Observation of Multinuclear Extra-framework Aluminum Species in Dealuminated Zeolite Catalysts

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Article

Keywords: extra-framework aluminum (EFAL), zeolitic catalysts, physicochemical properties

Posted Date: August 24th, 2020

DOI: <https://doi.org/10.21203/rs.3.rs-50498/v1>

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Abstract

Although the Lewis acidic extra-framework aluminum (EFAL) species usually play decisive roles in improving the thermal stabilities, acidity and catalytic performances of industrialized zeolitic catalysts, the structure of these important EFAL clusters has long been a subject of intense debate, and their characterization remains a challenging task. Particularly, the more stable and even more catalytic active multinuclear EFAL clusters have never been experimentally observed owing to the nearly indistinguishable physicochemical properties of mononuclear and multinuclear EFAL species detected by conventional techniques. Herein, by invoking advanced two-dimensional (2D) solid-state ^{31}P NMR spectroscopy in conjunction with a novel probe molecule, namely 1,2-bis(dimethylphosphine) ethane (DMPE), we demonstrated for the first time that the presence of multinuclear EFAL species in dealuminated zeolites. Furthermore, based on the comprehensive spatial interactions information from 2D ^{31}P - ^{31}P homonuclear correlation NMR experiments, the evolution and transformation mechanisms of various acidic sites during the dealumination treatment of zeolites have also been clarified.

1. Introduction

Heterogeneous zeolite catalysts have been extensively employed in chemical and petrochemical industries for various reaction processes such as cracking, alkylation, disproportionation, isomerization, *etc.*^[1–10] It is well-accepted that the Brønsted acid sites (BAS) originated from the framework bridging hydroxyl groups and Lewis acid sites (LAS) arising from extra-framework aluminum (EFAL) species are typical active sites, and thus are responsible for the catalytic performance (*e.g.*, activity, selectivity, and reaction mechanism) of zeolites.^[11–16] Therefore, understanding the detailed structures and properties of these active sites and their possible structural variations in zeolites is a critical step in developing fundamental insights into catalyst function and exploiting those insights for improved zeolite catalytic materials.^[15–19]

Post-synthetic dealumination treatment is a common tactic adopted to improve the thermal stabilities, acidity and catalytic performances of industrialized zeolitic catalysts through incorporating Lewis acidic EFAL species.^[20–30] However, the structure of these important EFAL clusters has long been a subject of intense debate. Thus far, various mononuclear Al-containing complexes, such as AlO^+ , $\text{Al}(\text{OH})_2^+$, $\text{Al}(\text{OH})_2^{2+}$, and Al^{3+} cations, as well as some neutral clusters including AlOOH and $\text{Al}(\text{OH})_3$ have been proposed as the possible intrazeolite EFAL species in dealuminated zeolites.^[24–29] For example, by using DFT theoretical calculations, Mota *et al.* investigated the structures and stability of all these mononuclear EFAL species, and proposed that the interaction of EFAL clusters with vicinal BAS would lead to enhanced acidity *via* hydrogen bonding.^[24, 25] Recently, the mononuclear Al^{3+} moieties in dealuminated Y zeolite has also been identified by a combination of solid-state NMR and DFT calculations.^[26] Note that aside from the mononuclear EFAL species, their multinuclear counterparts could also serve as LAS in dealuminated zeolites. Particularly, it has been demonstrated that the multinuclear oxygenated complexes are usually more stable and even more active for a variety of reactions than mononuclear

ones.^[31–34] However, although the presence of multinuclear EFAL clusters has been theoretically hypothesized,^[27,31] they have never been experimentally observed. Both the detailed structures of multinuclear EFAL species as well as their spatial interaction mechanisms in dealuminated zeolites are poorly understood. This strongly hampers the understanding of zeolite dealumination chemistry and catalytic reaction mechanism.

