h, then at 540 °C for 5 h to completely remove any organic residue. The calcined sample (15 g) was then converted to its sodium form, i.e., Naβ, by subjecting for four times to ion-exchange in 0.5 M $NaNO_3$ aqueous solution (300 ml) at 80 °C for 1 h. The solid product powders were filtered, dried overnight at 110 °C and calcined at 500 °C for 3 h, and were then used to prepare the Rb^+- and Cs^+-exchanged samples by ion-exchange with aqueous solutions of $RbNO_3$ and $CsNO_3$, respectively. Variation of the exchange degrees for Rb^+ or Cs^+ ions was done by adjusting the concentration of aqueous $RbNO_3$ or $CsNO_3$ (0.005–0.5 M), and repetition times (1–4 times) of the ion-exhange reaction. Typically, ca. 2 g of Naβ was dispersed and stirred in the $RbNO_3$ or $CsNO_3$ solution (40 ml) at 80 °C for 1 h. The ion exchange reaction was repeated for 1–4 times to achieve the desirable exchange degrees. At the termination of the final ion exchange, the sample was filtered, dried (110 °C, overnight) and calcined (500 °C, 3 h). The calcined samples are coded as $M_xNa_{1-x}\beta$ (M = Rb^+ or Cs^+), in which x refers to the fractional exchange degree of M (x = M/[M+Na] (molar)). In particular, an additional calcination step (500 °C, 3 h) should be added after the second ion-exchange reaction with 0.5 M $RbNO_3$ or $CsNO_3$ for preparing the $Rb_{1.00}\beta$ and $Cs_{1.00}\beta$ samples. Table 1 presents the different $M_xNa_{1-x}\beta$ samples investigated in this study.

The contents of alkali ions and SiO_2/Al_2O_3 ratio in the $M_xNa_{1-x}\beta$ samples were determined by X-ray fluorescence (XRF) analysis on a Shimadzu XRF-1800 fluorescence spectrometer. The BET surface areas, pore volumes and average pore diameters were derived from adsorption–desorption isotherms at −196 °C measured on a Micromeritics ASAP 2010C instrument after outgassing at 200 °C for 5 h. Surface acid–base properties of the samples were probed by temperature-programmed desorption of NH_3 (NH_3-TPD) and CO_2 (CO_2-TPD) on a Catalyst Analyzer (BEL JAPAN INC.) equipped with a well-calibrated quadrupole mass spectrometer (Inprocess Instruments, GAM 200) as the detector [9]. The sample was placed in a quartz microreactor and pretreated in a flow of 20% O_2/Ar (40 ml/min) at 500 °C for 1 h. After cooling the reactor to 100 °C, the reactor was switched to a flow of 2% NH_3/Ar or 2% CO_2/Ar (40 ml/min) for NH_3 or CO_2 adsorption (1 h). Then, the sample was purged with flowing Ar (40 ml/min) to remove weakly adsorbed NH_3 or CO_2 for 1–1.5 h (until the background signals of NH_3 and CO_2 became stabilized). The reactor temperature was then increased to 600 °C at a rate of 10 °C/min and the desorption profiles of NH_3 and CO_2 were monitored by recording the signals at m/z = 15 and 44, respectively. The calibration of the mass spectrometer and quantification of the desorbed NH_3 and CO_2 were documented earlier [9].

The gas-phase dehydration of LA was carried out under atmospheric pressure at 360 °C in a vertical down-flow fixed-bed tubular quartz reactor (50 cm × 9 mm (i.d.)). A constant weight of catalyst (500 mg, 20–40 mesh) was sandwiched in the middle of the reactor with quartz wools. About 2 ml of quartz sands (ca. 2 cm by height) were placed above the catalyst bed to ensure complete evaporation of the liquid feed. Prior to injection of the reaction feed, an aqueous solution containing 10 mol% (35.7 wt%) LA, the catalyst was pretreated at the reaction temperature for 1 h in flowing N_2 (25 ml/min). A flow of N_2 (15.5 ml/min) was used as the reaction carrier gas, which combined with the vaporized liquid feed to make a feeding gas mixture containing 7.4 kPa LA and 66.9 kPa H_2O (N_2 balance). The reaction weight hourly space velocity by LA ($WHSV_{LA}$) was 2.1 h^{-1}. Each run of the reaction was conducted for 10 h, during which the reaction effluents were condensed in an ice-water trap and collected hourly for off-line analysis by gas chromatograph (GC) and ion chromatograph (IC). The materials balance of the reaction was always higher than 95%, except in the very first hour. As reported earlier [9], the GC analysis would usually not be that reliable for the quantification of LA, especially when its conversion was higher than 70% or LA concentration in the condensate lower than 10 wt%. The IC analysis was instead established to accurately determine the LA conversion in all possible levels (0–100%) [9]. Further details of the GC and IC analyses including their cross calibrations can be found in Refs. [9,30].

The LA conversion, product selectivity and AA yield were calculated according to the following equations [9,30]:

$$\text{LA conversion}\,(\%) = \frac{\text{moles of LA consumed}}{\text{moles of LA in the feed}} \times 100,$$

$$\text{Product selectivity}\,(\text{mol\% or C\%}) = \frac{\text{moles of carbon atoms in the product defined}}{\text{moles of carbon atoms in LA consumed}} \times 100,$$

$$\text{AA yield}\,(\text{mol\% or C\%}) = \frac{\text{moles of AA produced}}{\text{moles of LA in the feed}} \times 100.$$

3. Results and discussion

3.1. Composition and physicochemical properties

The two series of samples ($Rb_xNa_{1-x}\beta$ and $Cs_xNa_{1-x}\beta$) prepared from the parent Naβ by ion-exchange with the aqueous solutions of $RbNO_3$ and $CsNO_3$, respectively, are listed in Table 1, together with their preparation descriptors (including the concentration of $RbNO_3$ or $CsNO_3$ and repetition times of the ion-exchange), fractional exchange degree (x) of Rb^+ or Cs^+, SiO_2/Al_2O_3 ratio, and textural properties. The exchange degree of Cs^+ in the $Cs_xNa_{1-x}\beta$ samples always appeared lower than that of Rb^+ in $Rb_xNa_{1-x}\beta$ when the ion-exchange reactions were conducted under the similar conditions. Compared with the preparation of the $K_xNa_{1-x}\beta$ samples of comparable x in our previous study [30], more severe conditions for the ion-exchange reactions had to be taken for producing the current $Rb_xNa_{1-x}\beta$ and $Cs_xNa_{1-x}\beta$ samples. For instance, the $K_{1.00}\beta$ sample was obtained by conducting at 80 °C the ion-exchanging reaction of Naβ in an aqueous solution of 0.5 M KBr for four times, while the $Rb_{1.00}\beta$ and $Cs_{1.00}\beta$ samples could not be obtained simply by repeating four times the ion-exchange reaction in 0.5 M $RbNO_3$ or 0.5 M $CsNO_3$ solution unless an interim high-temperature (500 °C) calcination step was added. This is because that some Na^+ ions in the parent Naβ are located inside the cages with small openings and are not accessible to the larger Rb^+ (1.48 Å) and Cs^+ (1.69 Å) ions but smaller K^+ ions (1.33 Å) [31], and the calcination of the partially exchanged samples can cause redistribution by thermal migration of the alkali ions within the zeolite, making those Na^+ accessible to and replaced by the coexisting Rb^+ or Cs^+

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Table 1
Preparation descriptors, fractional exchange degrees of the alkali ions, SiO_2/Al_2O_3 ratio, textural and acid–base properties of the exchanged zeolite samples.

