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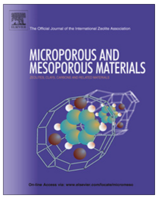

Influence of alkali cations on the inter-conversion of extra-framework aluminium species in dealuminated zeolites

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Dedicated to Dr. Michael Stöcker on the occasion of his retirement as Editor-in-Chief of Microporous and Mesoporous Materials.

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ABSTRACT

The common main factor of the Na^+ influence on the extra-framework aluminum (EFAL) transformations was observed while modeling partly hydrated zeolites at both periodic and cluster computational levels. It can be characterized as the attack of Lewis acid (Na^+) toward electron pairs of different O atoms. The limiting step of EFAL formation is assigned to the transformation between the $AlOH^{2+}$ and $Al(OH)_2^+$ species. It allows the explanation of the poisoning effect of Na^+ on the cracking reactions known experimentally. The role of electrostatic factor is also discussed.

1. Introduction

After the discovery of enhanced catalytic properties in hydrocarbons cracking over dealuminated zeolites with high Si/Al modulus the interest increased to extra framework aluminum (EFAL) species whose easy and non-expensive generation was demonstrated upon steaming or other dealumination treatments [1]. Various hypotheses have been discussed to provide a reasonable explanation of acidity growing upon dealumination: (I) EFAL species reveal catalytic Lewis acid activity [2]; (II) stabilization of the negative charges on the lattice due to the EFAL species after the removal of acidic proton [3] and (III) synergism between Brønsted and Lewis type acid sites owing to a close location of both sites together [1,4–9]. The last idea is linked with a problem to find any experimental evidence of the spatial neighborhood of the Brønsted and Lewis sites. Recent combined ^{27}Al double quantum (DQ)-magic angle spinning (MAS) nuclear magnetic resonance (NMR) studies and density functional theory (DFT) computations [10] allowed to assign four types of the ^{27}Al isotropic chemical shifts at 61, 55, 30, and 0 ppm to 4-, 4-, 5-, and 6-coordinated Al species originated from the framework Si–OH–Al, extraframework $AlOH^{2+}$, $Al(OH)_2^+$, and $Al(OH)_3$ (in the $Al(OH)_3(H_2O)_3$ form) moieties, respectively. The cross peaks [10] showed four types of spatial correlations between framework aluminum (FAL) and EFAL particles formed during consequent dealumination: (A) framework Si–OH–Al species and $Al(OH)_2^+$ with the most intense cross peaks showing the closest distances between respective Al atoms; (B) Si–OH–Al species and EFAL moieties $AlOH^{2+}$; (C) $Al(OH)_2^+$ species and 6-coordinated $Al(OH)_3$ moieties and (D) $Al(OH)_2^+$ and $AlOH^{2+}$ species [10].

All the mentioned species were already involved in possible hydrolysis scheme starting from Al^{3+} [11–13]:

$$Al^{3+}(H_2O) + (Si{-}O{-}Al)^- \rightarrow AlOH^{2+} + Si{-}O(H){-}Al \tag{1}$$

$$AlOH^{2+}(H_2O) + (Si{-}O{-}Al)^- \rightarrow Al(OH)_2^+ + Si{-}O(H){-}Al \tag{2}$$

$$Al(OH)_2^+(H_2O) + (Si{-}O{-}Al)^- \rightarrow Al(OH)_3 + Si{-}O(H){-}Al \tag{3}$$

The activation energies of the hydrolysis reactions in the zeolites were not yet discussed theoretically to our best knowledge and are usually postulated *via* referencing to the analogy with bivalent AE cations. In order to link all the FAL and EFAL species for explanation of dealumination process in Y zeolites, the authors [10] derived the alternative scheme which suggests that EFAL $Al(OH)_3$ species appear first from the zeolite according to the step (4) being the source of $Al(OH)_2^+$ and $AlOH^{2+}$:

$$(\equiv Si{-}O{-})_3Al({-}OH{-}Si\equiv) + 3H_2O \rightarrow Al(OH)_3 + 4(\equiv Si{-}OH) \tag{4}$$

$$Al(OH)_3 + Si{-}O(H){-}Al \rightarrow Al(OH)_2^+(H_2O) + (Si{-}O{-}Al)^- \tag{5}$$

$$Al(OH)_2^+ + Si{-}O(H){-}Al \rightarrow AlOH^{2+}(H_2O) + (Si{-}O{-}Al)^- \tag{6}$$

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This new scheme contains inverse reactions (2) and (3) as the steps (6) and (5), respectively. One should note that each step of the dealumination process [10] decreases the concentration of acidic protons and, at the first step, increases the concentration of silanols. Two acid protons should participate per each forming $Al(OH)_2^+$ group. Consequently, the complete realization of the scheme should decrease the H concentration that does not contradict to the known data [1,12]. The increase of the silanol concentration is confirmed by the data of Table S1 [10] obtained on the basis of ^1H MAS NMR spectra.

The importance of hydrogen bonding (HB) instead of the synergism between Brønsted and Lewis types was alternatively proposed in the work [14] of Mota et al. They pointed to the relatively small value of the deprotonation energy (DE) for the $Al(OH)_2^+ \times H6R(2Al)^-$ cluster as the indicator of high influence of the $Al(OH)_2^+$ on the acidity of the 6R fragment. However, this DE was nevertheless lower than that of bare H6R(1Al) cluster [14]. Hence, the selected model does not explain the role of the EFAL in the formation of super-acid sites after Y dealumination, which should lead to the higher DE of the new center. Additionally, the authors used the 6R fragment constructed of two 4R rings with a one common Si–O–Si side cut from the Y type including two Al sites in the next-neighbor position. Usually, such close Al sites lead to a lower acidity [15].