Solid-state nuclear magnetic resonance (SSNMR) spectroscopy has emerged as an important approach for the characterization of solid catalysts at the atomic scale.^[14,15,17,19,26,28–30,35–45] Particularly, the SSNMR spectroscopy in combination with probe molecule technique has been demonstrated to be one of the most practical and reliable methods for probing the local structure and acidity of various acid sites.^[15,17,26,28,37–45] However, conventional probe molecules such as NH₃, deuterated-acetonitrile, deuterated-pyridine, 2-¹³C-acetone, trimethylphosphine (TMP), and trialkylphosphine oxides usually contain only a sole basic group, thus merely capable of probing single active site. In order to further obtain the spatial proximity and interactions information between adjacent active sites, advanced two-dimensional (2D) SSNMR techniques^[46] were also invoked. For example, by utilizing ¹H double quantum (DQ) magic-angle spinning (MAS) NMR technique, the detailed structures of EFAL species in dealuminated HY zeolites and new insights on Brønsted/Lewis acid synergy have been fully disclosed.^[28] On the other hand, the interactions between the framework and EFAL species in dealuminated HY zeolites and relevant dealumination mechanism were revealed by ²⁷Al DQ-MAS NMR spectroscopy.^[29] Nonetheless, these approaches are incompetent in differentiating the mononuclear and multinuclear EFAL species in dealuminated zeolites.

In this work, we reported a novel technique for quantitative determination of spatial distances among various active sites, rendering a comprehensive insight on the characterization of multinuclear EFAL species, as well as the roles of their mutual interactions and relevant structure-activity correlation on catalytic performance and reaction pathway of heterogeneous acid-catalyzed systems. This was realized by invoking the adoption of a new ³¹P NMR probe molecule, namely 1,2-bis(dimethylphosphine) ethane (DMPE) having a fixed P-P interatomic distance of *ca.* 4.0 Å, as shown in Fig. 1a. It is noteworthy that the use of DMPE probe molecule features not only the analogous advantage of TMP which is sensitive to Lewis acidity,^[26,38,42] but also the merit of diphosphines that are feasible for distance measurement.^[39,40] Moreover, the smaller kinetic diameter (KD estimated to be *ca.* 5.5 Å^[47]) of DMPE is also favorable for its transport and coupling with various active sites in zeolite pore channels. Thus, the combined 2D ³¹P SSNMR and DMPE probe molecule method may be a desirable technique for characterizing multinuclear EFAL species, and for revealing detailed spatial interactions and evolution pathways of various acidic sites in zeolites during dealumination process.

2. Results And Discussion

2.1 Feasibility of DMPE for probing multinuclear EFAL species

It has been theoretically demonstrated that the self-organization of two mononuclear EFAL species into binuclear counterparts is a highly exothermic process, whereas the formation of trinuclear complex is also strongly exothermic inside the sodalite cage of Faujasite zeolite.^[27] Therefore, it is anticipated that these multinuclear EFAL species are readily formed inside the zeolite channels upon dealumination treatment. The multinuclear EFAL structures have similar Al – O distances at *ca.* 2.0 Å,^[27] thus a spatial distance between two adjacent Al atoms at *ca.* 3.0 ~ 4.0 Å may be inferred. Our DFT theoretical calculation results also confirmed that the nearest distance between two Al atoms respectively in two adjacent mononuclear EFAL species are larger than 5.0 Å, while that in aggregated multinuclear EFAL cluster are *ca.* 3.3 Å (Figure S1 of the Supplementary Information (SI)). On the other hand, as aforementioned, unlike conventional probe molecules that possess only a sole basic group, DMPE molecule ((CH₃)₂-P-(CH₂)₂-P-(CH₃)₂) contains two basic sites, corresponding to a P-P inter-atomic distance of *ca.* 4.0 Å, as illustrated in Fig. 1a. Considering the unique structure and adsorption configurations of DMPE probe molecules over dealuminated zeolites, as well as Al atoms in various EFAL species are usually responsible for their Lewis acidity, thus the similar spatial distances of Al-Al atoms in multinuclear EFAL species and P-P atoms in DMPE probe molecule lay a solid foundation for the investigation of multinuclear EFAL structures by the NMR approach.