Samples[a]	Exchange solution	Times of ion exchange	SiO_2/Al_2O_3 [c]	S_{BET}[d] ($m^2\ g^{-1}$)	PV[e] ($cm^3\ g^{-1}$)	PD[f] (nm)	EP[g] ($e\ Å^{-1}$)	Acidity by NH_3-TPD[h]		Basicity by CO_2-TPD[i]	
								Peak temp. (°C)	Density*10^2 ($mol_{NH_3}\ m^{-2}$)	Peak temp. (°C)	Density*10^3 ($mol_{CO_2}\ m^{-2}$)
Naβ	–	–	41.3	475	0.27	5.3	1.05	289	35.9	154	5.9
$Rb_{0.60}Na_{0.40}β$	0.05 M $RbNO_3$	1	40.6	438	0.26	5.4	0.83	214	21.3	157	10.4
$Rb_{0.73}Na_{0.27}β$	0.1 M $RbNO_3$	1	41.9	435	0.26	5.4	0.78	207	17.3	164	13.7
$Rb_{0.85}Na_{0.15}β$	0.1 M $RbNO_3$	2	40.8	427	0.25	5.3	0.73	206	13.9	168	17.0
$Rb_{0.90}Na_{0.10}β$	0.5 M $RbNO_3$	1	41.2	419	0.25	5.2	0.71	200	7.6	175	18.4
$Rb_{0.95}Na_{0.05}β$	0.5 M $RbNO_3$	2	40.8	388	0.22	5.3	0.69	190	7.2	175	24.5
$Rb_{0.98}Na_{0.02}β$	0.5 M $RbNO_3$	4	41.5	361	0.23	5.3	0.68	181	3.9	178	29.7
$Rb_{1.00}β$	0.5 M $RbNO_3$	4[b]	42.3	321	0.20	5.6	0.67	183	3.6	185	36.0
$Cs_{0.16}Na_{0.89}β$	0.005 M $CsNO_3$	1	42.5	437	0.26	5.3	0.98	239	28.8	157	9.2
$Cs_{0.55}Na_{0.45}β$	0. 05 M $CsNO_3$	1	42.7	415	0.25	5.3	0.80	209	19.9	161	12.2
$Cs_{0.71}Na_{0.29}β$	0.1 M $CsNO_3$	1	42.1	421	0.25	5.4	0.73	207	9.0	164	15.3
$Cs_{0.77}Na_{0.23}β$	0.1 M $CsNO_3$	2	41.9	411	0.26	5.5	0.70	191	6.3	162	21.2
$Cs_{0.81}Na_{0.19}β$	0.5 M $CsNO_3$	1	40.8	413	0.24	5.1	0.68	181	3.3	167	24.9
$Cs_{0.90}Na_{0.10}β$	0.5 M $CsNO_3$	2	40.9	397	0.25	5.2	0.64	180	2.4	174	34.8
$Cs_{0.95}Na_{0.05}β$	0.5 M $CsNO_3$	4	41.8	356	0.23	5.3	0.61	179	1.8	180	44.1
$Cs_{1.00}β$	0.5 M $CsNO_3$	4[b]	43.0	285	0.19	5.7	0.59	177	1.3	188	60.6

[a] The subscript numbers show the fractional exchange degree of each alkali ion.

[b] Twice calcinations were used during the preparation.

[c] Determined from XRF measurements.

[d] BET surface area.

[e] Pore volume measured at $P/P_0 = 0.975$.

[f] Average pore diameter measured from the desorption branch according to the BJH method.

[g] Electrostatic potential (EP) for the alkali ions in the exchanged zeolites = $\sum z_i/r_i \times f_i$, in which z_i, r_i and f_i stand, respectively, for the charge, radius and exchange degree of alkali ion i in the sample.

[h] Measured from NH_3-TPD measurement.

[i] Measured from CO_2-TPD measurement.

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ions [32,33]. The displaced Na^+ ions then became exchanged with the Rb^+ or Cs^+ ions during the later ion-exchange steps.

The $Rb_xNa_{1-x}\beta$ and $Cs_xNa_{1-x}\beta$ samples ($x > 0$) showed smaller surface areas (285–438 $m^2\,g^{-1}$) and pore volumes (0.19–0.26 $cm^3\,g^{-1}$) in comparison to their parent Naβ (475 $m^2\,g^{-1}$ and 0.27 $cm^3\,g^{-1}$). The increase in x generally led to lower surface area and pore volume among the $Cs_xNa_{1-x}\beta$ or $Rb_xNa_{1-x}\beta$ samples. On the other hand, the surface area and pore volume for the samples with similar x, also decreased according to the size of the alkali ions, i.e., $Cs_xNa_{1-x}\beta < Rb_xNa_{1-x}\beta < K_xNa_{1-x}\beta$, in consistent with many earlier observations [30,31,34,35]. The SiO_2/Al_2O_3 ratios for the $Rb_xNa_{1-x}\beta$ and $Cs_xNa_{1-x}\beta$ samples (40.6–43.0), measured by XRF analysis, were consistent with the ratio for the as-synthesized Beta zeolite (ca. 40) and its derived Naβ (41.3); the error of the measurement was within ±5%. The $Rb_xNa_{1-x}\beta$, $Cs_xNa_{1-x}\beta$, Naβ and the calcined as-received raw samples showed also very similar XRD patterns but the intensity for the $Rb_xNa_{1-x}\beta$ and $Cs_xNa_{1-x}\beta$ was significantly lower due to that the larger Rb^+ and Cs^+ ions had much lower X-ray absorptions [20,31,35]. These data indicate that the repeated ion-exchange reaction and calcination caused no significant changes in the zeolite framework and the SiO_2/Al_2O_3 ratio. Thus, the surface area and pore volume losses of the $Rb_xNa_{1-x}\beta$ and $Cs_xNa_{1-x}\beta$ with high ion-exchange degrees (e.g., $x > 0.7$) could be mainly attributed to partial pore blockage by the large Rb^+ and Cs^+ ions, though a contribution from loss of zeolite crystallinity could not yet be completely excluded [20,31,35,36].

