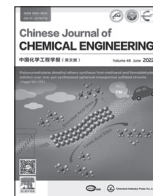




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Full Length Article

Comparative catalytic study on butene/isobutane alkylation over LaX and CeX zeolites: The influence of calcination atmosphere

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ABSTRACT

Lanthanum-containing (LaX) and cerium-containing X zeolites (CeX) were prepared by a double-exchange, double-calcination method. By changing the calcination atmospheres between nitrogen and air, the Ce^{IV} contents in CeX zeolites were adjusted and their impacts on physicochemical properties and catalytic performance in isobutane alkylation were established. The crystallinity of CeX zeolite was found to be negatively correlated with the Ce^{IV} content. This is believed to be due to the water formed during the oxidation of Ce^{III}, which facilitates the framework dealumination. As a consequence, calcining in air resulted in a great elimination of strong Brønsted acid sites while under nitrogen protection, this phenomenon was mostly hindered and the sample's acidity was preserved. When tested in a continuously flowed slurry reactor, the catalyst lifetime for isobutane alkylation was found to be linearly related to the strong Brønsted acid concentration. In addition, Ce³⁺ was found more benefit for the hydride transfer compared with La³⁺, which is ascribed to the stronger polarization effect on the CH bond of isobutane. Moreover, the decline of hydride transfer activity can be slowed down by the catalytic cracking of the bulky molecules. Based on the product distribution, a new catalytic cycle of dimethylhexanes (DMHs) involving a direct formation of isobutene rather than *tert*-butyl carbocation was proposed in isobutane alkylation.

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1. Introduction

The persistent upgrades in gasoline quality standards restrict the amounts of olefins and aromatics, which contribute to the octane number of the gasoline. To supplement the loss of anti-knock property, more alkylate oil is required in the gasoline pool. The alkylate oil is mostly composed of *iso*-paraffins typically generated from the alkylation reaction of isobutane with butenes. Industrially, this reaction is catalyzed by hydrofluoric acid and sulfuric acid. Hydrofluoric acid is hypertoxic and tends to form aerosols, which makes it extremely dangerous. For this reason, new HF alkylation plants are not approved by the authorities. Compared with hydrofluoric acid, the sulfuric acid process is quite safe. How-

ever, it suffers from high acid consumption, which may reach 70–100 kg per ton of alkylate oil [1]. The spent sulfuric acid contains about only 7% (mass) hydrocarbons, and is very difficult to handle. Most alkylation plants incinerate the waste acid and convert the resulting SO₂ to fresh sulfuric acid in a sulfuric acid plant. This process is quite costly and normally consumes about 25%–30% of the total operating cost [2]. Besides, liquid acids also lead to equipment corrosion and difficult separation problems.

To fundamentally overcome these drawbacks, solid acid-based alkylation catalysts have been desired for decades. As the reverse reaction of alkane catalytic cracking, the alkylation can certainly be catalyzed by zeolites with 12-membered ring pores such as faujasite zeolite which is widely used in the FCC unit. However, just like other solid acid catalysts, the faujasite zeolite also suffers from quick deactivation because of a tendency to generate bulk molecules.

It is well accepted that the hydride transfer between isobutane (*i*-C₄^H) and C₈ carbenium ions (C₈⁺) is the crucial step of the alkylation. By this approach, the carbon chain growth stops and the cat-

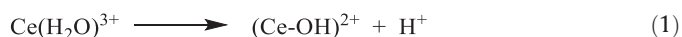
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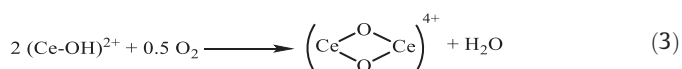
alytic cycle forms. However, the covalent nature of C–O bond suggests that the so-called “carbenium ions” are essentially alkoxides that require additional energy to be turned into carbonium ion-like transition states in the hydride transfer [3,4]. As a competing reaction, butene addition onto carbenium ions more easily occurs which finally leads to the formation of bulk molecules and catalyst deactivation. To prolong the catalyst lifetime, the hydride transfer should be promoted. This can be achieved by ion exchange with rare earth cations. Taking La^{3+} as an example, the introduction of La^{3+} enhances the acid strength [5] and polarizes the C–H bond of isobutane [6,7], both of which are beneficial for the hydride transfer. As a result, La^{3+} -modified Y zeolite exhibits superior alkylation performance in comparison with its protonic type.

The promotion effects of La^{3+} are closely associated with its content and accordingly, the framework Si/Al ratios. Our previous study on faujasite zeolite has demonstrated that X zeolite with a framework Si/Al ratio of *ca.* 1.2 can obtain the highest La^{3+} content after ion exchange, resulting in the longest catalyst lifetime [8]. Though LaX exhibits good alkylation performance and stability, the presence of Ce should be taken into consideration. This is because the traditional commercial rare earth precursors are a mixture primarily composed of lanthanum and cerium [9]. Different from lanthanum ions, which have only one valence state of +3, cerium ions possess two valence states: +3 and +4. The different valence states of cerium result in different cerium species, different cation locations, and probably, different alkylation performance.

Normally, Ce^{3+} is introduced into the supercage by ion exchange. Under normal conditions, one-step ion exchange can remove about 85% Na^+ at most [10]. The residual Na^+ not only reduces catalyst acidity but also facilitates side reactions [11]. To achieve a low residual sodium content, a subsequent calcination process is carried out, during which the hydrated Ce^{3+} cations gradually lose their hydration shells, migrate from supercage to small cages, and generate protons according to Eq. (1).



These protons not only act as Brønsted acid sites but also catalyze the hydrolysis of framework aluminum atoms which reduces the zeolite crystallinity [12]. When exposed to oxidizing atmospheres, Ce^{III} will be partially oxidized into Ce^{IV} , existing in the form of mononuclear hydroxy cerium [13] and binuclear oxygen-cerium complex [12] according to Eq. (2) and Eq. (3), respectively.



The water generated in reaction (3) is worthy of note. For zeolite with a Si/Al ratio as low as 1.2, framework dealumination is highly favored, especially in the presence of protons and water at high temperatures. Hence, one would suspect that calcining in air might cause more severe framework dealumination for cerium X-containing zeolite. On the other hand, it is well known that the oxidation of Ce^{III} will retard cerium ions from migrating into small cages [12]. As mentioned above, the ion migration during calcination is crucial to achieving low Na^+ content. Only by this approach can these residual sodium ions become exchangeable during the second ion-exchange step. Hence, calcining under oxidizing atmosphere might also influence the elemental composition of CeX zeolite.

For isobutane alkylation, the crucial importance of acidity has been well recognized and emphasized [11,14–16]. The change in crystallinity and elemental composition will undoubtedly influence the acidity of zeolite and its alkylation performance. However,

there are few studies involving Ce^{3+} exchanged X zeolite in isobutane alkylation and the impact of calcination atmosphere is seldom studied. A recent patent has reported the application of cerium-containing zeolites in isobutane alkylation [17], yet not concerning the impact of the calcination atmosphere. In this work, cerium-containing X zeolites were prepared by a two-step ion exchange and two-step calcination procedure. Each calcination step is operated under controlled atmospheres. The impact of calcination atmosphere on the physiochemical properties of CeX zeolites and their alkylation performance is discussed in detail.

2. Experimental

2.1. Materials

NaX zeolite with a mean particle size of *ca.* 4 μm and framework Si/Al ratio of 1.18 was supplied from Nankai University Catalyst Co., Ltd. Cerium (III) nitrate hexahydrate (99.5%) and lanthanum nitrate hydrate (99.9%) were obtained from Shanghai Macklin Biochemical Co., Ltd. Trans-2-butene ($\geq 99.9\%$) and isobutane ($\geq 99.9\%$) were obtained from Dalian Airichem Specialty Gases & Chemicals Co., Ltd.