Moreover, molecular dynamics (MD) simulations were also performed prior to the NMR experiments to evaluate the adsorption behavior of DMPE molecule inside Y zeolite. Radial distribution functions (RDF)^[48] were used to define the probability that two P atoms are separated by a distance *r* at various DMPE loadings. As shown in Figure S2, three peaks are observed, where regions I and I' with shorter distances (4.3 and 3.5 Å, respectively) are due to the adjacent two P atoms in the same DMPE molecule (intramolecular), while region II (*ca.* 6 Å) can be attributed to two P atoms that are relatively far apart from each other as they originated from two different DMPE molecules (intermolecular). This is also evidenced by increasing the DMPE loading from 1 to 2 molecules per Y zeolite supercell, leading to a notable increase in only the relative peak area of region II (intermolecular P-P atom pairs). As the atoms (*i.e.*, ³¹P-³¹P) within 5.0 Å are generally accepted to generate homo-nuclear correlation NMR signals, thus it can be concluded that the intramolecular P-P atom pairs govern the spatial interactions among the P atoms in the DMPE adsorption complexes, while that of intermolecular ones only play an negligible role, and may be excluded in the subsequent two-dimensional ³¹P-³¹P homo-nuclear correlation NMR experiments.

2.2 Structural and acidic properties of dealuminated zeolites

The structural properties of HY and HUSY zeolites before and after the dealumination treatment were first studied by X-ray diffraction (XRD) and ²⁹Si, ²⁷Al SSNMR experiments, as illustrated in Figure S3. In brief, the dealumination treatment could create abundant EFAL species, meanwhile, have negligible effect on

the structural integrity of HY and HUSY zeolites. The formation of EFAL species was further confirmed by the 1D ^1H and 2D ^{27}Al triple-quantum (3Q) MAS NMR experiments. As shown in Fig. 1b, a significant increase in the peak intensity of ^1H signals at 2.7 and 0.8 ppm due to EFAL species^[35, 41] was observed after the dealumination treatment. The ^{27}Al signal denoted as Al^{VI} in Fig. 2 also illustrated the presence of EFAL species. It has been widely accepted that the EFAL species in zeolite catalysts usually exert Lewis acidity.^[26, 28, 38] As such, these zeolite samples are beneficial for characterizing various EFAL species, and probing the interactions between BAS originated from the framework bridging hydroxyl groups and LAS arising from various mononuclear as well as multinuclear EFAL species.

After adsorption of DMPE probe, the parent HY exhibited two resonances with ^{31}P chemical shift ($\delta^{31}\text{P}$) of 2 and -47 ppm, as shown in Fig. 1c. Upon dealumination treatment at 450 °C, the spectrum of DMPE-loaded dealuminated HY-450 showed four main resonance peaks at 2, -25, -37, and -44 ppm. Similar behaviors were also observed for the parent HUSY and dealuminated HUSY-d450, as illustrated in Fig. 1c. On the basis of earlier reports on acidity characterization using the ^{31}P -TMP NMR approach,^[26, 38, 42] adsorption of TMP probe molecule on BAS in zeolites usually leads to the formation of protonated TMPH^+ complexes with $\delta^{31}\text{P}$ ranging from *ca.* -2 to -5 ppm. On the other hand, adsorption of TMP on LAS typically results in resonances with $\delta^{31}\text{P}$ in the range of *ca.* -20 to -60 ppm.^[26, 38, 42] Since DMPE and TMP possess rather similar physicochemical properties, it is anticipated that the $\delta^{31}\text{P}$ observed for these two probe molecules in analogous catalyst systems may be comparable. Thus, the ^{31}P resonance at *ca.* 2 ppm in Fig. 1 may be tentatively attributed to protonated DMPEH^+ ionic complexes associated with BAS. By the same token, the resonances with $\delta^{31}\text{P}$ ranging from -25 to -47 ppm are likely due to either DMPE bound to LAS with different acid strengths, or weakly acidic terminal hydroxyl groups (M-OH ; $\text{M} = \text{Si}$ or Al).

