Selective conversion of lactic acid to acrylic acid over alkali and alkaline-earth metal co-modified NaY zeolites

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Abstract

Alkali and alkaline-earth metal cation co-modified NaY zeolites are systematically synthesized and comprehensively investigated as catalysts for gas-phase dehydration of lactic acid (LA) to acrylic acid (AA). Long-term (time-on-stream > 55 h) catalytic performance in four repeated reaction-regeneration cycles is studied. The best performing catalyst shows consistently high AA selectivity of ~84 % at different weight hourly space velocity (WHSV) ranging from 0.48 to 4.8 hr⁻¹. Most importantly, the catalyst can still deliver a high AA selectivity of ~82% after four long-term reaction-regeneration cycles. Investigation shows that mild etching increases defect density of the zeolite and thus leads to poor hydrothermal stability in the long-term reaction-regeneration cycles. Strong acidic adsorbate/catalyst surface interaction (base property) and the acidity of the catalyst are responsible for the catalyst deactivation. The role of the alkali and alkaline-earth metal cations and the transformation of the cations during the reaction and regeneration process is presented.
Introduction

Shifting from fossil fuels to biomass derived feedstocks for the production of chemicals has been an important aspect in heterogeneous catalysis for achieving sustainable and environmentally friendly processes. One good example is the production of Acrylic Acid (AA) through selective dehydration/oxydehydration of bio-based feedstock, such as Lactic Acid (LA) and glycerol. This new route is a promising alternative to the current commercial route of AA production by the two-step selective catalytic oxidation of propylene.¹

The production of AA from LA can be achieved by selective elimination of the α-hydroxyl and β-hydrogen in gas phase with acid-base heterogeneous catalysts. However, due to the presence of highly reactive hydroxyl and carboxylic groups, the conversion of LA in the temperature range suitable for dehydration over solid acid-base catalysts usually leads to several competing reactions such as acid catalyzed decarbonylation/decarboxylation forming acetaldehyde; base-catalyzed condensation to produce 2,3-pentadione; hydrogenation of LA and intermolecular esterification to polymeric esters of LA.² Therefore, the selectivity towards AA is a major problem associated with the gas phase dehydration of LA.³ Tremendous efforts have been devoted to the development of heterogeneous catalysts for gas phase dehydration of LA. The most frequently investigated heterogeneous catalysts include modified zeolites,⁴¹³ sulfates,¹⁴⁻¹⁶ phosphates¹⁷⁻²⁴ and hydroxyapatites.²⁵⁻²⁷ Though acid-base properties for achieving high AA selectivity depend on the type of heterogeneous catalysts, it is generally agreed that well-balanced acid-base sites are critical to high AA selectivity. Recently, Lari et al. has produced a hierarchical NaY zeolite showing good AA selectivity (75%) within 6 hr of reaction.⁷ Xu’s group reported another promising heterogeneous catalyst based on alkali-
ion-exchanged ZSM-5. A high AA selectivity of 80% with LA conversion of 96% was reported on their best performing catalyst with good long-term stability for the first cycle of the reaction. Acetaldehyde (17% selectivity) was the main by-product, which is produced via decarbonylation/decarboxylation reaction over acidic sites along with the release of CO or CO₂.

On the other hand, catalyst deactivation and selectivity decay have usually been observed over the time-on-stream. However, most of the literature reports focus on only short-term catalytic reaction (generally < 30 hr). Indeed, low attention has been paid to the long-term catalytic performance in repeated reaction-regeneration cycles, thought this is a very important aspect since catalyst stability is crucial for its practical application.

In this work, step-by-step catalyst improvement has been carried out on a NaY zeolite. Alkali and alkaline-earth metal co-modified NaY zeolite has been developed, resulting in a good catalytic performance, with a high AA selectivity of ~84% (at various WHSV ranging from 0.48 to 4.8 hr⁻¹). Moreover, we have investigated the catalyst property-performance relationship through detailed and in-depth analysis. The role of the alkali and alkaline-earth cations is discussed. Most importantly, the catalysts have been subjected to four consecutive long-term reaction-regeneration cycles to assess catalyst stability/regenerability. The best performing catalyst retains a high AA selectivity of ~82% (at 100% LA conversion) after four reaction-regeneration cycles. Characterization techniques including N₂ sorption, temperature-programmed desorption of CO₂/NH₃ (CO₂-TPD and NH₃-TPD), ²⁷Al magic-angle-spinning nuclear magnetic resonance (MAS NMR), powder X-ray diffraction (XRD), Ca K-edge XANES, diffuse-reflectance infrared Fourier transform (DRIFT) were employed to understand the evolution of the catalyst
structure and the physiochemical properties. New insights into the parameters that govern the selectivity, catalyst activity and stability are discussed.