The acid–base properties of the $Rb_xNa_{1-x}\beta$ and $Cs_xNa_{1-x}\beta$ samples were probed by the NH_3- and CO_2-TPD measurements. Similar to the earlier study of the $K_xNa_{1-x}\beta$ samples [30], the desorption of either NH_3 or CO_2 from these $Rb_xNa_{1-x}\beta$ and $Cs_xNa_{1-x}\beta$ samples produced only one TPD peak, though the peak temperature and intensity (peak area) varied sensitively according to x of the sample (Figs. 1 and 2). NH_3 adsorbed on the parent Naβ zeolite would desorb in the temperature range of 140–450 °C, registering a peak at 289 °C (Fig. 1A) and a surface acidity of 3.59×10^{-1} $\mu mol\,m^{-2}$ (Table 1). The peak temperature of and the surface acidity registered from the NH_3-TPD profile for the $Rb_xNa_{1-x}\beta$ sample decreased from 289 °C and 3.59×10^{-1} $\mu mol\,m^{-2}$ to 183 °C and 3.6×10^{-2} $\mu mol\,m^{-2}$, respectively, when x was increased from 0 to 1.00 (Fig. 1A and Table 1). On the other hand, CO_2 adsorbed on the parent Naβ zeolite desorbed in the temperature range of 110–240 °C, registering a peak at 154 °C (Fig. 1B) and a surface basicity of 5.9×10^{-3} $\mu mol\,m^{-2}$ (Table 1). The peak temperature of and the surface basicity registered from the CO_2-TPD profile for the $Rb_xNa_{1-x}\beta$ sample increased from 154 °C and 5.9×10^{-3} $\mu mol\,m^{-2}$ to 185 °C and 3.6×10^{-2} $\mu mol\,m^{-2}$, respectively, when x was increased from 0 to 1.00 (Fig. 1B and Table 1). These data clearly indicate that the increase in the exchange degree of Rb^+ in the $Rb_xNa_{1-x}\beta$ sample reduced the surface acidity but improved the surface basicity, agreeing well with earlier documentations [19,30].

The NH_3- and CO_2-TPD profiles for the $Cs_xNa_{1-x}\beta$ samples (Fig. 2) are similar to those for the $Rb_xNa_{1-x}\beta$ samples (Fig. 1). Thus, increasing the value of x in $Cs_xNa_{1-x}\beta$ also led to smaller NH_3-TPD peak with lower peak temperature (acidity lower and weaker, Fig. 2A) but larger CO_2-TPD peak with higher peak temperature (basicity higher and stronger, Fig. 2B). The specific data for the peak temperature, surface acidity and basicity measured according to the NH_3- and CO_2-TPD profiles are also detailed for every $Cs_xNa_{1-x}\beta$ sample in Table 1. These observations on the dependences on x of the surface acidity and basicity for the $Cs_xNa_{1-x}\beta$ samples are consistent with those reported earlier for CsNaY zeolites [23,37].

Comparing the present NH_3- and CO_2-TPD results for $Cs_xNa_{1-x}\beta$ and $Rb_xNa_{1-x}\beta$ with those for $K_xNa_{1-x}\beta$ of similar x in our previous work [30] would show that the acidity of alkali-ion exchanged β zeolite ($M_xNa_{1-x}\beta$, M = K^+, Rb^+ and Cs^+) decreased but the basicity increased with the radius of the alkali ion, in line with many earlier reports in literature [18–20,38,39]. Specifically, the NH_3-TPD peak temperature was 200 °C for $K_{0.94}Na_{0.06}\beta$, 190 °C for $Rb_{0.95}Na_{0.05}\beta$ and 179 °C for $Cs_{0.95}Na_{0.05}\beta$, and the surface acidity measured as the number of desorbed NH_3 was

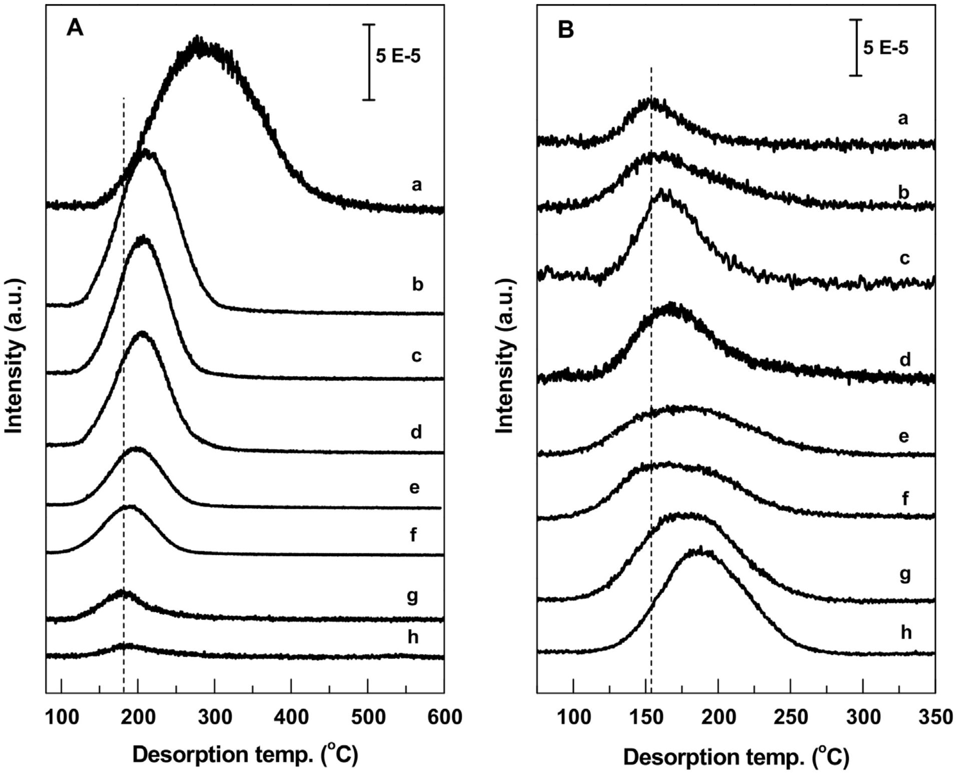

Fig. 1. NH_3-TPD (A) and CO_2-TPD (B) profiles from $Rb_xNa_{1-x}\beta$ of $x = 0$ (a), $x = 0.60$ (b), $x = 0.73$ (c), $x = 0.85$ (d), $x = 0.90$ (e), $x = 0.95$ (f), $x = 0.98$ (g) and $x = 1.00$ (h).

