Negative thermal expansion and cationic migration in zeolite Y used in FCC catalysts

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Abstract. The influence of extra-framework cations on the intrinsic negative thermal expansion (NTE) of calcined ultra-stable and lanthanum-exchanged zeolites Y was analysed. High-temperature thermal behaviour, cationic migration and dealumination were examined by *in situ* high temperature X-ray powder diffraction and thermogravimetric (TG) analyses. We analysed protonated ultra-stable zeolite Y and zeolite Y containing 13% La_2O_3 (LaY), and investigated how the presence of La^{3+} influences thermal behaviour of zeolite Y. Uncalcined LaY was also analysed to observe the La^{3+} migration before calcination. Mass loss up to 990°C was accompanied by TG analyses. X-ray powder diffraction data were analysed by Rietveld method. Our data show that lanthanum migration from supercages to sodalitic cavities is not reversible. However, some La^{3+} migration occurs above 400°C and we observe emptying of site I', migration to site I and to some extent to site II'. Furthermore, we examined the dealumination process as well. Both samples show two distinct thermal behaviours, positive or near-zero thermal expansion up to 500°C and NTE above this temperature. Together with intrinsic NTE in faujasite type zeolites, the dealumination process is largely responsible for NTE at high temperatures.

Keywords. Near-zero thermal expansion; *in situ* XRD; ultra-stable zeolite Y; extra-framework cation; lanthanum migration.

1. Introduction

Zeolites are open framework crystalline aluminosilicate structures. Their framework consists of corner sharing Si–O and Al–O tetrahedra joined in a porous three-dimensional structure. This structure creates their ion-exchange ability and allows for the facilitation of various extra-framework cations. Consequently, the use of zeolites is vast. Due to their ion-exchange ability, they are used as a remediation tool, in water softeners and filters, detergents, etc. One of the most important applications is in hydrocarbon cracking catalytic processes, namely fluid catalytic cracking (FCC), a key petroleum refining process. During the FCC process, the catalysts transform the heavy feedstock by breaking the long hydrocarbon chains at elevated temperatures into lighter petroleum products, such as liquefied petroleum gas. Thus, the catalyst must withstand the temperature and the steam partial pressure in the regenerator [1]. Ultra-stable zeolite Y (USY), a faujasite (FAU) structure type is one of the most important components in the FCC procedures. High hydrothermal and thermal stabilities of USY comes from dealumination and removal of sodium [2,3] and it is generally rare-earth

element (REE)-rich. Extra-framework REE in zeolites for FCC is responsible for enhancing hydrothermal stability, improving acidity and cracking activity [4]. There are usually five extra-framework sites that can be populated by extra-framework cations in FAU zeolites. These sites are located in supercages, sodalitic cavities and hexagonal prisms. The choice of an extra-framework site depends on the hydration level, and the type and the amount of extra-framework cations. Frising and Leflaive [5] formed a comprehensive list of possible extra-framework sites in the FAU structure. REE-rich USY is the most suitable for the FCC processes [2,6]. Due to its properties, La^{3+} -exchanged USY is used as the main component of FCC catalysts. The presence of REE, specifically Ce^{3+} and La^{3+} as the extra-framework cations improves the thermal stability of zeolite Y, as the zeolite collapse temperature increases with increasing content of REE [4]. Furthermore, the addition of REE not only increases thermal stability, but also the overall activity of the catalyst [7]. In La^{3+} -exchanged FCC zeolites, La^{3+} migration from supercages to sodalite cages at temperatures up to 400°C has been observed. At room temperature, hydrated rare earth ions $[\text{RE}(\text{H}_2\text{O})_x]^{3+}$ are too big to diffuse from the