Results and Discussion

Catalytic Performance of the modified zeolites

Fig. 1 Catalytic performance as a function of time-on-stream during LA conversion.
The catalytic performance as a function of time-on-stream during LA conversion over various NaY-based catalysts is shown in Fig. 1 and the major product selectivity is summarized in Table 1. The conversion of LA over parent NaY leads to the production of AA (highest selectivity is 56%) together with other side reactions. The conversion of LA over NaY drops quickly from 78% down to below 20% after 30 hr, showing a fast catalyst deactivation rate. Modification of NaY by KOH alone improves both AA yield and LA conversion. However, AA selectivity drops fast over KOH-NaY catalyst. When NaY is modified by alkaline-earth metal (Ca) alone, a stable AA yield and LA conversion is observed. High and stable AA selectivity of about 70% is obtained over the entire time-on-steam (30 hr), indicating a superior stability of the Ca-NaY catalyst. Since the introduction of calcium species improves the stability and selectivity of the catalyst while the addition of KOH improves the yield of AA and conversion of LA, the modification of NaY by both alkali and alkaline-earth metal was carried out resulting in KOH-Ca-NaY sample. Fig. 1 shows that a high AA selectivity of 84.2% with about 100% LA conversion is achieved over KOH-Ca-NaY catalyst. In addition, the catalyst retains a high AA selectivity of about 64% at TOS=30 hr. Further catalyst modification is carried out considering that small micropores in NaY may hinder the mass transfer and enhance catalyst deactivation by carbon deposition. As a proof-of-concept, mild base etching is employed to ‘open up’ the micropores in the parent NaY zeolite to generate some mesoporosity in the catalyst. The etched NaY, denoted as ENaY, is further modified by alkali and alkaline-earth metals to obtain KOH-Ca-ENaY catalyst. As displayed in Fig. 1, high AA selectivity of 83% is achieved over KOH-Ca-ENaY catalyst, with a slightly slower drop in AA selectivity over the total reaction time of 30 hr.
Table 1. Performance of modified zeolites for dehydration of LA\(^{[a]}\) and carbon balance

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Conversion (%)</th>
<th>Selectivity(^{[b]}) (mol%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>AA</td>
</tr>
<tr>
<td>NaY</td>
<td>78</td>
<td>43.4</td>
</tr>
<tr>
<td>KOH-NaY</td>
<td>89</td>
<td>62.9</td>
</tr>
<tr>
<td>Ca-NaY</td>
<td>68</td>
<td>70.3</td>
</tr>
<tr>
<td>KOH-Ca-NaY</td>
<td>100</td>
<td>84.2</td>
</tr>
<tr>
<td>KOH-Ca-NaY regen1x</td>
<td>100</td>
<td>83.3</td>
</tr>
<tr>
<td>KOH-Ca-NaY regen3x</td>
<td>100</td>
<td>82.2</td>
</tr>
<tr>
<td>KOH-Ca-ENaY</td>
<td>100</td>
<td>83</td>
</tr>
<tr>
<td>KOH-Ca-ENaY regen1x</td>
<td>100</td>
<td>83</td>
</tr>
<tr>
<td>KOH-Ca-ENaY regen3x</td>
<td>91</td>
<td>48.8</td>
</tr>
</tbody>
</table>

Carbon Balance

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>AA</th>
<th>AD</th>
<th>2,3 PD</th>
<th>PA</th>
<th>HA</th>
<th>ACEA</th>
<th>CO</th>
<th>CO(_2)</th>
<th>Carbon deposit(^{[d]})</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>KOH-Ca-NaY</td>
<td>84.2</td>
<td>1.5</td>
<td>0.4</td>
<td>2.7</td>
<td>0.8</td>
<td>0.2</td>
<td>0.9</td>
<td>3.3</td>
<td>3.4</td>
<td>97.4</td>
</tr>
<tr>
<td>KOH-Ca-ENaY</td>
<td>83</td>
<td>2.8</td>
<td>1</td>
<td>2.3</td>
<td>0.7</td>
<td>0.3</td>
<td>1.4</td>
<td>3</td>
<td>3.6</td>
<td>98.1</td>
</tr>
</tbody>
</table>