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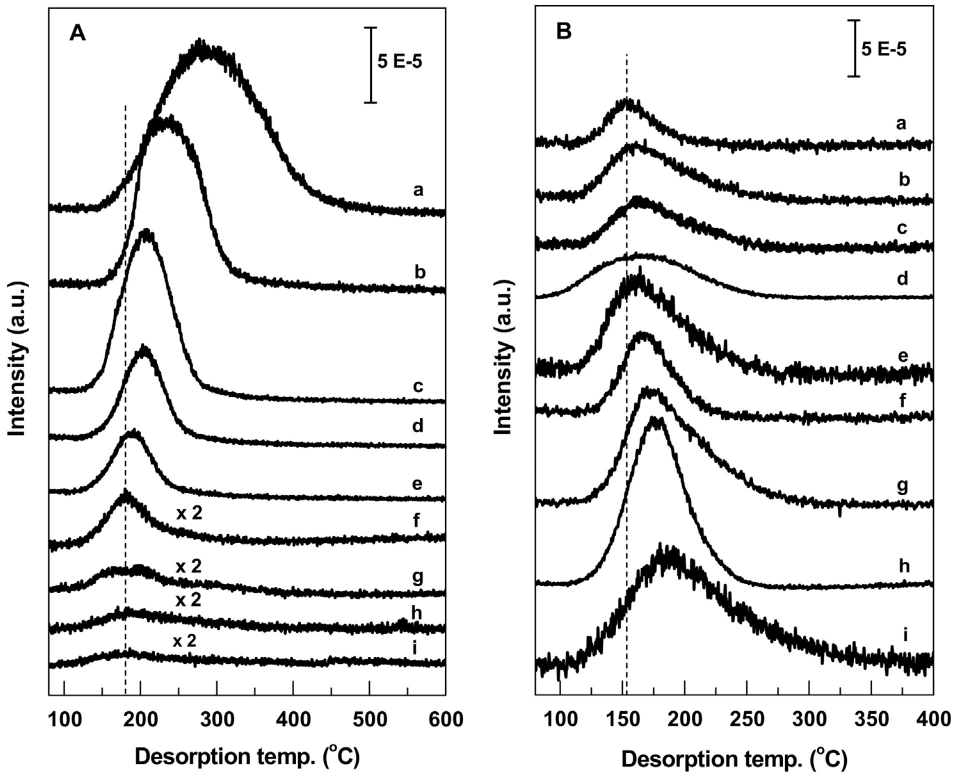

Fig. 2. NH_3-TPD (A) and CO_2-TPD (B) profiles from $Cs_xNa_{1-x}\beta$ of $x = 0$ (a), $x = 0.16$ (b), $x = 0.55$ (c), $x = 0.71$ (d), $x = 0.77$ (e), $x = 0.81$ (f), $x = 0.90$ (g), $x = 0.95$ (h) and $x = 1.00$ (i).

$2.41 \times 10^{-1}\ \mu mol\ m^{-2}$ for $K_{0.94}Na_{0.06}\beta$, $7.2 \times 10^{-2}\ \mu mol\ m^{-2}$ for $Rb_{0.95}Na_{0.05}\beta$ and $1.8 \times 10^{-2}\ \mu mol\ m^{-2}$ for $Cs_{0.95}Na_{0.05}\beta$. On the other hand, the CO_2-TPD peak temperatures were respectively 171, 175 and 180 °C, and the surface basicity data measured as the number of desorbed CO_2 were respectively 1.88×10^{-2}, 2.45×10^{-2} and $4.41 \times 10^{-2}\ \mu mol\ m^{-2}$ for $K_{0.94}Na_{0.06}\beta$, $Rb_{0.95}Na_{0.05}\beta$ and $Cs_{0.95}Na_{0.05}\beta$.

The acidity and basicity of the alkali-ion exchanged zeolites could be related to the electrostatic potential (EP) of the cations in the zeolites. As the acidity (strength and amount) would increase but the basicity (strength and amount) decrease with EP for alkali-ion exchanged X [40,41], Y [42,43] and β zeolites [30], the numbers of EP can be used as a comprehensively unified descriptor to evaluate the overall acid–base property or acidity–basicity balance of the cation-exchanged zeolites with varying exchange degrees [30,40–43]. When the overall acidity–basicity balance is expressed by the two ratios, acidity/basicity (acidity-to-basicity ratio) and $T_{NH_3\text{-TPD-peak}}/T_{CO_2\text{-TPD-peak}}$ (ratio of the NH_3-desorption-peak temperature to the CO_2-desorption peak temperature in degree Celsius), we obtain in Fig. 3 very clear correlations between the overall acidity–basicity balance and EP of the cations for all the $Rb_xNa_{1-x}\beta$ and $Cs_xNa_{1-x}\beta$ samples.

3.2. Catalytic performance

We showed previously that the exchange degree of K^+ significantly affected the catalytic performance of $K_xNa_{1-x}\beta$ for the LTA reaction and the samples with x in the window $x = 0.90$–0.98 were more effective for AA production [30]. The best performing catalyst $K_{0.94}Na_{0.06}\beta$ offered an AA yield of as high as 61% (selectivity: 64 mol%) for up to 8 h under optimized reaction conditions (gas-phase feed composition: 7.4 kPa LA, 66.9 kPa H_2O and 26.7 kPa N_2, 360 °C, $WHSV_{LA} = 2.1\ h^{-1}$) [30]. The catalytic reaction in this study was also conducted under the conditions optimized previously for the $K_{0.94}Na_{0.06}\beta$ catalyst. It should be noted that the $WHSV_{LA}$ ($2.1\ h^{-1}$) used in our studies [9,30] is 1.5–5 folds higher than those used in most literature [6–8,44–51]. Presented in Fig. 4 are the effects of x for the $Rb_xNa_{1-x}\beta$ catalysts on the time courses of LA conversion, AA selectivity and AA yield. The LA conversion (Fig. 4A) decreased slightly and remained higher than 96% during the reaction of up to TOS = 10 h for the samples of $x \leq 0.73$. The other samples of $x = 0.85$–1.00 produced lower LA conversion and faster deactivation. The time courses of AA selectivity (Fig. 4B) features an induction period of ca. 4 h for developing the stable AA selectivity over all the $Rb_xNa_{1-x}\beta$ samples except $Rb_{1.00}\beta$. Note that the Naβ sample ($x = 0$) always produced the lowest AA selectivity ($\leq$30 mol%) among the $Rb_xNa_{1-x}\beta$ catalysts. The stable

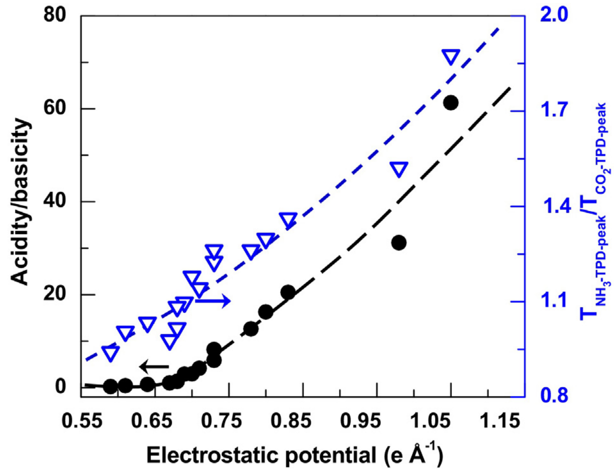

Fig. 3. Dependence of the surface acidity-to-basicity ratio (●) and the ratio of the NH_3-desorption-peak temperature to the CO_2-desorption-peak temperature (▽) on the electrostatic potential for the cations in the $Rb_xNa_{1-x}\beta$ and $Cs_xNa_{1-x}\beta$ samples.

