



Dealumination of Zeolite Frameworks and Lewis Acid Catalyst Activation for Transfer Hydrogenation

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Abstract

This study examines a selective removal of Al metal from Al-Beta (BEA), Al-Faujasite (FAU, type Y) and Al-Mordenite (MOR) whose frameworks have high and close Si/Al ratios ≥ 30 . Dealumination was performed using acid leaching (nitric acid, 13 M) solution at 100 °C for 20 h. Unlike Al-BEA, Al-FAU and Al-MOR were hardly dealuminated for their ultra-stable structure. Solid-state incorporation (SSI) method was applied to incorporate Lewis acidic Sn metal in dealuminated zeolitic frameworks. Newly formed zeolites have numerous vacant tetrahedral sites with a siliceous-rich framework. These zeolites were characterized by powder XRD, elemental analysis, N₂ sorption, DRIFT and ²⁷Al MAS NMR spectroscopies. Meerwein–Ponndorf–Verley (MPV) was selected as a reaction to assess the catalytic performance of prepared zeolites. While SSI-Sn-BEA exhibited superior catalytic activity for the presence of Lewis acid-Sn, FAU and MOR showed less catalytic activity due to their confined structural effects, presence of silanol nest and inadequate Sn incorporation.

Keywords Dealumination · Solid-state stannation · BEA · Zeolite · Faujasite · Mordenite

1 Introduction

Zeolites are aluminosilicates minerals that have a microporous crystalline structure with a large cavity built in their structure. They are efficiently used as catalysts in various chemical reactions such as petroleum catalytic cracking, oligomerization and fine chemistry for their unique activity and shape-selectivity [1]. The zeolites' activity is generally determined by Brønsted acid sites and the metal-phase actively deposit onto the zeolite structure [2]. The zeolites' selectivity is provided by their micropores (sizes are ranging from 3 to 12 Å), shapes relative to the channels and cages of the zeolite [3]. The catalytic and acidic properties of any zeolite are considerably affected by their Al content and Si/Al ratio; hence, controlling the aluminosilicate framework is remarkably important. It can be done by either dealumination (aluminous) or desilication (siliceous) to improve the active sites inside the zeolite frameworks

and tune the acidity siliceous or aluminous members of the substitutional series [4, 5]. In the case of obtaining a siliceous member, Brønsted acid Al metal was dealuminated by using silicon-containing species like (NH₄)₂SiF₆ in liquid phase and SiCl₄ in a solution from the zeolite framework [6]. Volatile non-siliceous compounds, such as COCl₂, CCl₄ and SO₂Cl₂, were applied to extract Al metal from zeolites [7]. By using acid and contacting with SnCl₄·5H₂O in dry isopropanol, Lewis acid Sn-BEA zeolites with a partial dealuminated BEA were synthesized [8]. However, these methods were not well satisfactory due to the generation of imperfect zeolite structures and possibly producing inadequate defect sites 'hydroxy nest' and consequently creating secondary mesoporous materials [9]. In the time, a selective removal of Al by acid leaching or dealumination of Al by nitric acid was diagnosed as a successful method for producing a siliceous-rich framework with vacant tetrahedral sites. Hence, Hammond's team has successfully used the silanol nests to incorporate the Sn metal in a free-Al-BEA zeolite framework by a solid-state incorporation (SSI) [10, 11]. The importance of the Sn-BEA heterogeneous catalysts is that they are used for activating a carbonyl group in a number of liquid phase reactions [12–14]. Based on DFT calculations, the possibility of dealumination for seven Brønsted acid sites in four MFI, FAU, CHA and MOR zeolites of lower Si/Al

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ratios (Extra-framework Al sites, EFAs) was theoretically estimated by Silaghi et al. [15]. The formation mechanisms of $\text{Al}(\text{OH})_3\text{H}_2\text{O}$ species and free energy were possible with increasing Al–O bonds.