\(^{[a]}\) Catalyst load, 500mg; reaction temperature, 350°C; 20 wt% LA at 0.02ml min\(^{-1}\); all values were taken at the 5th h during LA conversion. \(^{[b]}\) AA: acrylic acid; AD: acetaldehyde; 2,3 PD: 2,3-pentanedione; PA: propanoic acid; HA: hydroxyacetone; ACEA: acetic acid; \(^{[c]}\) Others: surface deposit and other minor products whose selectivity (mol%) =100 − \(\sum\) (selectivity for each listed products) \(^{[d]}\) Carbon deposit content is determined by thermogravimetric analysis (TGA) in the temperature range from 200°C to 550°C on an average hourly accumulation basis.
Fig. 2 Effect of WHSV on LA conversion and product selectivity.

The effect of the weight hourly space velocity (WHSV) was investigated over the KOH-Ca-NaY catalyst and the results are shown in Fig. 2. As expected, the LA conversion drops when WHSV is increased from 0.48 hr\(^{-1}\) to 4.8 hr\(^{-1}\) due to insufficient contact time of LA with the catalyst. However, the AA selectivity remains above 84% and slightly improved to 89% (LA conversion= 35%) at a WHSV ~ 4.8 hr\(^{-1}\), while the selectivity towards the main by-product (PA) remains low. This clearly indicates that our alkali and alkaline-earth metal cation co-modified NaY zeolite, is highly efficient, exhibiting a robust performance for selective dehydration of LA.
In view of the good AA selectivity of KOH-Ca-NaY and KOH-Ca-ENaY catalysts, long-term stability and regeneration of both catalysts were investigated and the results are presented in Fig. 3. In each reaction cycle, the reaction was terminated at TOS=55 hr and then the catalyst was
subjected to a two-step thermal regeneration process. The thermal regeneration was carried out in air with a ramping rate of 1°C min\(^{-1}\) to reach 120°C and stayed at 120°C for 1 h. The temperature was then further ramped to 450°C with the same ramping rate of 1°C min\(^{-1}\) and stayed at 450°C for 6 h. Both catalysts were subjected to four reaction-regeneration cycles. It can be clearly seen that KOH-Ca-ENaY shows a slightly better AA selectivity for the first reaction cycle. However, in the subsequent reaction cycles, both the LA conversion and AA selectivity is lower than that of KOH-Ca-NaY catalyst. Also, KOH-Ca-ENaY shows faster catalyst deactivation. On the contrary, the LA conversion over KOH-Ca-NaY catalyst remains at about 100% throughout the four reaction-regeneration cycles. The AA selectivity also remains as high as 82.2% for the 4th reaction cycle, indicating excellent catalytic performance of KOH-Ca-NaY catalyst after regeneration. To the best of our knowledge, this is the first work reporting four consecutive reaction-regeneration cycles with TOS >50 hr for the gas phase dehydration of LA to AA.
Physical-chemical properties of the modified zeolites