To afford a more reliable $\delta^{31}\text{P}$ assignments, additional ^{31}P CP/MAS NMR experiments were performed for weakly acidic SiO_2 and Lewis acidic Al_2O_3 samples. As depicted in Figure S4 (SI), the singlet at -47 ppm is clearly due to DMPE adsorbed on weakly acidic terminal Si-OH and Al-OH groups. Whereas the additional resonance at -42 ppm in Figure S4b arose from adsorption of DMPE on the LAS of Al_2O_3 catalyst. As such, the resonances at -25, -37, and -44 ppm in Fig. 1c may be ascribed due to DMPE bound to LAS with different acidic strengths. These assignments were further verified by $^{31}\text{P}\{^{27}\text{Al}\}$ CP rotational-echo adiabatic-passage double-resonance (REAPDOR) NMR experiments.^[49, 50] In the presence of ^{27}Al irradiation (see Fig. 1d,e), the ^{31}P resonances of the adsorbed DMPE that are in close proximity to ^{27}Al atoms should suffer a stronger dipolar dephasing associated with ^{31}P - ^{27}Al dipolar interaction, resulting in an overall reduction in the ^{31}P resonance signals. As shown in Fig. 1d,e, all resonance peaks were subjected to a strong dipolar dephasing during ^{31}P - ^{27}Al dipolar recouplings except for the resonance at -47 ppm. In other words, with the exception of weakly acidic Si-OH groups, resonance signals responsible for the peak occurred at 2, -25, -37, and -44 ppm correspond to ^{31}P atoms (on the DMPE probe molecule) that were in close proximity to the ^{27}Al species in dealuminated zeolites, which is in line with the peak assignments above.

2D ^1H - ^{31}P heteronuclear correlation (HETCOR) NMR spectroscopy (Figure S5a; SI)^[46] is also useful for assigning the ^{31}P signals of DMPE adsorbed on Brønsted and Lewis acid sites in solid acid catalysts. As shown in Fig. 3a, the HETCOR spectra of DMPE adsorbed on dealuminated HUSY-d450 zeolite recorded with a short contact time ($\tau_c = 0.1$ ms) showed an intense correlation peak at (2, 7.5) ppm. This correlation peak corresponding to ^{31}P resonance (F2 dimension; $\delta^{31}\text{P} = 2$ ppm) and ^1H resonance (F1 dimension; $\delta^1\text{H} = 7.5$ ppm) may be ascribed due to DMPE adsorbed on bridge hydroxyls (Si-OH-Al, *i.e.*, BAS) forming protonated DMPEH⁺ adsorption complexes. Upon increasing contact time to 4.0 ms, extra correlation peaks emerged in addition to the peak at (2, 7.5) ppm, as shown in Fig. 3b. The newly emerged correlation peaks at (2, 2.0), (-25, 2.0), and (-37 ~ -44, 1.8) ppm correspond to couplings of methyl protons ($\delta^1\text{H} = 1.8 \sim 2.0$ ppm) on the DMPE probe molecule with Brønsted ($\delta^{31}\text{P} = 2$ ppm) and Lewis ($\delta^{31}\text{P} = -25$, and $-37 \sim -44$ ppm) acid sites. Moreover, the appearance of correlation peaks at (-37 ~ -44, 7.5) ppm at longer contact time ($\tau_c = 4$ ms; Fig. 3b) indicates that LAS with varied strengths ($\delta^{31}\text{P} = -37 \sim -44$ ppm) are in close proximity to Brønsted acid protons ($\delta^1\text{H} = 7.5$ ppm). However, spatial correlation between Brønsted acid sites ($\delta^1\text{H} = 7.5$ ppm) and strong Lewis acid sites ($\delta^{31}\text{P} = -25$ ppm) was absent. Similar conclusions could also be drawn from the other Y zeolite catalysts, as shown in Figure S6 – S8.