The limited set of two EFAL species (6-coordinated AlO_6 ones are not catalytically active [8]) allows a discussion of the EFAL system (4)–(6) in the light of three important experimental facts selected below in order to test possible reaction scheme of the EFAL hydrolysis:

(1) The total OH concentration during dealumination of HZSM-5 zeolite (Si/Al = 20) decreases at 673 K relative to that without EFAL at 473 K [12]. Time programmed desorption (TPD) data [1] do not show increase of the total integral signal of acidic OH sites in the figure of Ref. [1], i.e., the redistribution of two TPD signals (673 and 843 K) takes place. These works [1,12] do not confirm at least an increase of the concentration of acid sites in the course of the treatment.

(2) The second important observation is the relation between the number of framework (N_{Al}) and extraframework (N_{EFAL}) Al atoms [4,7]. The variation of the EFAL atoms does not influence on the zeolite cracking activity if the N_{Al} number is small [4]. The total loss of activity at small N_{Al} is not approved in all the studies and seems to depend on the treatment conditions.

(3) The last point that we would like to mention is the poisoning of the part of the most active sites upon sodium addition [5]. Upon sufficient concentration of Na the EFAL activities for *n*-hexane [5] cracking goes to zero. In the case of iso-octane cracking [16], it was also shown that the selectivity depends on the Na concentration. The detrimental action of K cation instead of Na one is more effective for *n*-butane cracking at the MeHMOR zeolite, Me = Na, K [17]. The authors [5] estimated the activation energy in the temperature interval from 590 to 670 K at zero (0% relative to N_{Al}) and large (17%) of Na^+ concentrations, i.e., 36 and 39 kcal/mol, respectively, for the same type of the zeolite treatment. However, the errors (4 and 2 kcal/mol, respectively) of the activation energy calculation within the short T-range were too large so that these results cannot confirm any trend, i.e., decrease or increase, in the activation energy of the *n*-hexane cracking with the Na content. Evidently, these phenomenological evaluations cannot show which reaction should be tested as a candidate depending on the Na^+ concentration.

The role of Na^+ on EFAL activity is rarely discussed in modern studies and is assigned to possible electrostatic effects but the exact model for such influence is absent in the literature. Our recent calculations [18,19] for water dissociation over multi-valent cations demonstrated that even for tri-valent La^{3+} cation coordinated in the MOR zeolite the electrostatic effects are not the unique factor which explains the exothermic character of the dissociation. We have also shown that additional restrictions for water dissociation over divalent AE cations should be imposed, i.e., two FAL atoms should be spatially enough separated to stabilize the products of the dissociation. Regarding the lower charges of 0, +1, and +2, of the EFAL moieties, all the guesses about the conditions of water dissociations over them seem to require verification.

The goal of this paper is to check if the reaction schemes (4)–(6) proposed earlier [10] can be used to explain the effect of alkali cations (only Na^+) on the reactions between the EFAL particles. We will discuss the properties of the EFAL systems regarding important role of Na^+ cation in the reactions (5) and (6).

2. Computational details

Previously, it was found [20] that $AlOH^{2+}$ species occupy in the steamed USY the same cationic sites as the AE cations, therefore for the current analysis we can use the approaches already tested for the AE form zeolites [18,19]. The same 8T ($MAl_2Si_6O_8H_{16}$ and $MAl_2Si_6O_9H_{14}$ or 6R + 4R and 8R [18,19], respectively, where $M = AlOH^{2+}$) clusters and HMOR model with periodic boundary conditions have been used for modeling of the AE forms. One Si atom have been replaced by Al one to treat the neutral $MAlSi_7O_8H_{16}$ and $MAlSi_7O_9H_{14}$ systems for 6R + 4R and 8R, respectively, where $M = Al(OH)_2^+$. Together with these 8T systems a larger 10T cluster ($MAl_2Si_8O_{31}H_{22}$, where $M = AlOH^{2+}$) cut from ZSM-5 type was studied with two closely positioned Al sites earlier adopted for the analyses of the Cu^{2+} reactivity [21]. For the analysis of EFAL poisoning with Na^+ charged systems ($q = -1, +1$) have been analyzed to keep the same content upon Na^+ addition. Hence, the barriers in the cluster systems with and without Na^+ have different total charges (−1 and 0 or 0 and 1). DFT with different functionals (B3LYP, M06L, B97D) and MP2 with 6-31G* basis set have been applied for the cluster approach using GAUSSIAN 09 [22], Perdew–Burke–Ernzerhof (PBE) functional within the projector augmented waves (PAW) method was utilized with periodic boundary conditions as realized with VASP 5.2 [23]. In order to consider neutral periodic cells with and without Na^+ additional replacement Si by Al + H was realized at the remote T site of HMOR zeolite. The proton was replaced by Na^+ when the influence of the latter on the reactions (5) and (6) was modeled. QST3 [22] and nudged elastic bands (NEB) [24] methods have been respectively adopted for a search of the transition state (TS). Natural bond orbital (NBO) analysis [25] together with Mulliken charges was used to elucidate the role of electrostatic factors for the steps (5) and (6).

3. Results

We would like to mention that the reactions (5) and (6) discussed below will be considered as reversible ones so that the selection of the reagents and products will be inverted in some cases relative to the schemes (5) and (6) above. The drastic difference between the bi-valent alkaline earth (AE) and mono-valent alkali cations was shown many years ago on the basis of infrared (IR) data [26]. The alkali cations cannot split water in zeolites [26], while the bi-valent AE cations provide the cleavage upon recently shown conditions [18,19]. The similar double difference of the $AlOH^{2+}$ and $Al(OH)_2^+$ charges leads to analogous proposition about the possible higher activity of $AlOH^{2+}$ compared to that of