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supercages through the six-membered ring since there is not enough thermal energy to overcome activation energy of diffusion. The sodalite cages in zeolite Y are accessible from the supercages through six-membered rings of 0.25 nm free diameter. Therefore, the radius of hydrated $[\text{La}(\text{H}_2\text{O})_m]^{3+}$ ions is too large to diffuse through these windows, so most or all the hydration layers must be stripped to facilitate lanthanum cation migration to sodalite cages [8–10]. Thermal stability of lanthanum zeolite-Y is generally attributed to the so-called bridges between La and oxygen atoms in sodalite cages [9,11]; these bridges are postulated to consist of La atoms connected by bridging oxygens RE–O–RE [11–13]. Wang *et al* [14] noted that the distribution of REE in supercages and sodalite cages is closely related to the intensities of the diffraction lines at 11.8 and $12.4^\circ 2\theta$, attributed to the (311) and (222) crystallographic planes, respectively. Du *et al* [9] defined a parameter K as $K = I_{(311)}/I_{(222)}$ that measures the amount of REE inside these two cages, where the larger K value indicates more REE located in the sodalite cages. Most of the published studies have examined this behaviour up to 600°C . Marti *et al* [15] found that in hydrated NaY, most Na cations are located in site III', site I' is more populated than site I, while the smallest number of Na^+ cations are located in site II. Furthermore, they concluded that some Na^+ could be freely moving in the supercage. Haniffa and Seff [16] showed that extra-framework cations are located in I, I', II', III' and V sites in partially exchanged CuNaY. It has been suggested that introduction of REE in the FAU structure reduces the dealumination process under hydrothermal conditions and in turn increases the activity per weight of zeolite and enhances hydrogen transfer [7]. Nery *et al* [17] observed that in NaLaY, La^{3+} occupied site V before calcination. Smith *et al* [18] found that the majority of La^{3+} occupied site V, although some La was found in site I' in La-exchanged hydrated FAU. Zeolites are materials known to have negative thermal expansion (NTE) over a wide range of temperatures [19–22]. Materials with NTE contract upon heating under constant pressure, and exhibit a decrease in the unit cell volume. This property arises from the transverse vibration of rigid $(\text{Si},\text{Al})\text{O}_4$ tetrahedra [20,23]. Generally, several processes can occur in a zeolite structure during heating. Water loss up to $350\text{--}400^\circ\text{C}$ has been reported to cause contraction [3] or expansion [21] of the unit cell, phase transformation to a more stable phase [24], dealumination, extra-framework cation migration, intrinsic NTE and total or partial amorphization. To date, some published studies reported positive thermal expansion (PTE) of FAU type zeolites [23], while others reported NTE [20,25] for silico-alumino-phosphate (SAPO) with FAU type structure [22]. It is also worth to note that Couves *et al* [26] predicted theoretically that purely siliceous FAU and NaX varieties would both have NTE ranging from temperatures as low as -248°C up to 227°C , while experimentally verified that this behaviour for NaX is maintained between -248 and -56°C , while at near room temperatures, the unit cell starts to increase. We studied two types of calcined zeolite Y, protonated USY, an ultrastable zeolite Y, used as a precursor in the

Table 1. Sample composition.

Material	Number	XRF	SiO_2	Na_2O	Al_2O_3	La_2O_3
Zeolite	USY	%	73.11	1.12	22.86	—
Zeolite	LaY	%	65.97	0.59	20.45	13

preparation of REE-exchanged zeolites used in hydrocarbon catalytic processes, and La-exchanged zeolite LaY. The goal of our research was to determine the position and potential migration of extra-framework cations in two zeolite Y end members, USY and La-rich/Na-poor zeolite Y (LaY), over a wide range of temperatures. Furthermore, we examined a potential correlation between extra-framework cations and the NTE at high temperatures.

2. Methods

2.1 Materials

Chemical composition determined by X-ray fluorescence (XRF) of the two synthetic calcined at 550°C zeolite Y samples, protonated USY and LaY are shown in table 1, where the remaining 3 wt% of USY are attributed to hydrogen atoms. Materials are commercial, used in FCC catalysis and were kindly provided by Petrobras, where USY zeolite is the precursor for the synthesis of La-exchanged and other zeolites.

2.2 Characterization and data analysis

Samples were analysed *in situ* via high temperature X-ray powder diffraction (HT-XRPD) using a Bruker D8 Advance diffractometer with $\text{CuK}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$), and a Ni filter. Additionally, one uncalcined LaY sample was also analysed via HT-XRPD to observe the La^{3+} migration before calcination. Diffractometer was equipped with an Anton Paar XRK900 high temperature reaction chamber. Samples were analysed from 5 to $60^\circ 2\theta$, 2 s scan speed and step size 0.02° , at each 100°C from 25 to 900°C . XRPD data were subsequently analysed by Rietveld method using Topas 4.2 software. To obtain better refinement results, we excluded the (022) diffraction line from the calculations due to its asymmetry [9]. First, we modelled the XRPD patterns using the LeBail method to determine thermal expansion by calculating lattice parameter values at all temperatures ($25\text{--}800^\circ\text{C}$). Once we determined the coefficient of thermal expansion, we proceeded with Rietveld analysis, which takes into account the type of atoms and their positions in the structure and varied commonly refined parameters [27–29]. To fit the zeolite structures at each temperature, we refined zeolite Y samples in the $Fd\bar{3}m$ space group, and varied the following parameters: background, scale factor, cell parameters, average crystallite size and most importantly atomic site and occupancy

Table 2. Bond length constraints.