2.2. Catalyst preparation

NaX zeolite was converted to its Ce-form by ion exchange. A typical procedure was conducted as follows: NaX zeolite was exchanged with $0.2 \text{ mol} \cdot \text{L}^{-1} \text{Ce}(\text{NO}_3)_3$ solution with a liquid to solid ratio of $20 \text{ mL} \cdot \text{g}^{-1}$. The ion exchange step was carried out at 80°C for 2 h and repeated once. After filtration, washing, and drying at 120°C overnight, the resulting sample was calcined under flowing dry air or nitrogen ($300 \text{ mL} \cdot \text{min}^{-1}$) in a tube furnace with a heating rate of $0.5^\circ\text{C} \cdot \text{min}^{-1}$ up to 450°C . For the nitrogen-protecting calcination, the system was purged with nitrogen ($300 \text{ mL} \cdot \text{min}^{-1}$) for 3 h before heating to displace the oxygen in the tube. To achieve a high ion-exchange degree, the above procedure was once again repeated. The obtained sample was marked as CeX-A-B where A and B represent the calcination atmospheres of the first and second calcination step, respectively. For example, CeX-N-O describes a sample calcined under nitrogen in the first calcination step and in air in the second. For comparison, LaX zeolite was also studied in this study and was prepared using the same method described above. Since lanthanum can stably exist in trivalent state, the calcination steps were directly carried out in air.

2.3. Catalyst characterization

X-ray diffraction (XRD) was carried out on a Rigaku Smartlab XRD equipped with monochromatic $\text{Cu K}\alpha$ radiation (40 kV, 40 mA). Supposing the parent NaX zeolite was fully crystallized, the relative crystallinity was calculated according to ASTM D3906-03 (2013). Nitrogen adsorption-desorption isotherms were measured on an ASAP 2460 apparatus from Micromeritics. Prior to measuring, all samples were degassed under vacuum at 350°C for 12 h. The elemental compositions of CeX zeolites were measured by X-ray fluorescence (XRF). X-ray photoelectron spectra (XPS) were obtained on an ESCALab 250Xi electron spectrometer (ThermoFisher Scientific) using $300 \text{ W Al K}\alpha$ radiation. The spectra were curve fitted with a combination of Lorentzian and Gaussian lines. The amount of Ce^{III} was obtained from the intensity of the V_0 (U_0) and V' (U') lines according to [18]:

$$\text{Ce}^{\text{III}} = \frac{V_0 + V' + U_0 + U'}{\sum (V + U)} \times 100\% \quad (4)$$

H₂ temperature-programmed reduction (H₂-TPR) was performed on an ASAP 2920 analyzer with a heating rate of 10 °C·min⁻¹ from room temperature to 900 °C. The resulting water was condensed in an isopropanol-liquid nitrogen cold trap. The amount of H₂ consumption was determined by a thermo-conductivity detector (TCD). IR spectra of adsorbed pyridine (Py-IR) were recorded on a Thermo Fisher Nicolet 9700 spectrometer between 4000 and 1000 cm⁻¹ at a resolution of 4 cm⁻¹. Prior to the measurement, the zeolite powder was pressed into a self-supporting wafer and treated at 200 °C and 10⁻⁴ Pa for 4 h. After cooling to 150 °C, excess pyridine vapor was released into the cell and pyridine adsorption was carried out at this temperature for 4 h. The desorption of the probe molecule was successively monitored stepwise, by evacuating the sample for 1 h at 150 and 350 °C and cooling to room temperature between each step, to record the spectrum. The Brønsted acid concentrations were determined by using a molar extinction coefficient of 1.67 cm·μmol⁻¹ [19].

2.4. Reaction procedure

A continuous flow stirred tank reactor with an effective volume of 30 ml was used to evaluate the alkylation performance. The schematic diagram is displayed in Fig. 1. In a typical experiment, 1.5 g zeolite was activated at 200 °C under nitrogen flow (60 ml·min⁻¹) for 12 h. Afterward, the reactor was cooled to 60 °C and pressured to 2 MPa with nitrogen. Then liquified isobutane was pumped in and the slurry was stirred at a speed of 2000 r·min⁻¹. When the exhaust flow gradually got steady, the inlet was switched to the mixture of isobutane and 2-butene (I/O = 13). The mixture was pumped in with an olefin space velocity of 0.1 h⁻¹. The product was taken every 90 min and analyzed online using a gas chromatograph equipped with an FID detector. To successfully separate the isomers in the product, a 100 m PONA column (ID = 0.25 mm) and a time-consuming program (81 min) were used in this study.

To calculate the butene conversion, the buildup of butene concentration when no alkylation reaction takes place should be determined. In a previous study, Nivarthi *et al.* detected the butene concentration in a catalyst-free reactor [20]. However, it is worth noting that the butene concentration measured by this approach must be a little underestimated because it neglected the catalyst volume. Since NaX zeolite is inactive for the alkylation and pos-

sesses very close density to LaX and CeX zeolites, 1.5 g NaX zeolite was added into the reactor in the blank experiment and the buildup of butene concentration was examined at the same conditions as applied in a typical experiment. The obtained peak area of butene was denoted as $A_{\text{butene}}^{\text{NaX}}$ and the butene conversion can be calculated according to formula (5):

$$\text{Butene conversion} = \frac{A_{\text{butene}} - A_{\text{butene}}^{\text{NaX}}}{A_{\text{butene}}^{\text{NaX}}} \times 100\% \quad (5)$$

in which A_{butene} represents the peak areas of butene detected by GC using LaX or CeX as catalyst. The slurry reactor is an integral reactor, and as a result, only integral selectivity can be obtained. For component *i*, its integral mass selectivity can be calculated as follows:

$$\text{Integral mass selectivity} = \frac{A_i}{\sum_4 A_i} \times 100\% \quad (6)$$

3. Results and Discussion

3.1. Physicochemical characterization

Beginning with NaX zeolite, the color of CeX did not change after ion exchange with Ce(NO₃)₃ solution. After calcination in air, partial Ce^{III} was oxidized into Ce^{IV}, and consequently, CeX-O-N, CeX-N-O, and CeX-O-O turned to yellow with different shades as shown in Fig. 2. Even the sample calcined under nitrogen protection, namely CeX-N-N, showed very faint yellow rather than gray-white [13], which is probably attributed to the residual oxygen in the tube furnace. The existence of Ce^{IV} in CeX zeolites after calcination can be proved by the Ce 3d XPS spectra in Fig. 3. Peaks denoted as *U* and *V* correspond to Ce 3d_{3/2} and 3d_{5/2}, respectively, where *U* (*V*) and *U'* (*V'*) peaks are representative of Ce^{IV} [21]. As shown in Fig. 3, all samples exhibited an individual peak around 916.5 eV, attributable to Ce^{IV}, demonstrating the existence of Ce^{IV}. According to the results of XPS, the percentages of Ce^{IV} to the total Ce amount in CeX-N-N, CeX-N-O, CeX-O-N, and CeX-O-O were 43.2%, 45.9%, 48.4%, and 52.8%, respectively.

Since XPS gives only the surface information, H₂-TPR was used to evaluate the Ce^{IV} content in the samples. As shown in Fig. 4(a), reduction peaks at ca. 415 °C were observed for CeX-N-N and CeX-N-O while they moved to higher temperatures for CeX-O-N and CeX-O-O. Furthermore, when noticing the peak shape, it is inter-

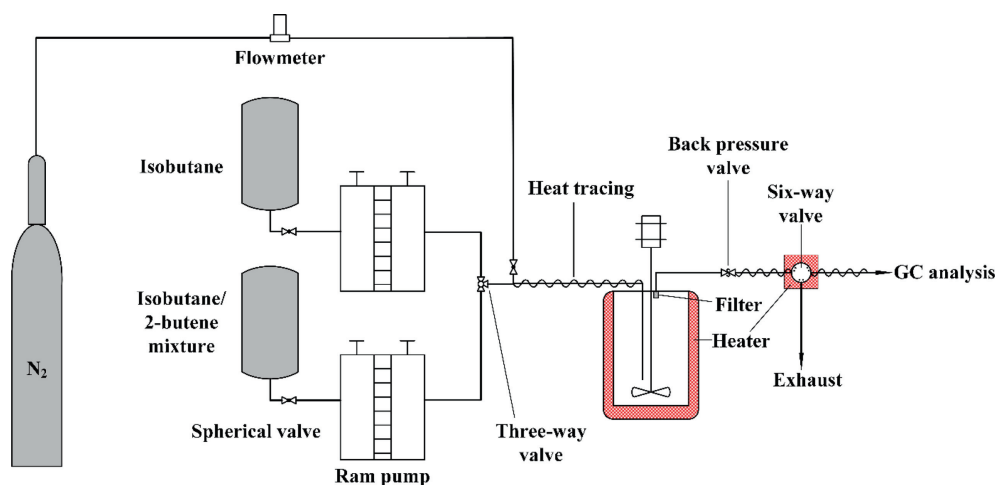


Fig. 1. The schematic diagram of the alkylation unit.