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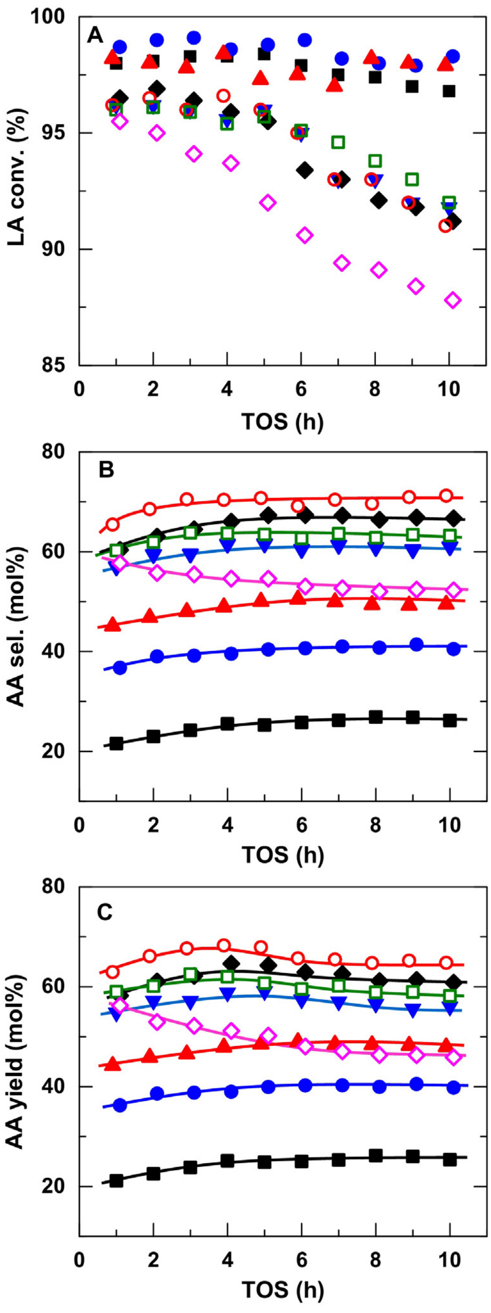

Fig. 4. Catalytic performance by the time courses of LA conversion (A), AA selectivity (B) and AA yield (C) of the $Rb_xNa_{1-x}\beta$ catalysts of $x = 0$ (■), $x = 0.60$ (●), $x = 0.73$ (▲), $x = 0.85$ (▼), $x = 0.90$ (♦), $x = 0.95$ (○), $x = 0.98$ (□) and $x = 1.00$ (◇).

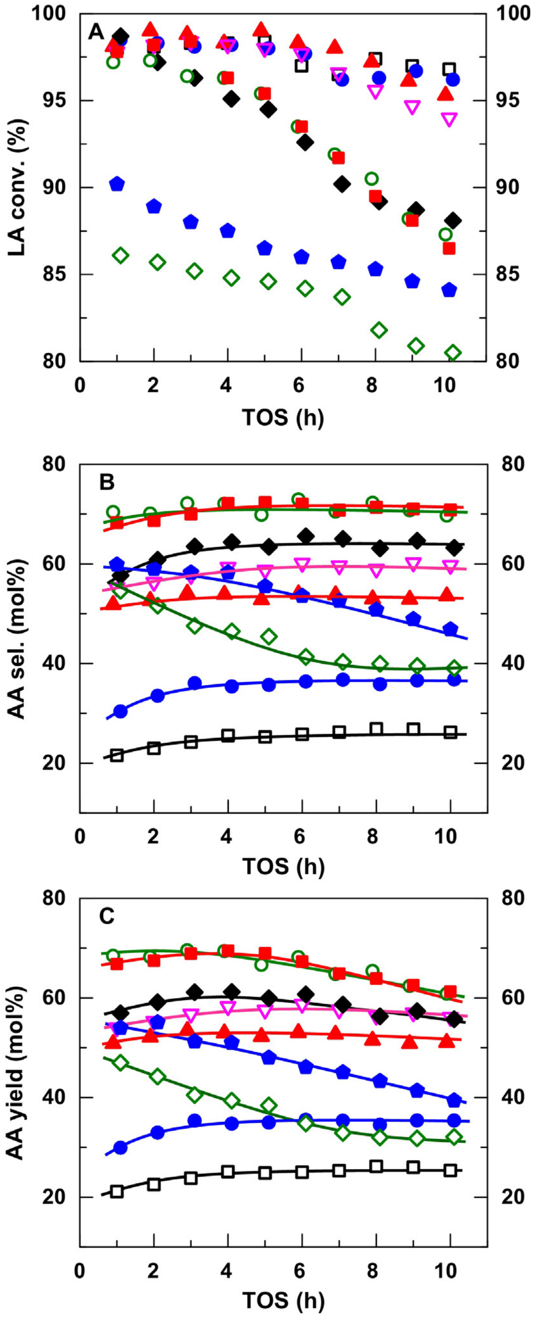

Fig. 5. Catalytic performance by the time courses of LA conversion (A), AA selectivity (B) and AA yield (C) of the $Cs_xNa_{1-x}\beta$ catalysts of $x = 0$ (□), $x = 0.16$ (●), $x = 0.55$ (▲), $x = 0.71$ (▽), $x = 0.77$ (♦), $x = 0.81$ (○), $x = 0.90$ (■), $x = 0.95$ (⬟) and $x = 1.00$ (◇).

AA selectivity (at TOS = 9–10 h) increased significantly from 26 mol% to 70 mol% with increasing x from 0 to 0.95 and then decreased to ca. 63 mol% and 52 mol% at $x = 0.98$ and 1.00, respectively. Thus, AA selectivity higher than 60 mol% and AA yields higher than 56 mol% (Fig. 4C) were obtained only over the samples of $x = 0.85$–0.98, which point to a specific window of x for making the $Rb_xNa_{1-x}\beta$ catalyst highly selective for the LTA reaction. Regardless of TOS, the highest AA selectivity (ca. 70 mol%) and yield (ca. 66 mol%) were always produced on the sample of $x = 0.95$, which identify $Rb_{0.95}Na_{0.05}\beta$ as the most efficient catalyst among the $Rb_xNa_{1-x}\beta$ samples for the LTA reaction.