The accessibility of Al atoms in the zeolite framework is limited by their pores' sizes and arrangements. For example, the BEA structure is constituted of a 3-dimensional 12-ring pores system and hence its framework has more malleable structure than the MOR structure that is built of a 1-dimensional 12-ring pore system with a limited malleability. The dealumination process is likely influenced by a number of the T-atoms in 4 rings where the smaller rings adhere into larger tension. Consequently, the dealumination of the BEA zeolite becomes easier, where three quarters of the structure in BEA consist of 4 rings. On the other hand, the 4-rings T-atoms construct only 25% of MOR structure [16]. The dealumination process via the SSI method was not experimentally attempted with several zeolitic frameworks having high molar Si/Al ratios such as mesoporous crystalline Al-Faujasite (Al-FAU), Al-Mordenite (Al-MOR) and Al-BEA. In this study, a selective removal of Al (dealumination) from these three zeolitic frameworks was performed by acid leaching (nitric acid) and the SSI method was utilized to obtain Lewis acid siliceous-rich structure. The possibility of dealuminating extra-framework silicon (EFSi) species (Si/Al ratios ≥ 30) Al-FAU and Al-MOR and forming hydroxyl nests by the SSI method in comparison with the Al-BEA was figured out. The catalytic activity of the newly zeolitic structures based on transferring hydrogenation in conversion of cyclohexanone to cyclohexanol through the Meerwein–Ponndorf–Verley (MPV) reaction was quantified.

2 Experimental Part

2.1 Catalyst Preparation

Three extra-framework Si species zeolites, namely Al-BEA (NH_4 -form, $\text{SiO}_2/\text{Al}_2\text{O}_3 = 38$), Al-MOR (a NH_4 -form, $\text{SiO}_2/\text{Al}_2\text{O}_3 = 45$) and Al-FAU (H-form, $\text{SiO}_2/\text{Al}_2\text{O}_3 = 30$), were

obtained from Zeolyst company. The NH_4 -BEA and the NH_4 -MOR were transferred to the protonic framework (H-form) via calcination in air at 550 °C for 5 h.

2.2 Dealumination Process

The dealumination process was achieved by treating the H-Al-(BEA, FAU, MOR) zeolites with 13 M HNO_3 (20 mL/g zeolite) at 100 °C for 20 h. The resulted zeolites were thoroughly washed with deionized water (500 mL/g zeolite) and dried at 100 °C overnight. The dealumination process of Al-BEA zeolite and the remetallation (incorporation) of De-Al-BEA with Sn(II)acetate to create the Lewis Sn-BEA site zeolite are schematically shown in Fig. 1.

2.3 The SSI Method

The SSI method was applied to incorporate Lewis acid Sn metal in the dealuminated zeolites. The method was described in detail in a previous published study [10] and is schematically shown in Fig. 1. It involves grinding the designated zeolites with an appropriate amount of tin(II)acetate in a pestle and mortar for about 10 min as shown in Fig. 2. Thereafter, the ground was heated in a combustion furnace at 550 °C (10 °C/min) under N_2 flow of 3 h and subsequently heated in air for 3 h for an ultimate dwell time of 6 h. The gas flow rates of 60 mL/min were used at all time.

2.4 Catalyst Characterization

The XRD analysis of all zeolite frameworks was performed by using a Siemens D-5000, with a Cu- α radiation (30 mA and 40 kV). Diffraction patterns (2θ) in the range of 5°–55°, step size 0.0167° and time to step of 150 s at 1 h were considered. The N_2 adsorption/desorption measurements were conducted to determine the effect of dealumination on the textural properties of Al-BEA, Al-FAU and Al-MOR. The adsorption/desorption isotherms were recorded at 77 K to determine the micro and/or mesoporosity changes. The structural distribution and the chemical elemental

Fig. 1 Postsynthetic dealumination technique for silanol nest formation in BEA zeolite framework by HNO_3 as dealumination agent and creation of stannosilicate by the SSI