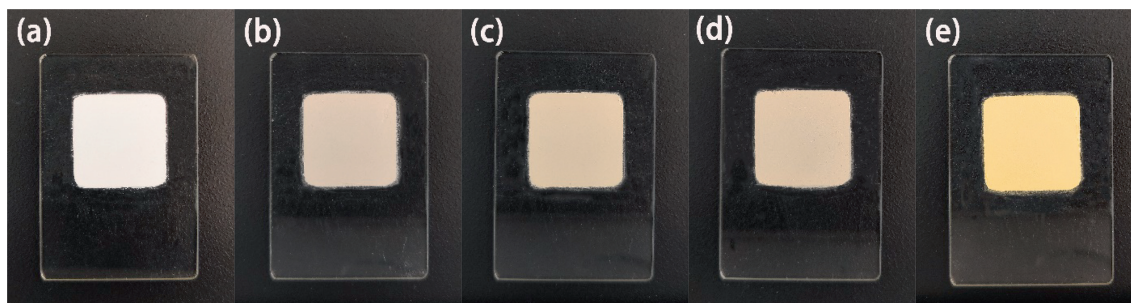


Fig. 2. Images of (a) CeX zeolite before calcination and four samples calcined under varying atmospheres: (b) CeX-N-N, (c) CeX-N-O, (d) CeX-O-N, and (e) CeX-O-O.

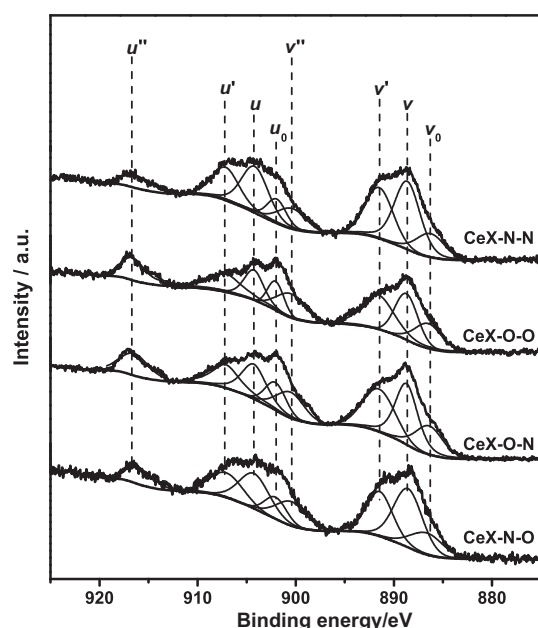


Fig. 3. Ce 3d XPS spectra for CeX zeolites.

esting to find that the reduction peaks of CeX-N-N and CeX-N-O were symmetrical and vanished before 600 °C while the other two exhibited asymmetric peaks which tailed to 770 °C, indicating the presence of Ce^{IV} species difficult to be reduced.

To identify the existing forms and locations of Ce^{IV} species, the TPR curves of CeX-O-N and CeX-O-O were fitted to low-temperature peaks at 415 °C and high-temperature peaks at around 535 °C. The hydrogen consumption of each peak was established and listed in Table 1. Interestingly, though suffering differently in the second calcination step, both CeX-O-N and CeX-O-O had a high-temperature hydrogen consumption of 0.15 mmol·g⁻¹, suggesting equal amounts of hard-reduced Ce^{IV} species. Furthermore, the high-temperature peak only appeared in CeX-O-O and CeX-O-N and did not emerge in CeX-N-O, which also suffered from oxidation during the second calcination step. Therefore, it is reasonable to speculate that the hard-reduced Ce^{IV} species was formed during the first calcination step operated in air. As mentioned above, upon heating in air, hydrated Ce^{3+} will migrate from supercage to small cages and be oxidized to $(\text{Ce-OH})^{3+}$ and $(\text{Ce}_2\text{O}_2)^{4+}$. Hunter *et al.* studied the cation locations in CeX zeolite calcined in air and found cerium only locates at SI in the hexagonal prism and SI' in the sodalite cage, with a population of 3.2 and 23.7 per unit cell, respectively [13]. Owing to the low population, Ce^{IV} in the hexagonal prisms would most likely exist in the form of $(\text{Ce-OH})^{3+}$ rather than $(\text{Ce}_2\text{O}_2)^{4+}$. The cavity size of the hexagonal prism

is only 0.27 nm [22]. Considering the diameters of Ce^{4+} and Ce^{3+} with six-coordination, which are, respectively, 0.20 and 0.23 nm [23], the reduction of Ce^{IV} is undoubtedly spatially restricted by the hexagonal prisms. For Ce^{IV} in the sodalite, however, this steric hindrance must be slighter owing to the larger cavity size of the sodalite cage which is 0.66 nm [24]. Consequently, the hard-reduced Ce^{IV} can probably be assigned to $(\text{Ce-OH})^{3+}$ locating at site SI in the hexagonal prisms.

For CeX-N-O, though $(\text{Ce-OH})^{2+}$ was also introduced into the hexagonal prisms after the first calcination in nitrogen, the second air calcination did not turn it into $(\text{Ce-OH})^{3+}$, reflected by the absence of high-temperature reduction peaks. Hunter *et al.* proposed the formation of $(\text{Ce-OH})^{3+}$ as Eq. (2) showed. However, this reaction occurred above 300 °C, at which water would have been dissociated in the electrostatic field of Ce^{3+} [12]. Accordingly, $(\text{Ce-OH})^{3+}$ might be formed in a more reasonable route as shown in Eq. (7).



Obviously, the oxidation of $(\text{Ce-OH})^{2+}$ requires the participation of protons. However, since there is only one site per hexagonal prism, $(\text{Ce-OH})^{2+}$ and protons would not be located in the same hexagonal prism and thus, the oxidation of $(\text{Ce-OH})^{2+}$ is prohibited during the second air calcination step.

For X zeolite, aluminum atoms can be easily extracted from the framework, resulting in a steep decline in relative crystallinity, which can be clearly reflected by the XRD patterns. As shown in Fig. 5, the parent NaX zeolite showed excellent crystallinity and diffraction peaks matching well with the FAU zeolite framework. However, the diffraction peaks significantly weakened after ion exchange, especially the (331) peak which almost vanished after ion exchange. Defining the parent NaX zeolite was fully crystallized, the relative crystallinities of LaX, CeX-N-N, CeX-N-O, CeX-O-N, and CeX-O-O were 27.7%, 22.5%, 19.4%, 17.6%, and 13.4% (Table 2), respectively. With the framework dealumination, the zeolite structure was corroded and as a result, the micropore volume decreased. As shown in Table 2, the micropore volume of the parent NaX zeolite was 0.36 cm³·g⁻¹ and dropped to 0.23, 0.21, 0.19, 0.17, and 0.16 cm³·g⁻¹ for LaX, CeX-N-N, CeX-N-O, CeX-O-N, and CeX-O-O, respectively.