Atoms	Maximum bond length (Å)
T–O	1.60
Al–O	1.90
O–O	2.75
La–O	2.80

parameters. Considering that zeolite Y is composed of light atoms with La^{3+} as an exception, thermal factors were determined at room temperature and fixed during the refinement to give sensible results [21,30,31]. Instrumental parameters were previously determined using a standard material, and were thus fixed during the refinement. To obtain meaningful atomic positions and to observe the cationic migration within the zeolite framework, we introduced bond length constraints in the calculation (table 2). Since Si and Al have almost identical X-ray scattering factors and it is not possible to determine their amounts using X-ray diffraction (XRD) techniques, we labelled tetrahedral sites T and included only silicon in the refinement, since it is prevalent at tetrahedral sites. Extra-framework aluminium in USY and lanthanum in LaY were allowed to vary, which allowed us to examine cationic migration within the zeolite structure and the dealumination process. Water molecules, considered as O^{2-} in Rietveld analysis, were included in the calculation at 25 and 200°C, in accordance with thermogravimetric (TG) data. Furthermore, above 800°C, we start to observe deterioration of the zeolite structure and could not obtain satisfactory agreement, thus Rietveld analyses were performed up to 800°C. To confirm the water departure temperature and to verify the thermal stability of zeolite Y samples, we performed DSC/TG analyses on a Perkin-Elmer STA 6000 in air flow 20 ml min^{-1} , and heated the samples at a rate of $20^\circ\text{C min}^{-1}$ from 30 to 990°C.

3. Results

HT-XRPD results (figure 1) show the behaviour of (311) and (222) diffraction lines during thermal treatment of calcined LaY from 25 to 900°C. For comparison, the inset in figure 1 shows the uncalcined sample, where all La^{3+} cations were in the hydrated state in supercages at room temperature. Figure 2 demonstrates the absence of the (222) diffraction line in zeolite USY, only the (311) line is present. Our results showed that thermal expansion properties vary depending on the type of extra-framework cations and temperature (figure 3). To calculate the CTEs, we used values of unit cell above 400°C to avoid accounting for the influence of water. USY and LaY CTEs between 500 and 800°C were determined to be $-3 \times 10^{-5} \text{ }^\circ\text{C}^{-1}$ and $-7.5 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$, respectively.

Figure 1. HT-XRPD *in situ* diffraction patterns showing the relationship between the (311) and (222) reflections in calcined LaY. The inset shows this relationship in uncalcined LaY.

Figure 2. HT-XRPD *in situ* diffraction patterns showing only the presence of (311) reflection in calcined USY.

Rietveld refinement results describing the migration of extra-framework cations are shown in figures 4 and 5, and related tables show the number of extra-framework cations in LaY and USY (tables 3 and 4). During Rietveld refinement of USY above 100°C, Al^{3+} extra-framework cations were allowed to migrate to sites that were initially occupied by water (sites Al3/O5 and Al4/O7; see supplementary file). Figure 6 shows TG curves for USY and LaY zeolites. Mass loss in both samples is similar, about 26% up to 990°C, while the DSC curves do not indicate any type of phase transition taking place. TG shows that mass loss due to water release up to 200°C is about 23 and 18% for USY and LaY zeolites, respectively.

4. Discussion

Several processes occur within the zeolite structure during heating. A major part of water loss occurs up to 200°C.

Figure 3. Lattice parameters of USY (left) and calcined LaY (right).

Figure 4. Migration of La^{3+} and Al^{3+} extra-framework cations in calcined LaY during heating; Al is located in hexagonal prism general position with multiplicity 32, defined in the CIF file [28].

At room temperature in zeolites, water is present on the surface as moisture and as structural water within the cavities at well-defined crystallographic sites. In uncalcined LaY hydration layer, surrounding La^{3+} ions begin to evaporate and the stripped La^{3+} cations migrate from supercages to sodalite cages and hexagonal prisms (figure 1, inset). This process is witnessed by the change in the intensity ratio between two distinct diffraction lines (311) and (222) [14]. During this process and up to 200°C LaY unit cell exhibits PTE (figure 3). The expansion of the unit cell represents the response of the crystal structure to water departure as suggested by Wang *et al* [32] for BaY zeolite. The authors presented a model that explained the increase of zeolite Y unit cell due to the loss of water from the centre of sodalite cages. These water molecules, located in the centre of sodalite cages, interacted with Ba^{2+} located at I' and II sites and were thus pulled closer together, and since Ba^{2+} cations were already interacting with framework O^{2-} , the entire framework contracted.