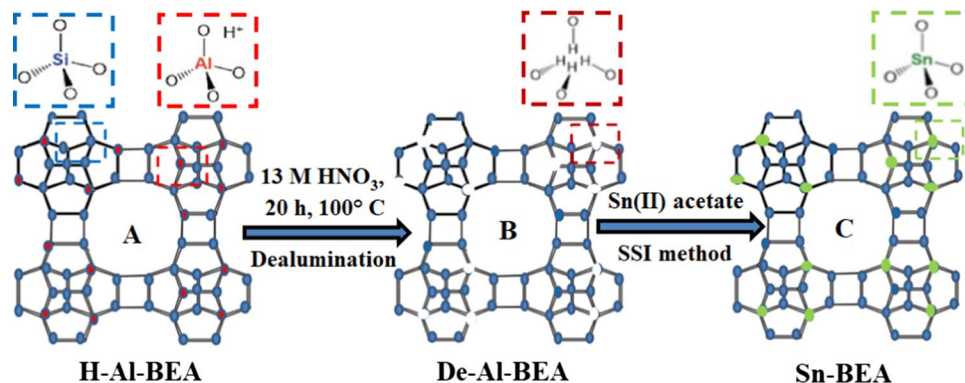
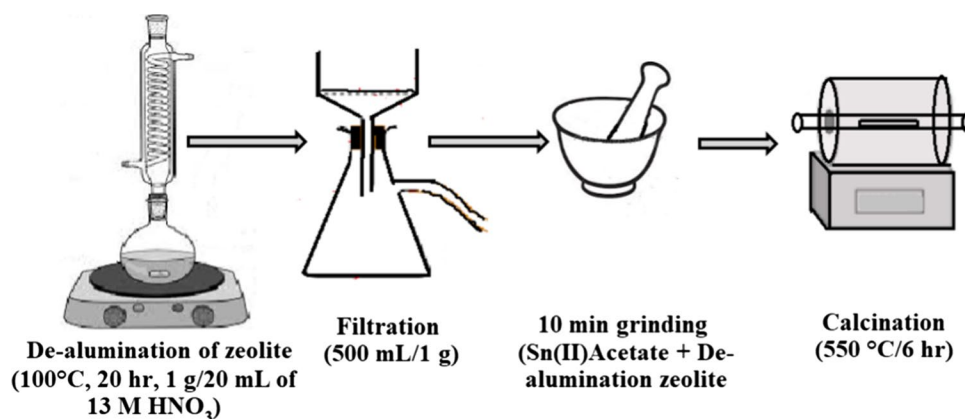


Fig. 2 A schematic showing the dealumination and Sn-incorporation process by the SSI method



composition of the zeolites were conducted by using SEM-JSM-6010 LV and ICP-AES analysis, respectively. Diffuse reflectance infrared Fourier-transform (DRIFT) spectra were performed and recorded on a Perkin-Elmer spectrometer in the range of 4000–650 cm⁻¹ at a resolution of 2 cm⁻¹. The CD₃CN measurements were recorded after pre-treating of zeolite powders at 550 °C for 1 h under 60 mL/min air flow. The samples were dosed by the CD₃CN vapor at 25 °C for 5 min and one spectrum was registered. Then, the sample chamber was evacuated in dynamic vacuum (around 10⁻⁴ torr), and spectra were registered at various temperatures of 25, 50, 100, 150, 200 and 250 °C. All spectra were background subtracted toward the pre-treated zeolite. The ²⁷Al MAS NMR spectrometer was measured for all samples at 104.2 MHz on a Varian VXR-400S spectrometer.

2.5 Catalytic Activity

The effect of dealumination process and SSI method for three stannosilicates zeolitic frameworks on their physicochemical characteristic and catalytic performance in hydrogenation conversion of cyclohexanone compound to cyclohexanol by using Meerwein–Ponndorf–Verley (MPV) reaction was evaluated. The MPV transfer hydrogenation was chosen for two reasons which are: (i) The reduction of aldehydes and ketones by the MPV is resulted in widely selective reactions since it can be carried out under mild conditions [11], and (ii) the MPV transfer hydrogenation of carbonyl compounds such as cyclohexanone (CyO) is a crucial reaction that can be efficiently catalyzed by the Sn-BEA zeolites or other Lewis acid analogues to determine the performance of the synthesized catalysts. To complete the MPV reaction, a 100-mL round-bottom flask provided with a reflux condenser and thermostatically controlled by immersing it in a silicon oil bath, was filled by a 10 mL of 0.2 M cyclohexanone solution dispersed in 2-butanol and 0.01 M biphenyl solvent. The solution was then heated up to 100 °C and continuously stirred at 800 rpm by a magnetic

bar with a catalyst amount equivalent to 1 mol % Sn relative to cyclohexanone.