It is worth noting that the crystallinities of CeX zeolites increased in the order of CeX-O-O < CeX-O-N < CeX-N-O < CeX-N-N, just opposite to the order of Ce^{IV} content in Table 1. As shown in Eq. (3) and Eq. (7), the oxidation of Ce^{III} is accompanied by the formation of water. The promotion effect of water on framework dealumination has been well established [25,26]. A study by Silaghi *et al.* demonstrated that the extraction of framework aluminum atoms is initiated by water adsorption on the Al atom in anti-position to the Brønsted acid site, allowing successive Al–O bond hydrolyses [27]. So, it is assumed that the more Ce^{III} be oxi-

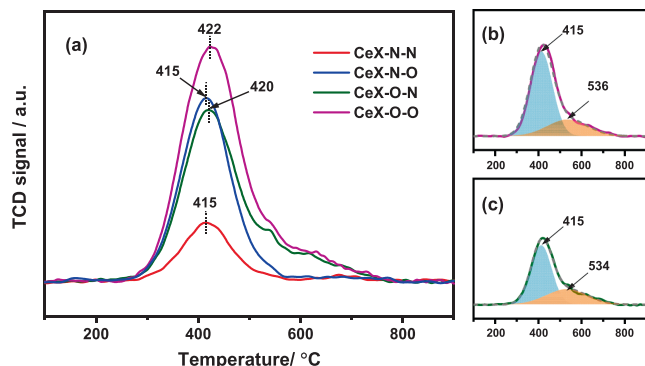


Fig. 4. (a) H_2 -TPR profiles of CeX zeolites and curve fitting of (b) CeX-O-O and (c) CeX-O-N. Solid lines: experimentally observed spectra. Dashed lines: simulated spectra.

Table 1
Hydrogen consumption of CeX zeolites

Sample	Hydrogen consumption/ $\text{mmol} \cdot \text{g}^{-1}$			$\text{Ce}^{\text{IV}}/\%$ (mass)
	Total	L	H	
CeX-N-N	0.12	0.12	–	3.36
CeX-N-O	0.35	0.35	–	9.81
CeX-O-N	0.44	0.29	0.15	12.33
CeX-O-O	0.60	0.45	0.15	16.81

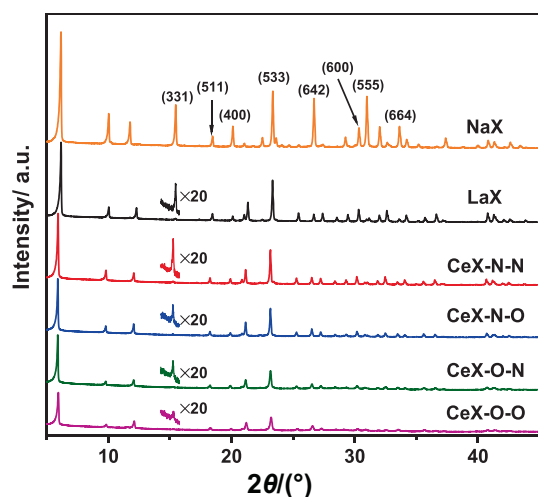


Fig. 5. XRD patterns of the parent NaX, LaX, and CeX zeolites calcined under varying atmospheres.

Table 2
Crystallinity and texture parameters of zeolites

Sample	$S_{\text{BET}}/\text{m}^2 \cdot \text{g}^{-1}$	$S_{\text{micro}}^{\text{①}}/\text{m}^2 \cdot \text{g}^{-1}$	$V_{\text{total}}^{\text{②}}/\text{cm}^3 \cdot \text{g}^{-1}$	$V_{\text{micro}}^{\text{③}}/\text{cm}^3 \cdot \text{g}^{-1}$	$V_{\text{meso}}^{\text{④}}/\text{cm}^3 \cdot \text{g}^{-1}$	Crystallinity ^⑤ /%
NaX	748	714	0.38	0.36	0.02	100
LaX	545	445	0.30	0.23	0.07	27.7
CeX-N-N	579	432	0.35	0.21	0.14	22.5
CeX-N-O	536	388	0.33	0.19	0.14	19.4
CeX-O-N	530	355	0.34	0.17	0.17	17.6
CeX-O-O	495	318	0.33	0.16	0.17	13.4

^① t -Plot micropore surface area; ^② pore volume at $P/P_0=0.995$; ^③ t -Plot micropore volume; ^④ $V_{\text{meso}}=V_{\text{total}}-V_{\text{micro}}$; ^⑤ by XRD.

dized, the more water generated, and consequently, more severe framework dealumination and lower crystallinity were obtained.

To verify our speculation, the elemental compositions of the samples were measured by XRF. As shown in Table 3, the Si/Al ratio of all samples increased compared with the parent NaX zeolite which is 1.18. Considering the relative stability of silicon, this increase is mainly due to the loss of aluminum atoms. The higher Si/Al ratios of CeX-O-N and CeX-O-O in comparison with CeX-N-N suggest that these two samples suffered more severe framework dealumination. Noting the common ground in preparing CeX-O-N and CeX-O-O relies on the atmosphere in the first calcination step, it can be concluded that the first air calcination could extract more aluminum atoms from the framework. This conclusion is quite reasonable because most Na^+ locates in the supercage in hydrated NaX zeolite which could be exchanged by La^{3+} after the first ion-exchange process. The consequent calcination in air would form more water, generate more extraframework aluminum species (EFAL), which would be washed off from the zeolite during the second ion-exchange step. While under nitrogen-protection during the first calcination, this phenomenon was mostly retarded and lower Si/Al ratios retained.

It was not shown in the table, but no residual sodium can be detected in LaX and all CeX zeolites. This indicates that high ion-exchange levels were achieved for all samples. The first calcination step is crucial in determining the exchange degree since sodium in the small cage will migrate to the supercage. This is the only way that these sodium ions will become exchangeable in the second ion exchange step. It is well known that the oxidation of Ce^{III} retards the cerium migration to sodalite cages [9,12]. If the effect is significant, the samples suffered from oxidation in the first calcination, namely CeX-O-N and CeX-O-O, would have significant amounts of residual sodium and lower Ce contents. However, the opposite results were obtained. As shown in Table 3, CeX-O-N and CeX-O-O exhibited significantly higher Ce contents than CeX-N-N and CeX-N-O. This unexpected result is probably attributed to the effective charge decline of cerium. When operating under nitrogen protection in the first calcination step, cerium mostly exists in the form of $(\text{Ce-OH})^{2+}$, with an effective charge of +3. This value drops to ca. +2 when calcining in air because of the transformation from $(\text{Ce-OH})^{2+}$ to $(\text{Ce}_2\text{O}_2)^{4+}$ [12]. It was suggested that more Ce^{3+} could be exchanged into zeolite during the second ion-exchange step. Based on the XRF results, it was indicated that the oxidation of Ce^{III} did not significantly influence the migration. This might be due to the high drying temperature and slow heating rate in the calcination step, which provides a long duration for Ce^{III} migration before oxidation occurs.

As illustrated above, the oxidation of Ce^{III} facilitate the framework dealumination which will certainly influence the acidity of the zeolites. Fig. 6 displays the NH_3 -TPD profiles of LaX and CeX

Table 3

Elemental composition of LaX and CeX zeolites measured by XRF

Sample	Elemental composition/% (mass)				Si/Al ratio
	SiO ₂	Al ₂ O ₃	La ₂ O ₃	CeO ₂	
LaX	51.35	30.61	18.04		1.30
CeX-N-N	49.86	31.05		19.09	1.36
CeX-N-O	50.56	30.98		18.56	1.38
CeX-O-N	48.36	27.72		23.92	1.48
CeX-O-O	47.85	27.15		25.00	1.50

zeolites calcined under varying atmospheres. All profiles were deconvoluted into three peaks corresponding to weak, medium, and strong acid sites. Generally, the acid strength is governed by the crystallinity, framework Si/Al ratios, and extraframework cations. Originating from the same parent NaX zeolite, the framework Si/Al ratio of the samples in this study must change in a small range. Thus, the acid strength distribution is mostly related to the relative crystallinity and extraframework cations in this study. Owing to the corresponding highest and lowest crystallinity, LaX and CeX-O-O, respectively, possesses the strongest and weakest acid sites. Although other samples' relative crystallinities differed from each other, they showed comparative acid strength, reflecting in their similar ammonia desorption temperatures. This unexpected result is probably attributed to the balance between relative crystallinity and positively charged EFAL. With more aluminum atoms extracted from the framework, the relative crystallinity decreased while the content of positively charged EFAL increased. The positively charged EFAL itself can act as strong Lewis acid and polarize the adjacent protons, enhancing the acid strength.