Table 2. Properties of the catalysts

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>$S_{\text{BET}}$ [m$^2$/g]</th>
<th>$V_{\text{pore}}$ [cm$^3$/g]</th>
<th>$V_{\text{mic}}$ [cm$^3$/g]</th>
<th>$S_{\text{meso}}$ [cm$^2$/g]</th>
<th>Total Acid [µmol/g]</th>
<th>Total Base [µmol/g]</th>
<th>Acid/Base [-]</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaY</td>
<td>737</td>
<td>0.36</td>
<td>0.32</td>
<td>45</td>
<td>1341</td>
<td>153</td>
<td>8.8</td>
</tr>
<tr>
<td>ENaY</td>
<td>772</td>
<td>0.51</td>
<td>0.34</td>
<td>53</td>
<td>1350</td>
<td>148</td>
<td>9.1</td>
</tr>
<tr>
<td>KOH-NaY</td>
<td>614</td>
<td>0.32</td>
<td>0.28</td>
<td>35</td>
<td>985</td>
<td>168</td>
<td>5.9</td>
</tr>
<tr>
<td>Ca-NaY</td>
<td>323</td>
<td>0.16</td>
<td>0.14</td>
<td>25</td>
<td>894</td>
<td>97</td>
<td>9.2</td>
</tr>
<tr>
<td>KOH-Ca-NaY</td>
<td>340</td>
<td>0.18</td>
<td>0.15</td>
<td>21</td>
<td>403</td>
<td>116</td>
<td>3.5</td>
</tr>
<tr>
<td>KOH-Ca-ENaY</td>
<td>294</td>
<td>0.18</td>
<td>0.13</td>
<td>24</td>
<td>400</td>
<td>123</td>
<td>3.3</td>
</tr>
<tr>
<td>KOH-Ca-ENaY@550</td>
<td>497</td>
<td>0.27</td>
<td>0.20</td>
<td>29</td>
<td>500</td>
<td>121</td>
<td>4.1</td>
</tr>
<tr>
<td>KOH-Ca-ENaY@700</td>
<td>140</td>
<td>0.08</td>
<td>0.06</td>
<td>9</td>
<td>149</td>
<td>69</td>
<td>2.2</td>
</tr>
<tr>
<td>KOH-Ca-ENaY regen 1x</td>
<td>438</td>
<td>0.27</td>
<td>0.20</td>
<td>27</td>
<td>442</td>
<td>58</td>
<td>7.6</td>
</tr>
<tr>
<td>KOH-Ca-ENaY regen 4x</td>
<td>420</td>
<td>0.23</td>
<td>0.18</td>
<td>24</td>
<td>416</td>
<td>34</td>
<td>12.2</td>
</tr>
<tr>
<td>KOH-Ca-NaY regen 4x</td>
<td>407</td>
<td>0.22</td>
<td>0.18</td>
<td>23</td>
<td>410</td>
<td>59</td>
<td>6.9</td>
</tr>
<tr>
<td>KOH-Ca-ENaY spent</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>n.d.</td>
<td>n.d.</td>
<td>n.d.</td>
</tr>
</tbody>
</table>

Table 2 shows porosity and acid-base properties of the zeolite-based catalysts. After mild base etching, an increase in the mesopore volume and surface area is clearly observed. $^{29}$Si NMR analysis (Table S1) shows that the framework Si/Al ratio drops from 2.6 to 2.2 and ICP results also indicate the decrease of Si, Al and Na amount. $^{28}$ Modification of NaY by KOH alone only slightly reduces the surface area of the catalyst while the loading of calcium onto the surface of the zeolite results in a large decrease in surface area and total volume. This indicates the partial blockage of the zeolite micropores by calcium-based compounds. XRD patterns (Fig. S1) of the modified NaY zeolites are similar, which implies that the structure of the modified zeolites was retained after the impregnation and calcination processes.

The acid-base properties of the NaY-based catalysts were investigated by NH$_3$ and CO$_2$-TPD measurements (Fig. 4). The modification by calcium and potassium species significantly reduces both the acid and base density of the catalysts. The ammonia desorption temperature of the modified zeolites slightly shifted down to lower temperature while the CO$_2$ desorption
temperature shows more prominent downshift towards a lower temperature, implying both the acid and base strength of the catalysts is weakened upon alkali and alkaline-earth metal cation modification. The addition of potassium and calcium cations is likely to hinder the access to sodalite cages and also the diffusion among supercages.\textsuperscript{29} The presence of the alkali and alkaline-earth metal cations could also modify the electron density of the framework oxygen atoms close to the extra-framework cation, leading to weaker interactions between the adsorbates and the catalyst surface.\textsuperscript{30-32} The improved catalyst activity of the modified catalysts could be related to the reduced basicity of the catalyst surface, which is less prone to be poisoned by the acidic adsorbates comparing to that of NaY. On one hand, the decrease in acid density and strength will restrain the acetaldehyde formation by acid-catalyzed decarbonylation and decarboxylation. On the other hand, the lower CO\textsubscript{2} desorption temperature of the modified catalysts implies a weaker carboxyl adsorption. As a result, the corresponding decarbonylation side reaction and polymerization of the reactant (lactic acid) and desirable product (acrylic acid) is minimized.