3 Results and Discussion

3.1 Structural Analysis

Figure 3 depicts the XRD patterns of the untreated and acid-treated Al-BEA, Al-FAU and Al-MOR zeolites. It shows that the crystalline structure of the zeolites kept almost without a change after the acid treating. This means that the long-range crystal ordering of materials kept their own structures after the nitric acid treatment. In the meantime, the role of acid treatment in the removal of Al from the BEA zeolite structure was more efficient than that from the other zeolitic structures as clearly shown within the elemental quantification in Table 1. This is obviously attributed to the molecular arrangements of the BEA structure compared to

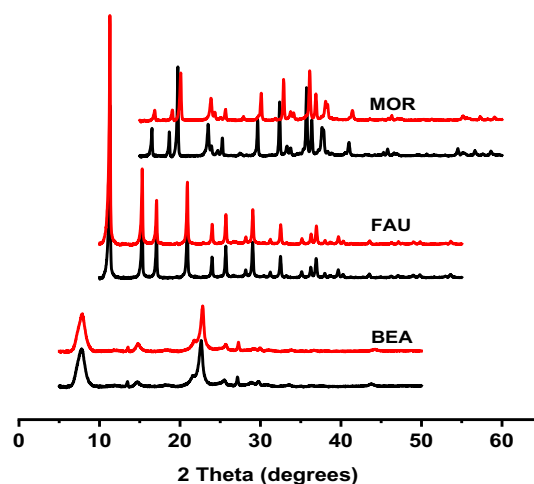


Fig. 3 The XRD powder patterns of the untreated (black line) and the acid treated (red line) zeolites



Table 1 Physicochemical characteristics of the untreated and the acid-treated Al-BEA, Al-FAU and Al-MOR zeolites

Zeolites frameworks	Channel dimensions (nm)	Molar ^c Si/Al ratio	S _{BET} ^d (m ² /g)	S _{meso} (m ² /g)	S _{micro} (m ² /g)	V _{micro} (cm ³ /g)	V _{total} (cm ³ /g)
Al-BEA ^a	0.66×0.67	19.54	550.88	197.63	373.04	0.193	0.448
Al-BEA ^b	0.56×0.56	1800.72	596.26	176.60	419.65	0.217	0.424
Al-FAU ^a	0.74×0.74	20.78	609.85	179.12	428.72	0.218	0.511
Al-FAU ^b	–	36.64	613.11	183.91	423.19	0.194	0.571
Al-MOR ^a	0.65×0.7	9.42	568.23	185.21	379.85	0.201	0.414
Al-MOR ^b	0.26×0.57	189.72	573.01	190.18	384.29	0.198	0.457

^aUntreated zeolites^bAcid-treated dealuminated zeolites^cICP-OES analysis^dBET surface area (S_{BET}) measured by the Brunauer–Emmett–Teller

ultra-thermodynamic stability formed in the structures for the other zeolites cavities.

From Table 1, it can be observed that the effect of nitric acid treatment (dealumination) on changing the BEA structure causes a large increase in its surface area, from 550.88 to 596.26 m²/g (8.23% increase), and creates a larger microporous and higher pore volume, from 0.193 to 0.217 cm³/g (12.3% increase). The increase indicates that after the successful removal of Al atoms from the BEA zeolite, the Al (OH)₃H₂O left the structure and created a vacancy with a tetrahedral BEA framework (larger hole) consisting of a silanol nest (or four Si–OH groups) surrounding it (see Fig. 1B). On the other hand, the effect of the acid treatment (dealumination) on the Al-FAU and Al-MOR zeolites resulted in marginal changes in their surface areas with lower micropores and minor pore volumes. Again, the dealumination's possibility of any zeolitic frameworks is dependent on the interaction of Brønsted acid sites (number of acid sites) with the oxygen atoms in the framework. For instance, the BEA framework has one Brønsted acid site and aluminum atom is located in its wall, while Al-FAU and Al-MOR structures are more stable for their two Brønsted acid sites (or two protons). These two Brønsted acid sites are shared between them by a strong hydrogen bond [17].