The effects of x for the $Cs_xNa_{1-x}\beta$ samples on the time courses of LA conversion, AA selectivity and AA yield are presented in Fig. 5, which are similar to those for the $Rb_xNa_{1-x}\beta$ samples in Fig. 4. However, the LA conversion data (Fig. 5A) show that these $Cs_xNa_{1-x}\beta$ catalysts presented a little faster deactivation than the $Rb_xNa_{1-x}\beta$ samples of similar x. An induction period (ca. 4 h) was also observed for developing the AA selectivity over the $Cs_xNa_{1-x}\beta$ samples of $x \leq 0.90$; for the other $Cs_xNa_{1-x}\beta$ samples (i.e., $x > 0.90$ or $Cs_{0.95}Na_{0.05}\beta$ and $Cs_{1.00}\beta$), the AA selectivity decreased steadily with TOS (Fig. 5B). The stable AA selectivity increased remarkably from 26 mol% to 70–71 mol% when x was increased from 0 to 0.77–0.81 and then decreased steadily to lower than 40 mol% when x was further increased to 1.00. Thus, AA selectivity higher than 60 mol% and AA yields higher than 55 mol% (Fig. 5C) were

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obtained only over the $Cs_xNa_{1-x}\beta$ catalysts of $x = 0.71–0.90$. Thus, these results uncover the appropriate window of x for obtaining highly selective $Cs_xNa_{1-x}\beta$ catalyst for the LTA reaction. However, the $Cs_xNa_{1-x}\beta$ catalysts of $x = 0.81–0.90$ always produced the highest AA selectivity (ca. 70 mol%) and yield (>60 mol%) during the reaction up to TOS = 10 h.

In our previous preliminary study of several $Rb_xNa_{1-x}\beta$ ($x = 0.87$ and 0.95) and $Cs_xNa_{1-x}\beta$ ($x = 0.80$ and 0.90) catalysts for the LTA reaction with a much lower $WHSV_{LA}$ (0.7 h^{-1}), the obtainable AA selectivity was always no higher than 50 mol% [30]. The significantly higher AA selectivity (ca. 70 mol%) obtained using a 3-fold higher $WHSV_{LA}$ (2.1 h^{-1}) in this work over the catalysts of the similar ion-exchange degrees (Figs. 4 and 5) would be not surprising as the much higher $WHSV_{LA}$ would mean a much shorter reaction contact time, which can significantly avoid many possible secondary reactions of AA, including decomposition and bi-molecular side reactions with the unreacted LA molecules and/or other products [9,30,31].

Therefore, our studies on alkali-ion exchanged β zeolite ($M_xNa_{1-x}\beta$) catalysts for the LTA reaction disclose that an appropriate window of exchange degree would exist for each kind of alkali ions in order to make the catalyst more selective for AA production. The exact range or width of the window is found specific to the nature of M in $M_xNa_{1-x}\beta$ samples ($M = K^+$, Rb^+ and Cs^+).

Presented in Table 2 are the catalytic reaction data at TOS = 1–2 h (number outside the parenthesis) and TOS = 9–10 h (number in the parenthesis) for all the $Rb_xNa_{1-x}\beta$ and $Cs_xNa_{1-x}\beta$ catalysts. Like in our earlier studies [9,30], AA, acetaldehyde (AD), 2,3-pentanedione (2,3-PD), propionic acid (PA) and 1-hydroxyacetone (1-HA) were always produced with selectivity of ≥1 mol%. Besides, a numbers of very minor (<1 mol%) products including gases and carbonaceous residues deposited on the catalyst surface were also detected. Except the clearly named products in Table 2, the other products including those in the gases and surface carbonaceous deposits were added up and shown as "Others" in the table. As the poorest catalyst for AA production, Naβ was characterized by showing the highest selectivity for AD (44∼46 mol%) and lowest selectivity for 2,3-PD production. This is not surprising with the consideration that Naβ is the most acidic and least basic catalyst; the high acidity of its surface would favor the AD producing decarbonylation/decarboxylation reaction of LA but suppress the 2,3-PD producing condensation reaction of LA [52,53]. The introduction of Rb^+ or Cs^+ ions by ion-exchange with the Na^+ ions continuously lowered the AD selectivity but improved the 2,3-PD selectivity as the consequence of increasing x in either $Rb_xNa_{1-x}\beta$ or $Cs_xNa_{1-x}\beta$ catalyst, due to that the increase of x in the $Rb_xNa_{1-x}\beta$ or $Cs_xNa_{1-x}\beta$ catalyst reduced the acidity and increased the basicity at the catalyst surface, as demonstrated by the NH_3- and CO_2-TPD data (Figs. 1 and 2, Table 1). Except over the Naβ and $Cs_{0.16}Na_{0.84}\beta$ catalysts, AA was always produced as the main product in Table 2; the most abundant by-product was AD over $Rb_xNa_{1-x}\beta$ of $x \leq 0.90$ and $Cs_xNa_{1-x}\beta$ of $x \leq 0.77$ but was changed to 2,3-PD over the other catalysts of higher x. On the basis of similar x, the $Cs_xNa_{1-x}\beta$ catalyst always produced more 2,3-PD and less AD than its counterpart $Rb_xNa_{1-x}\beta$ catalyst. The change in PA selectivity was parallel to that of 2,3-PD but opposite to that of AD over both $Rb_xNa_{1-x}\beta$ and $Cs_xNa_{1-x}\beta$ catalysts. Interestingly, the catalysts that offered the highest AA selectivity also produced the lowest selectivity for "Others"; the selectivity for "Others" was less than 3 mol% over the most selective $Rb_{0.95}Na_{0.05}\beta$ and $Cs_{0.81–0.90}Na_{0.19–0.10}\beta$ catalysts for AA production. These are also in line with our previous observations over hydroxyapatite [9] and $K_xNa_{1-x}\beta$ catalysts [30].