![Fig. 4 NH\textsubscript{3}-TPD (A) and CO\textsubscript{2}-TPD (B) profiles of the zeolite-based catalysts](image-url)
Traa et al. have recently shown that the decline of the LA conversion over NaY catalyst is due to the blocking of the active sites by accumulated acidic hydrocarbons.\textsuperscript{33} The strong adsorbate/catalyst interaction would result in fast hydrocarbon cluster formation that eventually results in the inaccessibility of the active sites. The uptake capability of acidic compounds is strongly related to the electronegativity of the framework oxygen, e.g. the basicity of the catalyst. When NaY is modified with potassium cation, the adsorbate/catalyst interaction becomes weaker as evidenced by the CO\textsubscript{2}-TPD result. Thus, the accumulation of the acidic hydrocarbons such as lactic acid and acrylic acid becomes slower compared to that on NaY, leading to slower decay of the LA conversion. However, due to the high acid density, the AA selectivity decreases along the time-on-stream due to the competing side reactions. Besides the reduction in the total basicity and acidity of the catalyst, another role of the calcium cations lies in the formation of relatively stable species that are more favorable to the production of AA. Sodium lactate species have been observed on NaY catalyst in several works.\textsuperscript{2,3} The additional calcium cations in our modified catalysts further improves the catalyst selectivity by suppressing other competing side reactions and moving the reaction equilibrium towards the production of AA through the formation of favorable intermediate. The detailed transformation of the calcium species during the reaction will be discussed in the next section. Carbonylation and polymerization are two thermodynamically favored and fast reactions that are catalyzed by acid sites in zeolites while dehydration is a relatively slower process.\textsuperscript{33} The ability to have stable adsorbed intermediates would shift the dynamic equilibrium towards the dehydration reaction. As a result, the fast conversion of LA through other side reactions could be inhibited.\textsuperscript{33}

The effect of the calcination temperature on the catalytic performance of KOH-Ca-ENaY is shown in Fig. S2. When the calcination temperature is above 500°C, the catalyst starts to show a
deteriorated performance with decreased AA yield and LA conversion. XRD analysis (Fig. S3b) indicates a large decrease in the crystallinity of the catalyst when it was calcined at 700°C. The total acid and base density of the catalyst calcined at 700°C drastically dropped to 149 and 69 µmol/g, respectively. The loss in the crystal structure of the catalyst is accompanied with a large decrease in the density of acid and base active sites due to the partial transformation of the zeolite into an amorphous phase.

Catalyst regeneration and deactivation

As discussed in section above, KOH-Ca-NaY possesses excellent catalyst activity throughout the four reaction-regeneration cycles while KOH-Ca-ENaY shows deteriorated catalytic performance from the second reaction-regeneration cycle onwards. KOH-Ca-NaY is by far the best performing catalyst being reported, still showing a high AA selectivity of 82.2% with almost 100% LA conversion after four long-term reaction-regeneration cycles. Various techniques were employed to characterize the fresh, spent and regenerated catalysts in order to reveal the catalyst property-performance relationship as well as the catalyst deactivation mechanism. ICP analysis (Table S2) shows no significant change in the amount of potassium, calcium and sodium cations in the spent and regenerated catalysts comparing to that of the fresh catalysts, indicating negligible leaching effect upon reaction-regeneration cycle. $^{27}$Al MAS NMR (Fig. S3) also shows no dealumination occurred during the reaction-regeneration cycle. However, the total basicity dropped for both KOH-Ca-ENaY and KOH-Ca-NaY catalyst after four reaction-regeneration cycles, with a more prominent drop in basicity observed over KOH-Ca-ENaY than that over KOH-Ca-NaY.
Fig. 5 XRD patterns of fresh and regenerated catalysts (A) KOH-Ca-ENaY and (B) KOH-Ca-NaY.

XRD (Fig. 5) reveals that the regenerated KOH-Ca-ENaY catalyst (KOH-Ca-ENaY regen4x) loses about 40% its crystallinity after four regeneration cycles, while KOH-Ca-NaY catalyst (KOH-Ca-NaY regen4x) retains almost 80% of its original crystallinity. This result implies a much better structural stability, especially the hydrothermal stability of the KOH-Ca-NaY catalyst than that of the KOH-Ca-ENaY catalyst. Though mild etching of NaY zeolite could open up some of the micropores, the etching process inevitably results in more defects. Resasco et al. have shown that the density of the defects in the zeolite is the most crucial factor that determines the hydrothermal stability of zeolites.\textsuperscript{34} Therefore, in the gas phase dehydration of LA, besides the appropriate acid-base properties, the hydrothermal stability of the catalysts plays crucial role in determining the long-term stability of the catalyst.
Fig. 6 Ca K-edge XANES spectra of (A) fresh (Cat. fresh), spent (Cat. spent) and regenerated (Cat. regen4x) KOH-Ca-ENaY catalyst and the catalyst calcined at 700°C (KOH-Ca-ENaY@700°C) (B) various crystalline reference compounds (C) fitting of the experimental data of spent KOH-Ca-ENaY (Cat. spent) and (D) fitting of experimental data of regenerated KOH-Ca-ENaY (Cat. regen4x).