The SEM micrographs and the EDS element maps of the untreated and dealuminated (acid treated) BEA, FAU and MOR zeolites are shown in Figs. 4A^a–C^a and 4A^b–4C^b, respectively. The EDS element maps for the BEA zeolite are indicated as darker images in the upper right corners of the SEM images (Figs. 4A^a, A^b), revealing that the Al atoms (white spots) have entirely left the BEA framework. The molar Si/Al (or SiO₂/Al₂O₃) ratio described in Table 1 supports this evidence where the ratio excessively raised up from 19.54 to 1800.72. The EDS element maps of the FAU and the MOR zeolites before (Figs. 4B^a, C^a) and after dealumination (Figs. 4B^b, C^b), respectively, showed no obvious

change in the zeolite frameworks or the octahedral structure. The SEM images depicted the uniform distribution of all zeolitic samples, and the dealumination protocol did not have noticeable change in the zeolite crystalline structures. This means no significant alterations in their particle sizes and crystal morphology occurred. Also, there were no signs of amorphous structure or phase species formed in all frameworks after the dealumination as per the XRD patterns (Fig. 3).

3.2 DRIFT Analysis: Lewis Acid Site

The DRIFT spectroscopy was utilized with CD₃CN (D3-acetonitrile) to confirm the presence of Lewis acidic framework Sn^{IV} in all zeolites under study. The CD₃CN is highly useful probe molecule for Lewis acidic zeolites due to its interaction with the framework heteroatoms, resulted in an acid–base adduct which shows an intense absorbance at 2311 cm⁻¹. This feature is not particularly noticed for the extra-framework Sn species nor the SnO₂, and its occurrence can thus confirm the existence of the Sn^{IV} framework atoms [12, 18, 19]. In Fig. 5a, two intense features (peaks) are observed in the DRIFTS spectrum after dosing the materials with the CD₃CN solvent. The first peak 2275 cm⁻¹ resulted from the physisorbed CD₃CN, which is freely desorbed from the zeolites after heat treatment where the temperatures were ranged from 50 to 250 °C. The other peak (feature) of 2311 cm⁻¹ indicates the existence of the Sn^{IV} framework atoms after interacting with the CD₃CN molecules. This in turn indicates the existence of framework atoms isomorphously replaced the Sn atoms in the Al-free BEA structure. This specific DRIFT peak was not shown for the dealuminated FAU and MOR zeolites (see Fig. 5b, c). Subsequently, it can be concluded that the Lewis acid Sn^{IV} sites are not part of these materials.