Figure 5. Behaviour of extra-framework Al^{3+} in USY. Al is located in hexagonal prism, general position multiplicity 32, and Al1 and Al2 are located in O5 and O7 water sites after dehydration.

Table 3. Number of La^{3+} extra-framework cations per unit cell during heating.

	T ($^{\circ}\text{C}$)							
	25	200	300	400	500	600	700	800
$\text{La}^{3+}/\text{U.C.}$	16	13	13	15	15	14	14	14

Therefore, as the water molecules depart, the structure relaxes and the volume increases. In the case of LaY, La^{3+} located at I' plays the same role as Ba^{2+} and through the interaction with water, contracts the framework. Marinkovic *et al* [21] reported this type of complex thermal behaviour in HZSM-5 structure. Similarly, Bhange and Ramaswamy [33] observed a similar response of silicalite-2 to dehydration. Conversely, USY zeolite unit cell does not respond to the departure of water from its cavities in such a way. Surface moisture is lost up to 100°C , while structure water leaves the structure up to 200°C . Figure 6 shows divergence between LaY and USY TG curves above 100°C implying higher pore water release from USY cavities. However, due to the lack of extra-framework La^{3+} , water molecules do not strongly interact with the USY framework and the unit cell does not expand or contract significantly up to 500°C ($\alpha = 9.3 \times 10^{-7} \text{ }^{\circ}\text{C}^{-1}$ for this temperature range), when NTE effect becomes dominant. Furthermore, protonated USY zeolite contains a certain amount of extra-framework hydrogens; we can assume that the presence of these protons influences the thermal expansion properties of USY. Thermal behaviour up to 500°C can be explained by the interaction of hydrogens with both water molecules and the framework, although weaker than the interaction of highly charged cations such as La^{3+} . Therefore, the intrinsic NTE is partially attenuated when water is lost and the overall behaviour shows thermal expansion close to zero ($\alpha = 9.3 \times 10^{-7} \text{ }^{\circ}\text{C}^{-1}$). Kirschhock *et al* [34] examined water desorption behaviour in partially dehydrated Y and X zeolites with various alkali metal cations and found that the quantity of absorbed water depends on the type of extra-framework cations. They showed that Na^{+} has a high affinity towards water, and the formation of SII–water–SIII interaction. Similarly to zeolite HZSM-5 [21], the presence of water molecules contracts LaY structure, which reflects on the thermal expansion properties. Once all the structural water leaves the zeolite LaY structure, CTE changes very little between 200 and 400°C , when the dealumination process becomes prominent (figure 3a). Together with intrinsic NTE, the dealumination process is largely responsible for NTE at high temperatures in FAU-type structure. As Al^{3+} leaves the framework, it enters the structure as extra-framework cations leaving behind empty tetrahedra with excess negative charge. At the same time, oxygen anions from the empty tetrahedra are drawn to silicon in the neighbouring tetrahedra and the unit cell contraction becomes more apparent, thus, further contributing to NTE [21,35]. NTE coefficients in USY and LaY differ by one order of magnitude i.e., USY

Table 4. Number of Al^{3+} extra-framework cations per unit cell during heating.

	T ($^{\circ}\text{C}$)								
	25	100	200	300	400	500	600	700	800
$\text{Al}^{3+}/\text{U.C.}$	54	53	56	51	49	51	58	64	84

Figure 6. TG curves of LaY and USY zeolites.

exhibits stronger NTE from 500°C . When there are no extra-framework cations, pure siliceous FAU and SAPO exhibit similar NTE around -4×10^{-6} [22,25]. USY exhibits much stronger NTE above 500°C than both pure siliceous FAU and LaY. In both USY and LaY, significant amount of dealumination causes additional framework contraction and enhances the intrinsic NTE. Therefore, a higher dealumination rate (figures 3 and 4) causes higher NTE coefficient in USY ($-3 \times 10^{-5} \text{ }^{\circ}\text{C}^{-1}$) than in LaY ($-7.5 \times 10^{-6} \text{ }^{\circ}\text{C}^{-1}$). Furthermore, the extra-framework Al^{3+} cations do not attenuate the NTE as previously suggested [23]. Our data show that the amount of extra-framework aluminium in USY extra-framework sites remains more or less constant during heating up to 500°C . Above this temperature, dealumination becomes significant and an additional population of extra-framework Al^{3+} sites is documented by Rietveld analysis (figure 5). Conversely, extra-framework La^{3+} starts to migrate during heating from 400°C in calcined LaY. Specifically, we observe the emptying of site I' and the migration to site I and to a certain extent to site II'. In addition, dealumination starts at 400°C , and we observed the formation of one extra-framework Al site in LaY (figure 4). Frising and Leflaive [5] determined that for pure NaY, site II is the preferred location and is almost always completely populated with 32 Na atoms because it minimizes cation–cation repulsion. Regarding La^{3+} , they report that it is located in site V which is not the case for the analysed LaY zeolite. On the contrary, Rietveld analysis showed that La^{3+} preferentially fills sites I, I' and II' (figure 4). Furthermore, our analyses on calcined LaY showed