2.3 Identification of multinuclear EFAL species

The spatial interactions between P atoms in various adsorption configurations of DMPE over dealuminated HY and HUSY zeolites were further studied by 2D ^{31}P - ^{31}P proton driven spin diffusion (PDSD)^[51] MAS NMR experiments (Figure S5b; SI). As shown in Fig. 4a, in addition to the two autocorrelation peaks (*i.e.*, peaks along the diagonal axis; F2 = F1) at (2, 2) and (-47, -47) ppm, a set of off-diagonal correlation peak pairs at (2, -47) and (-47, 2) ppm were also observed for DMPE adsorbed on the parent HY zeolite. These results indicated that Brønsted acid sites and weakly acidic Si - OH groups are in close spatial proximity with each other. Upon dealumination treatment, new correlation peak pairs at (2, -44) and (-44, 2) ppm were observed for DMPE adsorbed on dealuminated HY-d450 (Fig. 4b). Thus, the formation of weaker Lewis acid sites ($\delta^{31}\text{P} = -44$ ppm) as well as their spatial interactions with Brønsted acid sites ($\delta^{31}\text{P} = 2$ ppm) may be inferred for dealuminated HY-d450 zeolite. Similar conclusions may also be drawn for the parent HUSY zeolite (Fig. 4c) and dealuminated HUSY-d450 (Fig. 4d). For the latter, up to four autocorrelation peaks at (2, 2), (-25, -25), (-37, -37), and (-44, -44) ppm were identified as well as three off-diagonal correlation peak pairs at (2, -37) and (-37, 2), (2, -44) and (-44, 2), and (-37, -44) and (-44, -37) ppm. By comparison, the formation of stronger Lewis acid sites ($\delta^{31}\text{P} = -37$ and -25 ppm) may be inferred for the dealuminated HUSY-d450 compared to that of the dealuminated HY-d450 ($\delta^{31}\text{P} = -44$ and -37 ppm). Moreover, results obtained from ^{31}P - ^{31}P PDSD MAS NMR correlation spectra also revealed that the strong Lewis acid site at -25 ppm is relatively isolated compared to the other active centers, in close agreement with the results obtained from ^1H - ^{31}P HETCOR NMR (Fig. 3) and previous work using TMP as the NMR probe.^[26] Again, the strong Lewis acid

site observed at $\delta^{31}\text{P} = -25$ ppm may be attributed to tri-coordinated EFAL- Al^{3+} species formed due to excessive dealumination treatment.

As aforementioned in Part 2.1, the self-organization of two mononuclear EFAL species into binuclear counterparts is a highly exothermic process, whereas the formation of trinuclear complex is also strongly exothermic inside the sodalite cage of Y zeolite.^[27] Therefore, it is conclusive that these multinuclear EFAL species are readily formed inside the zeolite channels during post-synthetic dealumination treatment. Herein, the combination of ingenious DMPE probe molecule and advanced 2D NMR techniques opens up new possibilities for probing multinuclear EFAL species in dealuminated zeolites. As illustrated in Fig. 4, for both the DMPE-loaded dealuminated HY-d450 and HUSY-d450 zeolites, the 2D ^{31}P - ^{31}P PDSO NMR spectra clearly revealed the spatial correlations between Lewis acid sites with different acid strengths (-37 and -44 ppm). Therefore, our NMR results reported herein, for the first time, provide experimental evidence for the presence of multinuclear EFAL species in dealuminated zeolites.