Therefore, the exchange of Naβ with Rb^+ or Cs^+ ions led to reduced acidity but increased basicity in the resultant zeolite catalyst, which exhibited better catalytic performance for the selective production of AA mainly by inhibition of the AD producing decarbonylation/decarboxylation reaction of LA. However, excessive or complete exchange of Na^+ ions with either Rb^+ or Cs^+ ions would "over-reduce" the acidity and make the zeolite catalyst too basic for the LTA reaction due to that the 2,3-PD producing condensation reaction would become considerably favorable over the too basic catalyst. On the other hand, the too basic sites would also become more or less poisoned by LA and AA during the reaction [6,7,30], resulting in the formation of increasing amounts of unwanted and/or unknown products (Table 2) and faster catalyst deactivation. In fact, a higher amount of "Others", including some insoluble "oil" in supernatant of the condensate was always observed when $Rb_{1.00}\beta$, $Cs_{0.95}Na_{0.05}\beta$ or $Cs_{1.00}\beta$ was the catalyst. Similar observations also appeared when the same reaction was conducted by Onda et al. on other strongly basic catalysts like MgO and Pb-P hydroxyapatites [6,7]. Thus, $Rb_{0.95}Na_{0.05}\beta$ and $Cs_{0.81–0.90}Na_{0.19–0.10}\beta$ were identified as the best performing catalysts for AA production among the $Rb_xNa_{1-x}\beta$ and $Cs_xNa_{1-x}\beta$ catalysts, respectively.

The stable selectivity data for AA, AD and 2,3-PD were correlated in Fig. 6 with EP of the alkali ions in all the $Rb_xNa_{1-x}\beta$ and

Table 2
Catalytic performance of Rb^+- and Cs^+-exchanged β zeolite catalysts for gas-phase dehydration of aqueous LA.[a]

Catalyst	Conv. (%)	Product selectivity (mol%)[b]						AA yield (mol%)
		AA	AD	2,3-PD	PA	1-HA	Others[c]	
Naβ	98 (97)	23 (26)	44 (46)	3 (4)	1 (2)	1 (1)	28 (21)	23 (25)
$Rb_{0.60}Na_{0.40}\beta$	99 (98)	39 (40)	36 (35)	4 (5)	1 (2)	1 (1)	19 (17)	39 (40)
$Rb_{0.73}Na_{0.27}\beta$	98 (97)	47 (49)	32 (30)	6 (8)	1 (2)	1 (1)	13 (10)	46 (48)
$Rb_{0.85}Na_{0.15}\beta$	96 (92)	59 (61)	24 (20)	9 (12)	2 (2)	1 (1)	5 (4)	57 (56)
$Rb_{0.90}Na_{0.10}\beta$	97 (91)	63 (66)	17 (15)	11 (13)	2 (3)	1 (1)	6 (2)	61 (59)
$Rb_{0.95}Na_{0.05}\beta$	96 (91)	69 (70)	14 (12)	12 (14)	2 (2)	1 (1)	2 (1)	66 (65)
$Rb_{0.98}Na_{0.01}\beta$	97 (92)	62 (63)	14 (10)	18 (20)	2 (3)	1 (1)	3 (3)	60 (58)
$Rb_{1.00}\beta$	95 (88)	56 (52)	8 (7)	22 (23)	4 (5)	1 (1)	9 (12)	53 (46)
$Cs_{0.16}Na_{0.84}\beta$	98 (96)	34 (37)	38 (39)	3 (3)	1 (1)	1 (1)	23 (19)	33 (36)
$Cs_{0.55}Na_{0.45}\beta$	99 (95)	53 (54)	30 (29)	7 (8)	1 (2)	1 (1)	8 (7)	52 (51)
$Cs_{0.71}Na_{0.29}\beta$	98 (94)	56 (60)	23 (21)	9(10)	2 (3)	2 (1)	8 (5)	55 (56)
$Cs_{0.77}Na_{0.23}\beta$	97 (88)	61 (63)	18 (17)	10 (12)	2 (3)	1 (1)	8 (4)	59 (55)
$Cs_{0.81}Na_{0.19}\beta$	97 (87)	70 (70)	12 (10)	12 (13)	2 (4)	1 (1)	3 (2)	68 (61)
$Cs_{0.90}Na_{0.10}\beta$	98 (86)	69 (70)	10 (8)	16 (15)	3 (4)	1 (1)	1 (2)	67 (60)
$Cs_{0.95}Na_{0.05}\beta$	95 (84)	59 (47)	9 (7)	22 (28)	3 (7)	1 (2)	6 (9)	56 (39)
$Cs_{1.00}\beta$	86 (80)	52 (39)	7 (6)	25 (30)	6 (9)	1 (1)	9 (15)	44 (31)

[a] Catalyst loading: 500 mg; $WHSV_{LA}$: 2.1 h^{-1}; Rxn temp.: 360 °C; TOS = 1–2 h (number outside the parenthesis) and 9–10 h (number in the parenthesis).
[b] AA: acrylic acid; AD: acetaldehyde; PA: propionic acid; 2,3-PD: 2,3-pentanedione; 1-HA: 1-hydroxyacetone.
[c] Selectivity for "Others" including surface carbonaceous deposits and uncondensed gas products (mol%) = $100 - \sum$(selectivity for each listed product).

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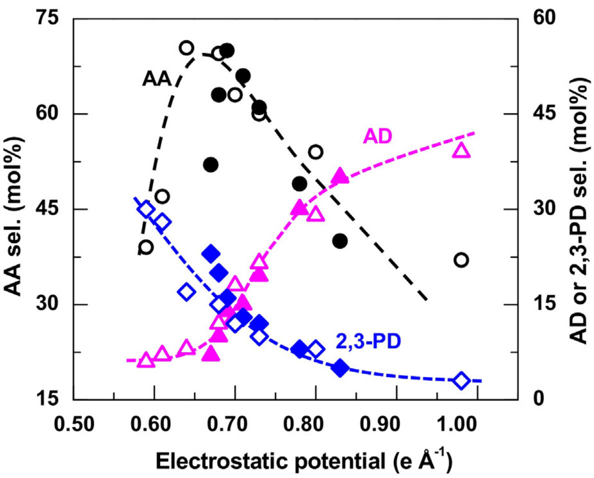
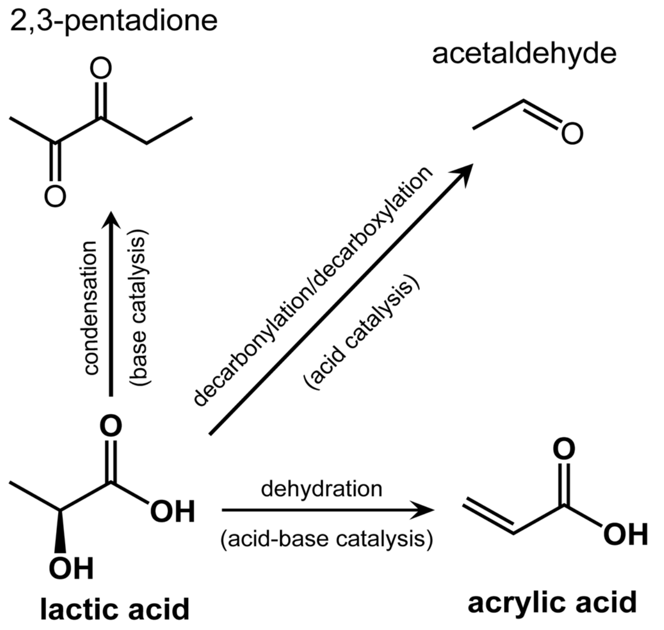


Fig. 6. Dependence of the selectivity levels for AA (●, ○), AD (▲, △) and 2,3-PD (◆, ◇) at TOS = 9–10 h on the electrostatic potential for the alkali ions in the $Rb_xNa_{1-x}\beta$ (solid data pionts) and $Cs_xNa_{1-x}\beta$ (open data points) catalysts.