Further investigation of the acidity was carried out by pyridine adsorption IR (Py-IR). As shown in Fig. 7(a), four bands were observed for all samples. The absorption bands at 1444, 1454, 1540, and 1490 cm⁻¹ were assigned to pyridine reacting with extraframework cations [25], pyridine coordinated to Lewis acid

sites, pyridinium ions formed on Brønsted acid sites, and the combined contribution of Brønsted and Lewis acids, respectively [28]. As illustrated above, the oxidation of Ce^{III} into Ce^{IV} is accompanied by the formation of water which facilitates the framework dealumination. Since acidic protons are directly related to framework aluminum atoms, framework dealumination would undoubtedly reduce the concentration of Brønsted acid. On the other hand, according to Eq. (7), the formation of (Ce-OH)³⁺ was obtained at the expense of protons. Therefore, the more Ce^{IV} generated, the fewer Brønsted acid sites were obtained. As seen in Table 4, the total Brønsted acid concentrations (B₁₅₀) of CeX-N-N, CeX-N-O, CeX-O-N, and CeX-O-O were, respectively, 0.110, 0.098, 0.087, and 0.057 mmol·g⁻¹, decreasing with the increasing Ce^{IV} content. The difference between CeX-N-N and CeX-O-O became more pronounced when strong Brønsted acid sites (B₃₅₀) were noticed. As shown in Fig. 7(b), when evacuated at 350 °C, the 1540 cm⁻¹ bands for CeX-N-O and CeX-O-O were obviously weaker than that of CeX-N-N. Noteworthy, this band almost vanished for CeX-O-O, suggesting very few strong Brønsted acid sites. The concentration of strong Brønsted acid of CeX-O-O was 0.005 mmol·g⁻¹, only one-sixteenth of that for CeX-N-N. It is interesting to note that though CeX-N-O was less dealuminated compared with CeX-O-N, it exhibits a slightly higher concentration of strong Brønsted acid as displayed in Table 4. This is probably because that the Brønsted acid sites after the first calcination mainly located in the supercage [25], which could participate in the oxidation of Ce^{III} and be consumed according to Eq. (7).

Since the Lewis acid sites have not been fully absorbed by pyridine, their concentrations cannot be obtained in this study. As seen in Fig. 7(b), with the desorption temperature increasing from 150 °C to 350 °C, the intensity of the band at 1454 cm⁻¹ markedly increased, suggesting the presence of pyridine readsorption [29]. This is probably because that the steric hindrance caused by extraframework cations inhibits pyridine adsorbed onto some Lewis acid sites. While under higher temperatures, these Lewis acid sites become accessible and pyridine desorbed from Brønsted acid sites or extraframework cations re-adsorbed onto them [29]. Above all, the crystallinity, porosity, composition, and acidity of CeX zeolite can all be significantly affected by the calcination atmospheres.

3.2. Catalyst performance of LaX and CeX zeolites calcined under varying atmospheres

3.2.1. The stability of catalysts in butene/isobutane alkylation

The most concerning feature of a solid alkylation catalyst is its stability. As seen in Fig. 8(a), there is a big difference in their stability. For CeX-O-O, the initial 2-butene conversion was only 90.1% and decreased to 66.5% within 3 h, suggesting a very poor activity and fast deactivation. While for other samples, butene can be completely consumed within 1.5 h. Afterward, CeX-N-O and CeX-O-N deactivated in turn. As for CeX-N-N and LaX, they both can keep a high butene conversion for a long period of time. Defining the time of butene conversion higher than 99% as catalyst lifetime,

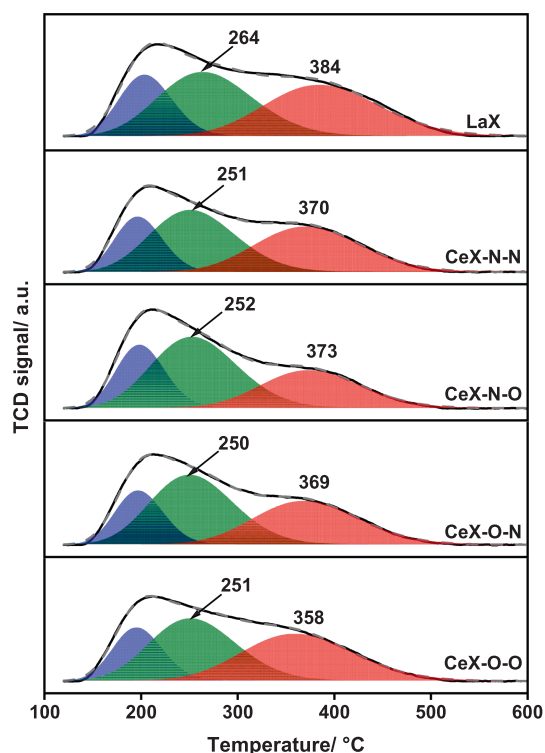


Fig. 6. NH₃-TPD profiles of LaX and CeX zeolites calcined under varying atmospheres.

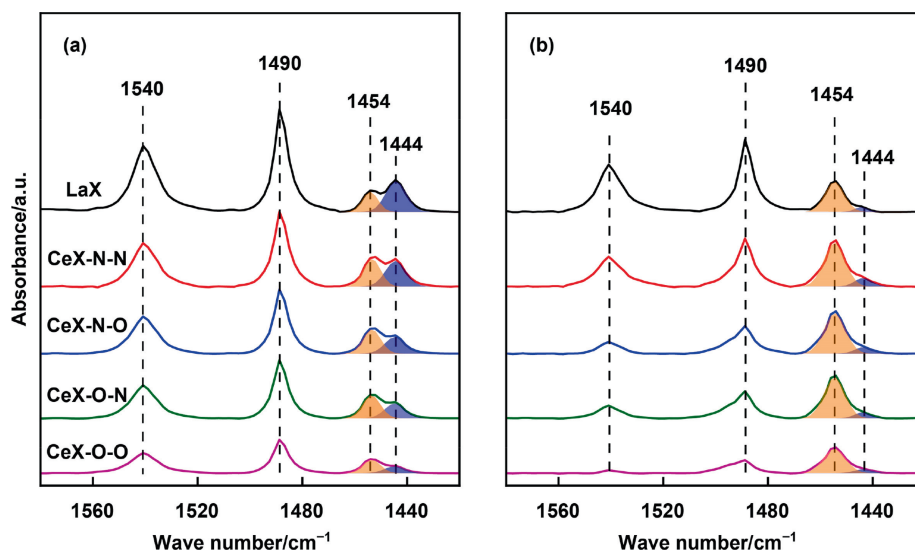


Fig. 7. IR spectra after pyridine adsorption on LaX and CeX zeolites calcined under varying atmospheres, followed by evacuation at (a) 150 °C and (b) 350 °C.

Table 4
Acidity of CeX zeolites by Py-IR

Sample	Acidity/mmol pyridine (g catalyst) ⁻¹		B ₃₅₀ /(B ₁₅₀ -B ₃₅₀)
	B ₁₅₀	B ₃₅₀	
LaX	0.140	0.110	3.67
CeX-N-N	0.110	0.080	2.67
CeX-N-O	0.098	0.023	0.31
CeX-O-N	0.087	0.030	0.53
CeX-O-O	0.057	0.005	0.10

the lifetimes of CeX-N-N and LaX were 12 h and 16.5 h, respectively.