The Ca K-edge XANES analysis was performed on the fresh, spent and regenerated KOH-Ca-NaY and KOH-Ca-ENaY catalysts. The spectra are shown in Fig. 6 and Fig. S4. The pre-edge (feature A) transition is observed at 4039 eV which corresponds to the 1s-
The main resonance (feature C) appears at about 4049 eV with a shoulder (feature B) at about 4044 eV, corresponding to the 1s-4p transition. The intensity of the pre-edge provides complementary information on the calcium site geometry. The intensity of KOH-Ca-ENaY@700 is higher than the other catalysts, suggesting the Ca environment in KOH-Ca-ENaY@700 is more distorted. In order to interpret the XANES spectra of our catalysts, the Ca K-edge XANES spectra of several reference compounds, including Ca(NO$_3$)$_2$, CaCO$_3$, CaO and calcium lactate, were also measured and they are shown in Fig. 6B. Considering the main-edge features, the XANES spectrum of the fresh catalyst (Cat. fresh) is close to that of the Ca(NO$_3$)$_2$ and the XANES spectrum of the regenerated catalyst (Cat. regen4x) clearly shows the features of CaCO$_3$. KOH-Ca-ENaY@700 has a XANES spectrum that is very similar to the amorphous Na-Ca aluminosilicate glasses reported in the literature. Fitting the experimental Ca K-edge XANES spectra of the spent and regenerated catalysts with various standards and our fresh catalysts shows that the calcium in the spent catalyst consists of 66 wt% of the Ca$^{2+}$ in the fresh catalyst and 34 wt% of the Ca$^{2+}$ in calcium lactate. The presence of the lactate in the spent catalyst is clearly shown by the FTIR analysis in Fig. S5. The bands at ~ 1580 and 2970 cm$^{-1}$ are ascribed to lactate and polylactate species, respectively. The catalyst that has been regenerated for four times consists of 66 wt% Ca$^{2+}$ in CaCO$_3$, 32 wt% of Ca$^{2+}$ in the KOH-Ca-ENaY@700 and 2wt% of the Ca$^{2+}$ in the fresh catalyst. The fitting results for various spent and regenerated catalysts are shown in Table S3. It is seen that KOH-Ca-NaY regen4x is less prone to the transformation of calcium cations into amorphous-like Na-Ca aluminosilicate.
These results clearly demonstrate the role and the transformation of the calcium cation during the reaction and regeneration processes. Part of the calcium cations have undergone through proton exchange with the adsorbed lactic acid to form calcium lactate, a stable intermediate which can help to shift the dynamic equilibrium to the dehydration reaction. The lactate is then dehydrated to calcium acrylate and finally to acrylic acid by proton exchange with the lactic acid. Upon regenerations, calcium lactate is converted to CaCO$_3$. After a few cycles of reactions and regenerations, the calcium cations gradually transformed into CaCO$_3$, while a fraction of the calcium cations undergo a phase transformation resulting in a similar surrounding environment as the one in amorphous Na-Ca aluminosilicate glass.$^{36}$ In order words, these calcium cations can be viewed as ‘structural’ or network-forming element rather than the modifier.$^{37}$ The stronger interaction between the calcium cation and the NaY substrate in KOH-Ca-ENaY@700 or amorphous Na-Ca aluminosilicate will limit the mobility of the Ca cation, thus leading to a deteriorated catalytic performance. Further improvement on the catalyst to improve its stability is important to make it suitable for industrial processes. Since we have identified that the gradual loss of calcium cations (promoter or modifier) into amorphous-like Na-Ca aluminasilicate moieties lead to the deteriorated catalytic performance, the possible approaches such as use of other cation promoters such as Ba, Cs and/or the use of other type of Lewis-acid based catalyst which is hydrothermally stable such as hydroxyapatite could be carried out to further improve the stability of the catalyst.
Fig. 7 DRIFT spectra of fresh and regenerated KOH-Ca-NaY and KOH-Ca-ENaY.
Comparing the DRIFT spectra (Fig. 7) of the fresh catalyst with the regenerated catalyst, it can be seen that the bands related to the bridging Si-OH-Al groups (3630 cm\(^{-1}\)) are reduced while the bands related to the hydroxyl groups on extraframework species (3690 cm\(^{-1}\)) are increased upon regeneration.\(^{38, 39}\) Analysis in the range of 2000-1200 cm\(^{-1}\) (carbonate range) shows additional peak (e.g. \(\sim 1583 \text{ cm}^{-1}\)) upon regeneration. The peak persists at 350\(^\circ\)C, indicating stable carbonate species present in the regenerated catalyst. These results are consistent with the XRD and XANES analysis results showing that calcium carbonate is present in the regenerated catalyst and more defects are formed within the zeolite structure after a few cycles of reaction-regeneration.