$Cs_xNa_{1-x}\beta$ catalysts. Apparently, the AD selectivity increased but the 2,3-PD selectivity decreased with increasing EP, conforming that the more acidic catalyst favors to promote the formation of AD but the more basic catalyst prefers the production of 2,3-PD [6–9,30,42–51]. Miller et al. made the first observations that the catalyst with a higher basicity would produce more 2,3-PD, and strong solid bases such as $CsOH/SiO_2$ and $CsCl/SiO_2$ could produce 2,3-PD with a selectivity higher than 60% [52,53]. On the other hand, the AA selectivity showed a volcano-type dependence on the EP of the cations for the $Rb_xNa_{1-x}\beta$ and $Cs_xNa_{1-x}\beta$ catalysts in Fig. 6. The AA selectivity became maximized when the EP was near 0.67 e Å^{-1}. A similar correlation was obtained previously for the $K_xNa_{1-x}\beta$ catalysts though the maximum AA selectivity was obtained at EP = 0.77 e Å^{-1} [30]. Thus, the present results are in support of the earlier conclusion that a balanced co-presence of acidic and basic sites is required for the selective formation of AA in the gas-phase LTA reaction [6–9,30]. In other words, this present study further confirms that the dehydration reaction of LA for AA production proceeded in a cooperative acid–base bifunctional catalysis mechanism over the $Rb_xNa_{1-x}\beta$ and $Cs_xNa_{1-x}\beta$ catalysts [9,30]. Scheme 1 summarizes the main reactions of LA and their related acid–base catalysis in the gas-phase LA conversion over alkali-ion exchanged β zeolites.

Fig. 7 compares the correlations between the stable AA selectivity and the EP of the alkali ions for the three series of $M_xNa_{1-x}\beta$ catalysts (M = K$^+$, Rb$^+$ and Cs$^+$). The AA selectivity data for the $K_xNa_{1-x}\beta$ samples, which were obtained at $WHSV_{LA} = 0.7\ h^{-1}$ in our previous work [30], were generally much lower than that for $Rb_xNa_{1-x}\beta$ and $Cs_xNa_{1-x}\beta$ obtained at $WHSV_{LA} = 2.1\ h^{-1}$. The three correlation curves are in common to show the volcano-type dependences of the AA selectivity on the EP of the alkali ions in the catalysts, however, the EP number for offering the highest AA selectivity (i.e., the maximum of the volcano curve) depends sensitively on the nature of the alkali ion (M), being 0.77 e Å^{-1} for $K_xNa_{1-x}\beta$, 0.69 e Å^{-1} for $Rb_xNa_{1-x}\beta$ and 0.66 e Å^{-1} for $Cs_xNa_{1-x}\beta$ samples. These EP numbers indicate that the balanced acidity and basicity for selectively catalyzing the LTA reaction would be different or specific for each type of the catalysts.



Scheme 1. Reactions and their related acid–base catalysis for LA conversion over alkali-exchanged β zeolite catalysts [30].

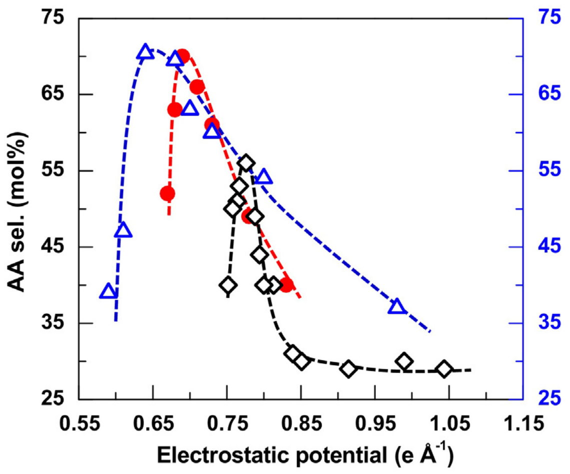


Fig. 7. AA selectivity (TOS = 9–10 h) as a function of the electrostatic potential for the alkali ions in $K_xNa_{1-x}\beta$ (◇), $Rb_xNa_{1-x}\beta$ (●) and $Cs_xNa_{1-x}\beta$ (△) catalysts (Rxn conditions: 360 °C; 10 mol% LA; $WHSV_{LA} = 0.7\ h^{-1}$ over $K_xNa_{1-x}\beta$, $WHSV_{LA} = 2.1\ h^{-1}$ over $Rb_xNa_{1-x}\beta$ and $Cs_xNa_{1-x}\beta$).

4. Conclusions

This work demonstrates that the Rb$^+$- and Cs$^+$-exchanged Naβ zeolites with appropriate exchange degrees can be highly efficient for catalyzing the gas-phase dehydration of bio-derivative LA for sustainable AA production. Measurement of the surface acid–base of the catalyst samples by NH_3- and CO_2-TPD showed that the weakly acidic and weakly basic surface sites with suitably balanced acidity and basicity are essential to the selective LTA reaction. The decarbonylaiton/decarboylation of LA to AD and condensation of LA to 2,3-PD, which were catalyzed over the acidic and basic sites, respectively, were shown as the main competing reactions to the desired LTA reaction. $Rb_{0.95}Na_{0.05}\beta$ and $Cs_{0.81-0.90}Na_{0.19-0.10}\beta$ are identified as the best performing catalysts for AA production by optimizing the exchange degrees for Rb$^+$ and Cs$^+$, respectively, to uncover the suitable acidity–basicity balance, offering the AA selectivity as high as 69–70 mol% and AA yields higher than 65 mol%

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for longer than 10 h. These $Rb_{0.95}Na_{0.05}\beta$ and $Cs_{0.81-0.90}Na_{0.19-0.10}\beta$ catalysts are superior to the best K^+-exchanged $Na\beta$ zeolite catalyst ($K_{0.94}Na_{0.06}\beta$) in our previous study. Comprehension of the acid–base property by the EP of the zeolite catalysts disclosed that the number of EP for enabling the highest AA selectivity for the LTA reaction on the $M_xNa_{1-x}\beta$ ($M = K^+$, Rb^+ and Cs^+) catalyst was dependent of the nature of the alkali ions; the rank was $Cs_xNa_{1-x}\beta < Rb_xNa_{1-x}\beta < K_xNa_{1-x}\beta$.

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