Since the alkylation is catalyzed by strong Brønsted acid site, an attempt to correlate the catalyst lifetime with strong Brønsted acid concentration was made. As shown in Fig. 8(b), catalyst lifetime has a significant linear relationship with B₃₅₀, except for CeX-O-O, whose strong Brønsted acid concentration is too low. Such a linear correlation has also been observed in our previous study on LaFAU zeolites with varying framework Si/Al ratios [8]. Besides, some researchers ascribed the longer catalyst lifetime to a higher ratio of strong to weak acid concentration [30–32]. This explanation

relies on the fact that only strong Brønsted acid sites are active for the alkylation while weak Brønsted acid sites only catalyze butene oligomerization which deactivates the catalyst. As shown in Table 4, the ratio of strong to weak Brønsted acid concentration increased in the order of CeX-O-O < CeX-N-O < CeX-O-N < CeX-N-N < LaX, in line with the catalyst lifetime. However, it should be pointed out that this explanation is probably only suitable for catalysts with comparable acid concentrations.

Assuming that strong Brønsted acid sites in different catalysts act the same, the line should go through the origin, which is contrary to the result in Fig. 9(b). Therefore, this linear relationship also implies that strong Brønsted acid sites in different samples are not equivalent. To evaluate the lifetime of individual strong Brønsted acid site, TON (total butene turnover number for individual strong Brønsted acid site among the catalyst lifetime) was used. The TON can be calculated using the expression:

$$\text{TON} = 1000 \cdot \frac{yW}{xM} \quad (8)$$

in which W and M stand for the olefin space velocity and molar mass of 2-butene, respectively. Hence, the TONs for CeX-N-O, CeX-O-N, and CeX-N-N are calculated to be 11.6, 178.6, and 267.9, respectively. This result suggests that even with similar acid strength, the lifetimes of individual strong Brønsted acid sites in dif-

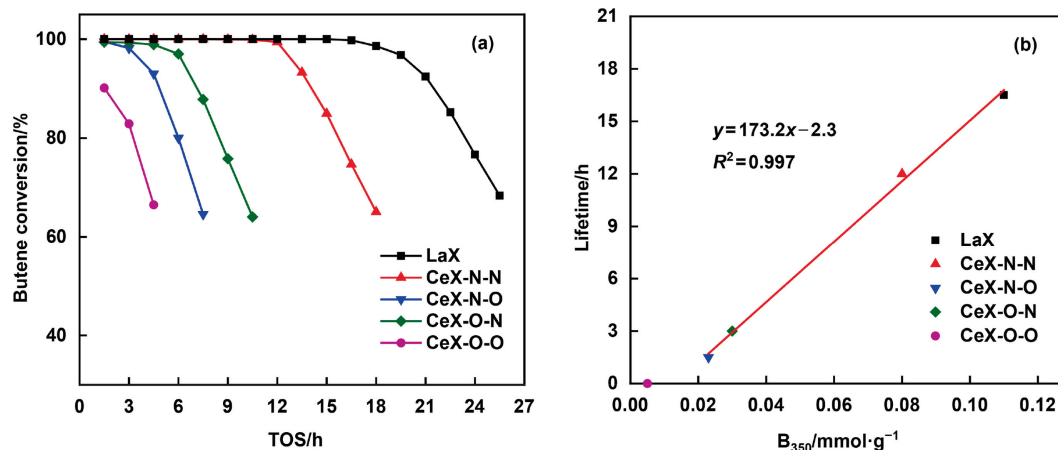


Fig. 8. (a) Butene conversion versus time on stream over LaX and CeX zeolites calcined under varying atmospheres; (b) The correlation between catalyst lifetime and B₃₅₀.

ferent catalysts can also differ from each other, being influenced by their concentrations. Theoretically, the lifetime of an active site depends on the relative rate of hydride transfer to butene addition [33]. For catalysts with higher acid concentrations, more 2-butene in the channels can be turned into carbocations, resulting in lower free 2-butene around the active site. Accordingly, the carbon chain growth, which deactivates the catalyst, was suppressed and higher TON was obtained. However, such a rule did not fit for LaX: though possessing more B_{350} , LaX showed equal TON to CeX-N-N, indicating lower hydride transfer activity. It is well recognized that the hydride transfer requires Brønsted acid site with high strength. However, it should be pointed out that the acid strength is not the only factor that influences the hydride transfer activity. This is quite evident when noticing that LaX was more acidic than CeX-N-N as illustrated in Fig. 6. Noting the difference between LaX and CeX-N-N mainly relies on the different rare earth cations, the different hydride transfer activity of LaX and CeX-N-N would likely be ascribed to the difference between La^{3+} and Ce^{3+} . Besides the hydrolysis of rare earth cation which generates protons, rare earth cation locating in the supercage can polarize the C–H bonds of isobutane and facilitate the hydride transfer between isobutane and carbocations [6,7]. Such polarization effect is probably related to the intensity of electric fields and therefore, the rare earth cation radius. Because of the smaller cation radius of Ce^{3+} , CeX-N-N would possess stronger electric fields and give a stronger polarization effect on the C–H bond of isobutane [34]. Thus, CeX-N-N containing Ce^{3+} was speculated to be more active in the hydride transfer reaction than LaX.

3.2.2. Product distributions over LaX and CeX-N-N

During the alkylation, side reactions such as butene oligomerization and catalytic cracking take place as well. For samples with low strong Brønsted acid concentration, namely CeX-O-O, CeX-N-O, and CeX-O-N, butene oligomerization will be quite dominating which is responsible for their low TON. Hence, comparing products over catalysts with huge lifetime differences would be meaningless. In this study, only CeX-N-N and LaX are discussed because they possess identical TON for individual strong Brønsted acid sites. As mentioned above, the identical TON for CeX-N-N and LaX were achieved via different paths. LaX benefitted from its high B_{350} concentration while CeX-N-N is supposed to be more active on hydride transfer. The preference for different reactions will lead to different product selectivities. As shown in Fig. 9, the alkylation product is usually divided into four fractions, i.e., *n*-butane, C_5 – C_7 fraction, C_8 fraction, and C_9^+ fraction. Generally, the alkylation is initiated by the protonation of 2-butene (2-C), forming

sec-butyl carbocation (*s*-C) (Eq. (9)). Such *sec*-butyl carbocations can accept a hydride from isobutane (*i*-C) and be freed in the form of *n*-butane (*n*-C). In the meantime, isobutane turns into a *tert*-butyl carbocation (*t*-C) (Eq. (10)).



Normally, catalysts with more acidic sites often lead to higher *n*-butane selectivity. This relies on two facts. First, higher acid strength is more favorable for hydride transfer reaction [35]. Second, *tert*-butyl carbocation is more easily decomposed on stronger acid site (Eq. (11)), which frees the protons that can again protonate 2-butene and produce *n*-butane via Eq. (10) [33,36].



Considering the result of NH_3 -TPD in Fig. 6, LaX was expected to show higher *n*-butane selectivity than CeX-N-N. However, the opposite result is observed in Fig. 9. The initial *n*-butane selectivity is 7.6% and 9.3% for LaX and CeX-N-N, respectively. With time on stream, the *n*-butane gradually decreased to 6.0% for both samples at 7.5 h. Since *n*-butane can only be produced via Eq. (10) [33], the higher *n*-butane selectivity of CeX-N-N directly proves its higher hydride transfer activity, which is in line with the conclusion obtained from the stability. As shown in Fig. 9, the C_9^+ selectivity over CeX-N-N is around 0.5% during the initial several hours, slightly lower than that over LaX.