Through thorough and in-depth analysis, the following conclusions can be drawn. 1) hydrothermal stability of the catalyst is a crucial factor, being responsible for the long-term stability of catalyst in the reaction-regeneration cycles for gas phase dehydration of LA; 2) acidic adsorbate/catalyst surface interaction (base property) and the acidity of the catalyst are responsible for the catalyst deactivation. Too strong adsorbate/surface interaction results in fast hydrocarbon cluster formation while strong acidity favors the coke formation, both leads to catalyst deactivation; 3) the formation of the stable intermediate (lactate) will shift the dynamic equilibrium to the dehydration reaction, resulting in high AA selectivity; 4) the gradual loss of crystallinity, basic site and calcium cations into amorphous-like Na-Ca aluminasilicate of the KOH-Ca-ENaY are the main reasons for the deteriorated catalyst performance. The retained crystallinity and the acid-base property of KOH-Ca-NaY catalyst ensure its excellent catalytic performance throughout the four long-hour reaction-regeneration cycles. The slightly faster decline in
AA selectivity with TOS in the 4th cycle could be related to the transformation of some calcium cations, inhibiting the Ca effect.

Conclusions

In summary, we have demonstrated that alkali and alkaline-earth metal co-modified NaY zeolite KOH-Ca-NaY possesses excellent catalytic performance for gas phase dehydration of LA. High AA selectivity of about 84.2 mol% with 100% LA conversion is obtained over the fresh catalyst while the AA selectivity can still reach 82.2 mol% with 100% LA conversion after four long-term reaction-regeneration cycles. The importance of the hydrothermal stability of the catalyst in the dehydration of LA has also been addressed. Although mild etching of parent NaY could open up the micropores which are prone to pore blockage, the increased defect density would lead to poor hydrothermal stability of the catalysts in the repeated long-term reaction-regeneration cycles. On one hand, too strong adsorbate (i.e. lactic acid, acrylic acid)/catalyst surface interaction leads to hydrocarbon cluster formation; while strong acidity catalyzes other side reactions. Thus, stabilizing the reactive carboxylic group by the formation of stable intermediate, i.e. calcium lactate, is important to shift the dynamic equilibrium to the dehydration reaction. This ensures high selectivity of AA by suppressing other side reactions. The role and the transformation of calcium cations during the reaction and regeneration process has also been clearly shown. The gradual loss of the calcium cations into the amorphous-like Na-Ca aluminasilicate is responsible for the decline in AA selectivity. This work provides not only fundamental insight into the selectivity control and deactivation mechanism, but also sheds light and provides guidance for further catalyst improvement for the gas phase dehydration of lactic acid.
Experimental Section

Catalyst preparation

NaY (CBV100, SiO$_2$/Al$_2$O$_3$ molar ratio is 5.1) was obtained from Zeolyst International and calcined at 550°C for 8 hours before use. Base etching of NaY was performed by adding 1.6g of NaY (calcined) into 50 ml NaOH (1mol L$^{-1}$) aqueous solution and stirred at 70°C for 4 hours. The resulting slurry was filtered, washed with deionized water and dry at 60°C in oven overnight. The etched NaY was denoted as ENaY. Single alkali metal modified NaY was obtained by adding 1ml KOH (0.8mmol ml$^{-1}$) dropwise onto 1g of NaY (calcined). The well-mixed mixture was then dried at 60°C overnight. The sample was named as KOH-NaY. 1ml of Ca(NO$_3$)$_2$ (1.45 mmol ml$^{-1}$) solution was added dropwise onto 1g of NaY (calcined). The well-mixed mixture was then dried at 60°C overnight. The dried sample was further calcined at 450°C for 5 hours with a ramping rate of 1°C/min. The calcined alkaline-earth metal modified zeolite was denoted as Ca-NaY. The alkali and alkaline-earth metal co-modified catalyst was prepared by adding 1ml KOH (0.8mmol ml$^{-1}$) dropwise onto 1g of Ca-NaY. After drying at 60°C overnight, final product was obtained and denoted as KOH-Ca-NaY. The same modification was done for ENaY and the alkali and alkaline-earth metal co-modified ENaY was denoted as KOH-Ca-ENaY.