that after calcination, migration of La^{3+} to sodalitic cavities is a non-reversible process. Once the water layer surrounding La^{3+} ions is stripped and they migrate to their favoured locations, such as I' and I, and further temperature treatment does not have significant effect on their location, as witnessed by the Rietveld analysis. We do, however, observe slight redistribution of La^{3+} between hexagonal prism and sodalitic cavity, along the [111] direction over I, I', II' sites, 16 (I) and 32 (I' and II') fold sites that increase coordinative RE–O–RE bonding and in turn increase the hydrothermal stability of LaY [28]. Lee and Rees [8] described La^{3+} cation migration as irreversible; however, Wang *et al* [14] suggested the reversal of this process. They performed *in situ* XRPD during heating at 550°C, cooling and after rehydration and concluded that diffraction intensity variation of two characteristic lines is related to both LaY hydration status and the La^{3+} location. They suggested that the $[\text{La}(\text{H}_2\text{O})_m]^{3+}$ ions in the supercages can strengthen the (222) diffraction line and reduce (311) diffraction line dramatically. Reappearance of the (222) diffraction line after rehydration dubbed the process reversible. Complete absence of the (222) peak in USY suggests that this peak is indeed related to the presence of La at supercages (figure 1). However, we found that it could also be related to the presence of water. Since La ions do not migrate after calcination to supercages, water molecules enter the porous zeolite structure; at room temperature polar water molecules are drawn to existing framework charge inside supercages. Even though both USY and LaY contain approximately the same amount of water (figure 6), we do not see the (222) diffraction line in USY at room temperature (figure 2). Therefore, our data suggest that the existence of (222) diffraction line in already calcined LaY samples at room temperature in the presence of atmospheric water reflects the position of water molecules in supercages and the corresponding response of the lattice. Furthermore, we could assume that water molecules do not have much influence on the USY framework since the cell parameter remains more or less constant up to 500°C (figure 3). Figure 4 shows even distribution of extra-framework aluminium in USY. There is no migration during thermal treatment until 500°C when the dealumination process begins to take place. Above this temperature, we can first observe a slight and then a sharp increase in the number of extra-framework aluminium cations. On the other hand, reappearance of (222) diffraction line above 550°C in LaY (figure 1) cannot be related to the presence of water at these temperatures. Furthermore, since the migration of lanthanum is irreversible i.e., we do not see reappearance of La in supercages, and the appearance of (222) diffraction line above this temperature is related to another process, possibly dealumination.

5. Conclusions

1. Cation migration between supercages and sodalitic cavities in calcined zeolites Y is an irreversible process.

We observe some migration of extra-framework La^{3+} between sites I' and I/II', located within sodalite cages and hexagonal prisms during heating from 400°C in calcined LaY. Most importantly, at temperatures similar to those of the FCC process, extra-framework La^{3+} ions remain in previously mentioned 16 and 32 fold positions in sodalitic cavities and hexagonal prisms, crucial for the improvement of hydrothermal stability of LaY FCC catalysts.

2. NTE of FAU type zeolites with framework Al increases due to dealumination above 400°C in comparison with pure siliceous FAU and SAPO. Below 400°C, thermal expansion of both zeolites LaY and USY, is dominated by indirect interaction of water with the framework, mediated by extra-framework cations, principally La^{3+} and to a lower extent H^+ .
3. *K* factors, as an indication of the occupation of rare earth cations in supercages and sodalitic cavities, can only be considered in the case of uncalcined REE-rich zeolites Y. The relationship between (311) and (222) reflections does demonstrate the location of REE and their migration to sodalitic cavities. However, once this process is finished, it becomes irreversible i.e., REE do not migrate back to supercages. The existence of (222) at room temperature in calcined LaY zeolite is most probably related to the presence of water in supercages. Furthermore, the reappearance of (222) diffraction line at the temperatures > 500°C could be attributed to dealumination process and thus, occupying one of the supercage extra-framework sites, responsible for this reflection.

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