Though the higher acid strength of LaX did not lead to higher hydride transfer activity, it promoted the cracking reaction. As shown in Fig. 9, LaX exhibits a higher C_5 – C_7 selectivity than CeX-N-N over the whole lifetime. More importantly, as the reactant of catalytic cracking, more C_9^+ carbocations were consumed, resulting in less C_9^+ fraction. After 7.5 h, the C_9^+ selectivity over CeX-N-N sharply increased to 11.7% in just 4.5 h. While for LaX, the C_9^+ selectivity increased by 12.2% from 9 h to 16.5 h, suggesting a much slower rate. Due to the diffusion resistance, the heavy end would partially stay in the supercages. With the accumulation of deposits, the effective size of the supercage decreased, leading to stronger steric inhibition of the larger reaction intermediates for hydride transfer [37]. Through catalytic cracking, these deposits would be partially transformed into small molecules and the deactivation slows down. Thus, the cracking activity seems to play a protective role in maintaining the hydride transfer activity. As for the C_8 fraction, it can be obtained in large amounts for both catalysts over the catalyst lifetime, especially when the C_9^+ selectivity has not raised, the C_8 selectivity can be as high as 85%. With time on stream, the

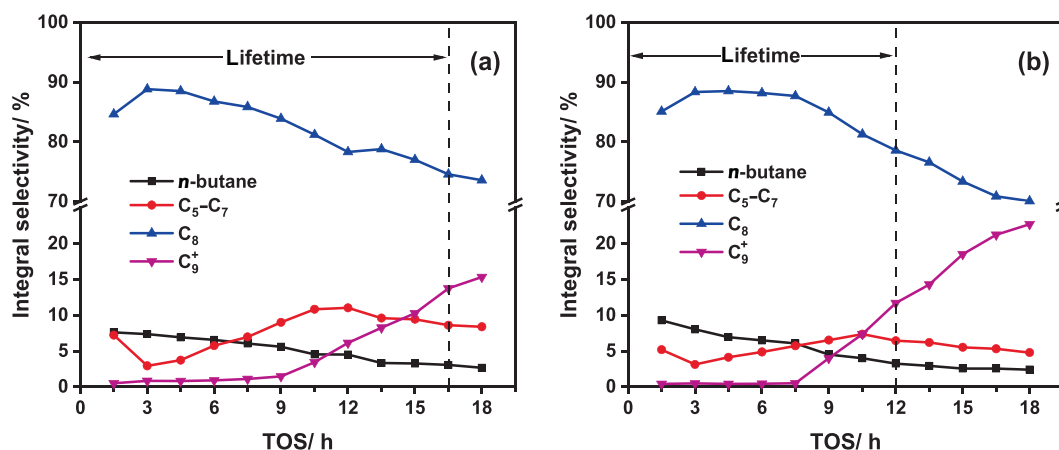
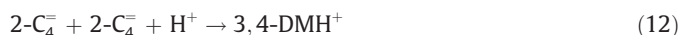


Fig. 9. Variation of product distribution with time on stream over (a) LaX and (b) CeX-N-N.

catalyst gradually deactivated and the P/O ratio in the reactor increased, leading to a continuous drop of the C₈ selectivity.

The composition of the C₈ fraction deserves more attention because it directly determines the anti-knock property of the alkylate. As shown in Fig. 10, the C₈ fraction is composed of trimethylpentanes (TMPs), dimethylhexanes (DMHs), olefins (C₈⁼), and other C₈ alkanes. The latter two were generated in small amounts, totally covered less than 5% of the C₈ fraction over the catalyst lifetime. TMPs were the most dominating component in the C₈ fraction and occupied 93.5% and 94.8%, respectively, for LaX and CeX-N-N at 1.5 h. With time on stream, they gradually dropped, respectively, to 84.3% and 88.1% at the end of catalyst lifetime. Meanwhile, the DMHs selectivity increased to 11.5% and 8.5% for LaX and CeX-N-N, respectively. The ratio of TMP/DMH can more intuitively reflect the quality of the alkylate. Normally, the TMP/DMH ratio is around eight for alkylate oil obtained using sulfuric acid as catalyst [38]. In this study, it went to ca. 7.3 and 10.4, respectively, for LaX and CeX-N-N at the end of catalyst lifetime, indicating that CeX-N-N was more favorable to producing high-quality alkylate oil regardless of its shorter lifetime.

The formation of DMHs is worthy of note since they are the most abundant low-octane components in the C₈ fraction. Restraining the formation of DMHs is significant for improving the quality of alkylate. Most studies discussed the catalytic cycle of TMPs while discussions on the continuous formation of DMHs is scarce. Generally, DMHs are generated through successive adsorption of two 2-butene onto the Brønsted acid site, resulting in a 3,4-DMH⁺ carbocation (Eq. (12)), which would quickly isomerize to other DMH⁺ carbocations via methyl and hydride transfer [8].



Afterward, these DMH⁺ carbocations can accept hydride ions from isobutanes and be released in the form of DMHs, meanwhile, the isobutane turns into a *tert*-butyl carbocation (Eq. (13)).



To complete the catalytic cycle, the resulting *tert*-butyl carbocation must suffer from a decomposition step as illustrated earlier in Eq. (11) to recover the Brønsted acid site. The overall catalytic cycle of DMHs is shown as Path I in Fig. 11.

However, there are still some ambiguities on this mechanism. First, the resulting *tert*-butyl carbocation can not only undergo decomposition but also butene addition, generating a 2,2,3-TMP⁺ carbocation (Eq. (14)), which will finally turn into TMPs after isomerization and consequent hydride transfer.

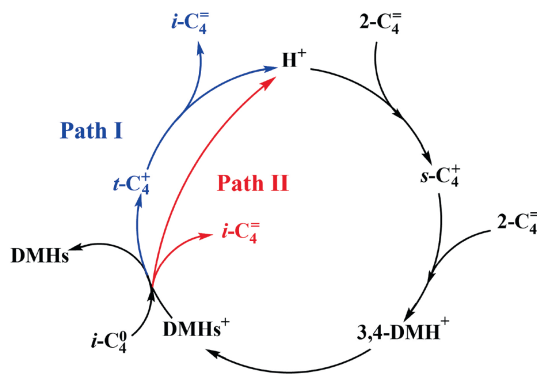


Fig. 11. The catalytic cycle of DMHs completed by the formation and decomposition of *tert*-butyl carbocation (Path I) and by the direct recovery of Brønsted acid site (Path II).

Since the reactor was filled with isobutane, butene concentration in the reactor was extremely low within the initial several hours, which makes this reaction occur in a low probability. With the feedstock pumping in, butene concentration rapidly increased and butene addition would become more significant. Thus, the TMP/DMH ratio would increase with time on stream, which is contrary to the fact.

Second, the higher DMHs selectivity over LaX zeolite suggests that this sample is more active on *tert*-butyl carbocation decomposition. Though the *tert*-butyl carbocation decomposition is usually observed more easily take place on catalysts with higher acid strength, it should be pointed out that other properties must contribute to the decomposition as well [4]. The decomposition is supposed to undergo a scheme as illustrated in Fig. 12. The *tert*-butyl carbocation first transfers into a zeolite-bound *tert*-butoxy intermediate, from which a proton can be transferred to the zeolite lattice with a concomitant formation of isobutene [39]. The stability of the intermediate plays a critical role in carbocation decomposition. As a conjugate acid-base pair formed with positive-charged carbocation and negative-charged zeolite lattice acting as Lewis acids and Lewis base, respectively, the stability of the intermediate is surely influenced by the basicity of zeolite lattice. With a more basic lattice, the intermediate gets more stable and consequently, carbocation decomposition becomes more difficult. In our case, the basicity of zeolite lattice increases with increasing cation size [40]. Considering the smaller cation radius of Ce³⁺, the zeolite lattice of CeX-N-N was speculated to be less basic compared with LaX. Consequently, the *tert*-butoxy intermediate bonded with CeX-N-N zeolitic lattice would be less stable. So, CeX-N-N is supposed to be

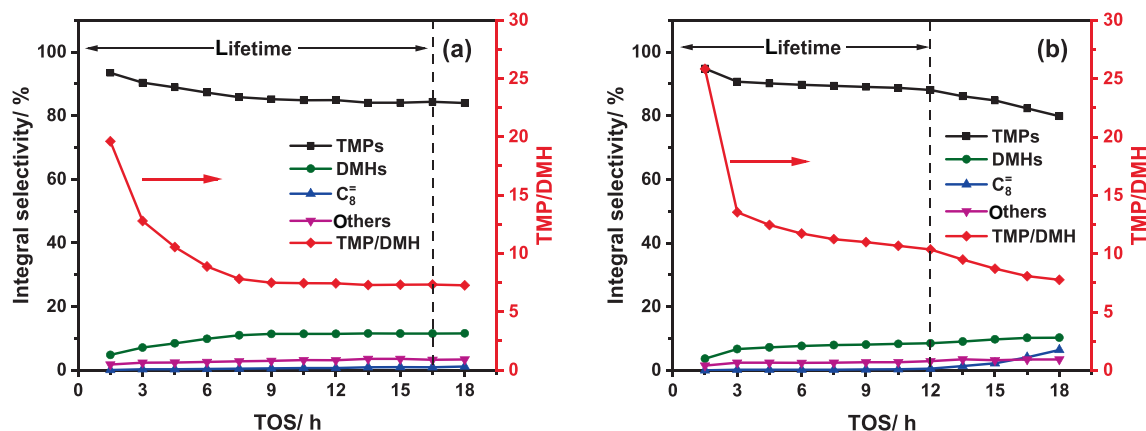


Fig. 10. Compositions of the C₈ fraction and TMP/DMH ratios over (a) LaX and (b) CeX-N-N.