It is noteworthy that ^{31}P - ^{31}P PDSO MAS NMR of the adsorbed DMPE is capable of providing only correlation information of ^{31}P atoms at different chemical environments (*i.e.*, different $\delta^{31}\text{P}$). In other words, it is incapable of identifying proximity of ^{31}P atoms that have the same chemical environment (*i.e.*, same $\delta^{31}\text{P}$). In this context, 2D ^{31}P DQ MAS NMR (Figure S5c; SI)^[39] is a viable approach for probing interactions among various adsorption DMPE structures in dealuminated zeolites. Although nearly null ^{31}P DQ signal was observed for DMPE-adsorbed HUSY and HUSY-d450 samples, results obtained from dealuminated HY-d450 (Figure S9; SI) revealed that Brønsted ($\delta^{31}\text{P} = 2$ ppm) and weak Lewis acid sites ($\delta^{31}\text{P} = -44$ ppm) are respectively in close proximity and are spatially correlated. Thus, by invoking the advanced NMR technique together with ingenious DMPE probe, spatial correlations between various active sites (B/B, L/L, B/L) in dealuminated zeolites, as well as relevant transformation from B/B acid pairs into B/L and L/L acid pairs during dealumination treatment of zeolites may readily be obtained. Particularly, the observed spatial interaction among various Lewis acid sites (-37 ppm vs. -44 ppm; -44 ppm vs. -44 ppm) provide an experimental clue that the occurrence of condensation between various EFAL species (*i.e.*, the formation of multinuclear EFAL species) during post-synthetic dealumination treatment. Such atomic-scale proximities and interactions among various acidic sites (Brønsted acidic protons & Lewis acidic mononuclear and multinuclear EFAL species) provide strong support toward the rate enhancements observed for dealuminated zeolites, which feature vicinal Brønsted and Lewis acidic entities in numerous reports.^[4,13,20–23,52–56]

2.4 Evolution mechanisms of various acid sites during dealumination process

The experimental NMR results reported herein also provide direct evidence for the migration and evolution mechanisms of various Al species in dealuminated Y zeolites. As illustrated in Fig. 5a, at the initial stage of dealumination (HY-d450), due to the breaking of framework Si-O-Al bridges and successive hydrolysis of the three-coordinated framework Al species, mononuclear extra-framework $\text{Al}(\text{OH})_3$ species (*i.e.*, Lewis

acidity with $\delta^{31}\text{P} = -44$ ppm) tend to form firstly. This notion is in support by the observed correlation peak pairs at (2, -44) and (-44, 2) ppm in Fig. 4b. Upon further increasing the severity of dealumination treatment, the mononuclear $\text{Al}(\text{OH})_3$ species may readily migrate toward the vicinity of Brønsted acid sites, followed by gradual removal of water molecules to generate Lewis acid sites with modest strengths (*e.g.*, $\text{Al}(\text{OH})_2^+$ and AlOH^{2+} species; $\delta^{31}\text{P} = -37$ ppm). Likewise, further elimination of water molecule between Brønsted acidic site and AlOH^{2+} species would result in the formation of mononuclear tri-coordinated EFAL- Al^{3+} species with strong Lewis acidity ($\delta^{31}\text{P} = -25$ ppm). It is noteworthy that the formation of tri-coordinated EFAL- Al^{3+} Lewis acid sites occurred at the expense of three adjacent Brønsted acid sites. As a result, no spatial interaction between the EFAL- Al^{3+} and Brønsted acid sites ($\delta^{31}\text{P} = 2$ ppm) was observed. Furthermore, the self-organization of mononuclear EFAL species into multinuclear EFAL counterparts may also simultaneously proceed (Fig. 5b), as evidenced by the appearance of correlation peaks among various Lewis acid sites (-37 ppm *vs.* -44 ppm; -44 ppm *vs.* -44 ppm) in Fig. 4 and Figure S9. Therefore, it is conclusive that both the mononuclear and multinuclear EFAL species are formed during the dealumination treatment of zeolites. All the structural geometries of various acid sites (including Brønsted acidic bridging hydroxyl groups and Lewis acidic mononuclear as well as multinuclear EFAL species) were further confirmed by DFT theoretical calculations (shown in Figure S1 and S10).