Catalyst characterization

N$_2$ physisorption was measured at -196°C with Micromeritics ASAP 2020. The specific surface area was estimated by the Brunauer-Emmett-Teller (BET) method, and the pore size was calculated by the Barrett-Joyner-Halenda (BJH) method, using the desorption branch of the isotherms. Powder X-ray diffraction (XRD) measurements were collected using Cu K$_\alpha$ radiation with a Bruker D8 X-ray diffractometer over a 2θ range of 10-60°, employing a step size of 0.017° and a step time of 1 s. Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) spectra were recorded with Bio-Rad FT-IR 3000 MX equipped with a mercury cadmium
telluride (MCT) detector. Every spectrum was obtained based on 128 scans with a resolution of 4 cm\(^{-1}\). Before each measurement, the sample was pre-treated at 200°C in helium for 1 h to remove surface moisture and contaminants. Acid and base sites were evaluated using temperature programmed desorption of NH\(_3\) (NH\(_3\)-TPD) and CO\(_2\) (CO\(_2\)-TPD), respectively. In a typical TPD experiment, 0.1 g of sample was pre-treated in helium flow at 400°C for 2 h. Then, the temperature was lowered to 100°C, and the sample was treated under flowing 5% NH\(_3/\)He mixture or CO\(_2\). Afterwards, the sample was purged with helium to remove physisorbed NH\(_3\) or CO\(_2\). TPD measurements were then carried out from 100 to 500°C using a heating rate of 5°C min\(^{-1}\). \(^{27}\)Al and \(^{29}\)Si MAS NMR spectra were recorded on a Bruker Advance 400D spectrometer using a standard Bruker solid MAS probe, with a spinning speed of 15 kHz and a recycling delay of 0.5 s. X-ray absorption spectra (XAS) at Ca K-edge were measured on reference compounds and catalysts using the XAFCA facility at the Singapore Synchrotron Light Source (SSLS). This beamline has a flux of 1.6 x 10\(^{10}\) photons per second at 7 keV and covering the photon energy range from 1.2 keV to 12.8 keV using two sets of monochromater crystals, a Si(111) crystal for the range from 2.1 to 12.8 keV and a TKiOPO4 crystal (KTP(011)) for the range between 1.2-2.8 keV.\(^{40}\) The energy resolution was about 5.1x10\(^{-4}\) at 10 keV. The X-ray absorption data were processed using Winxas.

**Catalyst testing**

The dehydration of LA was carried out using a vertical, down-flow, packed bed reactor. 0.5 g of NaY-based catalyst was loaded in the middle of the reactor. Before each reaction, the loaded catalyst was pre-treated at 400°C for 1 h under a flowing mixture of 5% N\(_2/\)He. Nitrogen was used as internal standard for the gas phase analysis using online gas chromatography (GC). The flow rate of the carrier gas (5% N\(_2/\)He) was kept at 30 ml min\(^{-1}\)
1. 20wt.% of an aqueous solution of LA was fed and vaporized at top of the reactor along with the carrier gas. Gas phase products such as CO, CO$_2$ and a fraction of acetaldehyde were determined by online GC (Shimadzu 2014), whereas the other products were condensed in a stainless steel trap located at the outlet of the reactor. The liquid products were collected on an hourly basis and were analyzed by offline GC (Agilent 6890N) and HPLC (Shimadzu CTO-20A). For long-term catalytic reaction, the overnight reaction was analysed based on the average result of the liquid products collected overnight. Carbon content in spent catalysts was estimated by thermal gravimetric analysis (TGA). The conversion of LA and the selectivity toward AA were calculated based on the following equations:

$$\text{Conversion of LA (\%)} = \frac{\text{fed LA in mole} - \text{unreacted LA in mole}}{\text{fed LA in mole}} \times 100\%;$$

$$\text{Yield of product (\%)} = \frac{\text{Amount of carbon in the product (mole)}}{\text{Amount of carbon in fed LA (mole)}} \times 100\%;$$

$$\text{Selectivity of product (\%)} = \frac{\text{Amount of carbon in the product (mole)}}{\text{Amount of carbon in converted LA (mole)}} \times 100\%.$$  

**Supporting Information**

Additional characterization data by XRD, MAS-NMR and Ca K-edge XANES are included. This material is available free of charge via the Internet at xxx.

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References


High AA selectivity of 84% was achieved through environmentally friendly and sustainable catalytic process.