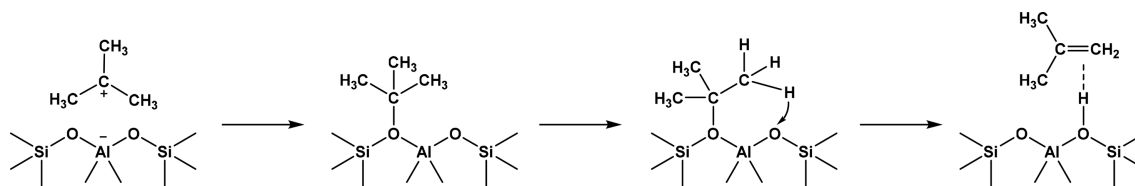
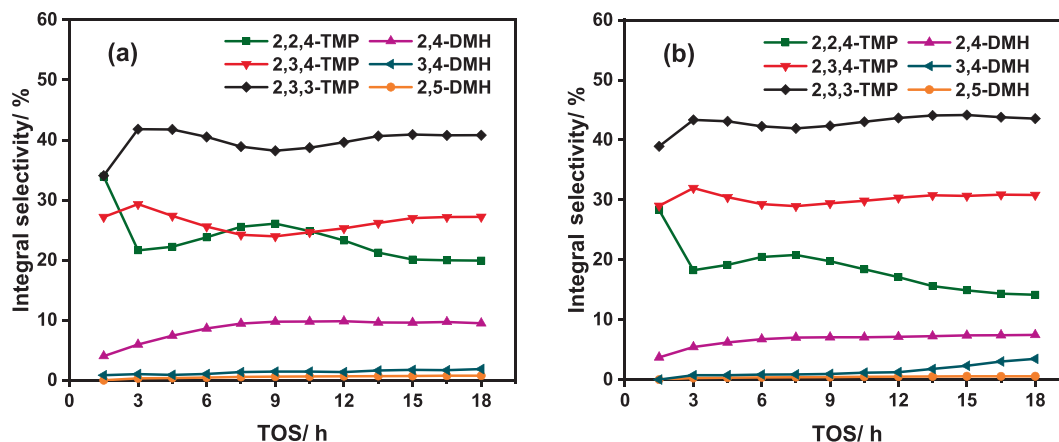
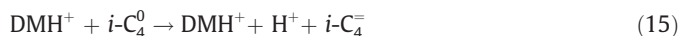
Fig. 12. Schematic presentation of the *tert*-butyl carbocation decomposition.

Fig. 13. Constitution of TMPs and DMHs over (a) LaX and (b) CeX-N-N with time on stream.

more active on *tert*-butyl carbocation decomposition and should yield more DMHs. As displayed in Fig. 10, DMHs occupy 8.5% of the C₈ fraction over CeX-N-N, lower than that over LaX which is ca. 11.5%. The discrepancy between the speculation and the reality suggests that the catalytic cycle of DMHs might be completed in another way.

Liu *et al.* simulate the reaction mechanism of propene/isobutane alkylation and found two reaction routes for the hydride transfer. One involves the formation of a three-molecule complex of “carbocation-isobutane-propene” and another route occurs between carbocation and isobutane with the direct formation of isobutene rather than *tert*-butyl carbocation [39]. Accordingly, the hydride transfer between isobutane and DMH⁺ carbocation is suggested *via* a route as shown in Eq. (15) and the catalytic cycle of DMH is as shown in Path II in Fig. 11.



Such reaction route directly yields isobutene and recovers the Brønsted acid site that does not go through *tert*-butyl carbocation formation and decomposition. The resulting isobutene can certainly re-adsorb onto the Brønsted acid site, which would turn to TMP⁺ carbocations after a 2-butene addition. However, due to the competitive adsorption by 2-butene, isobutene readsorption could largely be suppressed. Hence, the TMP/DMH ratio reduces with time on stream.

Instead, the resulting isobutene would mainly react with another *tert*- or *sec*-butyl carbocation, forming 2,2,4-TMP⁺ or 2,4-DMH⁺ carbocation, respectively.



Normally, the addition of 2-butene onto *tert*- and *sec*-butyl carbocation would give 2,2,3-TMP⁺ and 3,4-DMH⁺ carbocation, respectively, as the primary product. Afterward, they quickly isomerize into other carbocations by methyl and hydride transfer

[8]. As for 2,2,4-TMP⁺ and 2,4-DMH⁺, besides the normal isomerization route, they can also directly be formed according to Eq. (16) and Eq. (17), respectively. Thus, the more DMHs generated, the more isobutene formed and as a result, more 2,2,4-TMP and 2,4-DMH were obtained. Since LaX yielded higher DMHs selectivity, accordingly, it would produce more 2,2,4-TMP and 2,4-DMH which can be clearly illustrated in Fig. 13. The recovered Brønsted acid site could repeat the butene addition and hydride transfer as illustrated in Eq. (9) and Eq. (10), resulting in *n*-butane and *tert*-butyl carbocation. Owing to its higher hydride transfer activity, this reaction is preferent over CeX-N-N and as a result, more *n*-butane and higher TMP/DMH ratio were obtained.

4. Conclusions

In this study, CeX zeolites with varying Ce^{IV} contents were prepared by calcining under controlled atmospheres. The impacts of calcination atmosphere on the physiochemical properties were determined. The relative crystallinity and micropore volume were found to decrease with the increasing content of Ce^{IV}. This is believed to be due to the *in situ* formed water, which caused more severe framework dealumination. This would further decrease the acidity. Meanwhile, the sacrifice of protons during the Ce^{III} oxidation should also be responsible for the reduce the concentration of Brønsted acid sites as well. As a result, the oxidized CeX zeolites exhibit much lower strong Brønsted acid concentrations. Comparing with CeX zeolite calcined under nitrogen protection, CeX zeolite suffered two-step oxygen calcination exhibited only one-sixteenth strong Brønsted acid concentration and consequently, deactivated at the very beginning while the lifetime of CeX-N-N was as high as 12 h. Therefore, cerium-containing zeolites should be prepared carefully to avoid cerium oxidation.

Combining with the alkylation performance of LaX zeolite, the catalyst lifetime was found to be strongly dependent on the concentration of strong Brønsted acid sites. In comparison with LaX zeolite, CeX-N-N was found to be more active for hydride transfer.

This difference was attributed to a stronger polarization effect on the C–H bond of isobutane caused by the smaller cation radius of Ce^{3+} . Though LaX was not as active for hydride transfer as CeX–N–N, benefiting from its stronger acid sites, it yielded a lower C_{9+} fraction which would deposit in the cavity, reduce the effective size of the supercage, and restrain the hydride transfer. As a consequence, LaX exhibited a slower decline rate on the hydride transfer activity. Further investigation on the C_8 composition suggested that the catalytic cycle of DMHs might be completed by a direct formation of isobutene, rather than tert-butyl carbocation.

These results provide valuable knowledge for the preparation of alkylation catalysts using cerium-containing rare earth elements. In addition, when using such catalysts, the regeneration approach should also be noted: the coke burning method may change the catalyst properties and is undesirable.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

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