3. Conclusions

In summary, the spatial interactions and evolution mechanism of various active sites in dealuminated HY and HUSY zeolites have been comprehensively investigated by advanced ^{31}P SSNMR experiments using 1,2-bis(dimethylphosphine) ethane as the probe molecule. Considering the unique structure of DMPE molecule, it is experimentally demonstrated for the first time that the presence of multinuclear EFAL species in dealuminated zeolites. Such a combined NMR probe molecule technique may open up a new avenue for exploring the spatial interactions among various acid sites and revealing the fine structure of undiscovered active centers in heterogeneous catalysts such as zeolites, metal oxides, functionalized silica/carbon materials, and heteropolyacids. Further work on the fine structure and their synergistic catalytic effects of multinuclear EFAL species are currently underway.

Declarations

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Acknowledgments

This work was supported by the National Natural Science Foundation of China (No. 91645112, 21802164, 21902180, 21991092, and U1832148), and Natural Science Foundation of Hubei Province of China (No. 2018CFA009), Key Research Program of Frontier Sciences, CAS (No. QYZDB-SSW-SLH026). The authors are grateful to SINOPEC Shanghai Research Institute of Petrochemical Technology (No. 417012-4) for their support in computing facilities.

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Figures

Figure 1

(a) Illustrations of three possible chemisorbed adsorption configurations of DMPE probe molecules over dealuminated zeolites: (i) on two adjacent Brønsted acid sites, (ii) on adjacent Brønsted and Lewis acid centers, and (iii) on two adjacent Lewis acid sites (e.g., multinuclear EFAL structures), respectively. (b) ^1H MAS NMR spectra of HY and HUSY zeolites before and after the dealumination treatment. (c) ^{31}P CP/MAS NMR spectra of DMPE adsorbed on the parent HY, dealuminated HY-d450, parent HUSY, and

dealuminated HUSY-d450 zeolites, respectively. $^{31}\text{P}\{^{27}\text{Al}\}$ CP/REAPDOR NMR spectra of DMPE adsorbed on (d) the parent HY, and (e) the dealuminated HUSY-d450 zeolites. The red and green lines represent the spectra observed with (S) and without (S0) $^{31}\text{P}\{^{27}\text{Al}\}$ CP/REAPDOR dipolar dephasing, respectively, whereas $\Delta S = S0 - S$ represents their difference spectrum.

Figure 2

Sheared 2D ^{27}Al 3Q MAS NMR spectra of (a) parent HY, (b) dealuminated HY-d450, (c) parent HUSY, and (d) dealuminated HUSY-d450 zeolites.

Figure 3

2D ^1H - ^{31}P HETCOR NMR spectra of DMPE adsorbed on dealuminated HUSY-d450 zeolite recorded with a contact time of (a) 0.1 ms, and (b) 4.0 ms. The appearances of the correlation peaks at $(-37 \sim -44, 7.5)$ ppm only at longer contact time indicate that the Lewis acid sites associated with signals at $-37 \sim -44$ ppm are in close proximity to the Brønsted acid protons bound to the DMPE probe molecule.

Figure 4

2D ^{31}P - ^{31}P PDSD MAS NMR spectra of DMPE adsorbed on the (a) parent HY, (b) dealuminated HY-d450, (c) parent HUSY, and (d) dealuminated HUSY-d450 zeolites. All correlation spectra were recorded with a mixing time of 100 ms. The rows extracted at -47 ppm for DMPE-loaded parent HY, and -37 ppm for DMPE-loaded dealuminated HY-d450, parent HUSY, and dealuminated HUSY-d450 zeolites from the respective 2D plot are also shown on the right, indicating the spatial correlations between Lewis acid sites with different acid strengths (-37 and -44 ppm), i.e., the presence of multinuclear EFAL species in dealuminated zeolites.

Figure 5

Proposed migration and evolution mechanism of (a) mononuclear and (b) multinuclear EFAL species inside Y zeolites upon dealumination treatment.

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