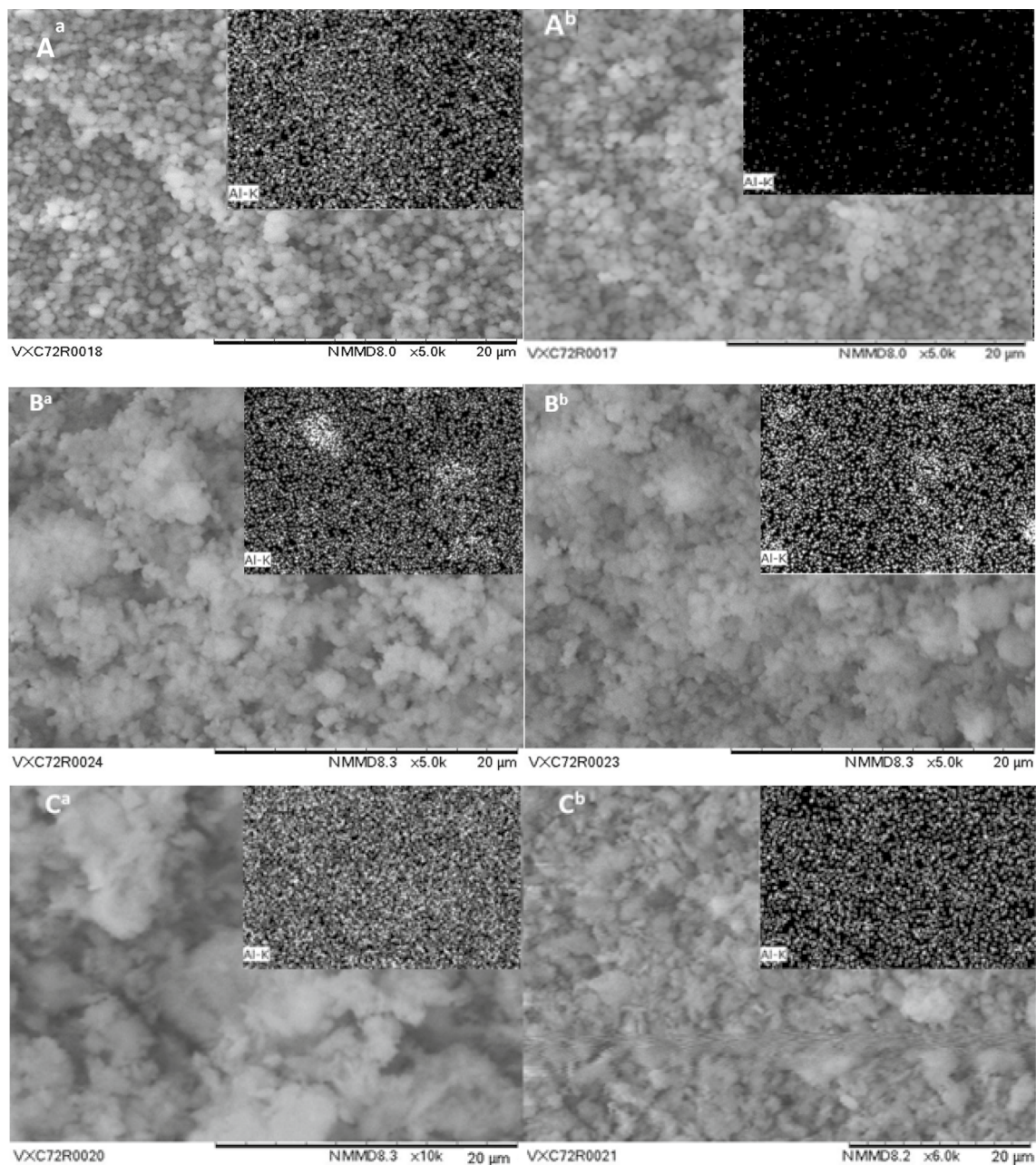


Fig. 4 SEM micrographs and EDS element maps, light spots in the EDS maps correspond to the distribution of Al in the untreated (A^a) and the acid-treated (A^b); **A** BEA, **B** FAU and **C** MOR zeolites

The ^{27}Al MAS NMR spectroscopy is an efficient investigation for determining the coordination and local structure of particular aluminum species in zeolite materials. Tetrahedral and octahedral Al species can be distinguished easily based on their different chemical shifts [20]. For example, tetrahedral coordination framework aluminum (FAI) atoms show a signal around 55 ppm, whereas octahedral coordination extraframework aluminum (EFAI) atoms typically provide a signal at about 0 ppm. The ^{27}Al MAS NMR spectra are depicted in Fig. 6 from which a signal with a chemical

shift around 55 ppm can be observed for the tetrahedrally coordinated Al atoms. Other bands around 0 ppm represent the octahedral extra-framework Al species. The decrease in tetrahedrally coordinated aluminum signal intensity (signal at 55 ppm) for BEA acid treatment and the increase in octahedral coordinated aluminum signal intensity (signal at 0 ppm) compared to Al-BEA untreated confirm the removal of Al from parent BEA after nitric acid treatment. ^{27}Al MAS NMR spectra for the parent FAU and MOR materials and samples dealuminated with nitric acid are shown in

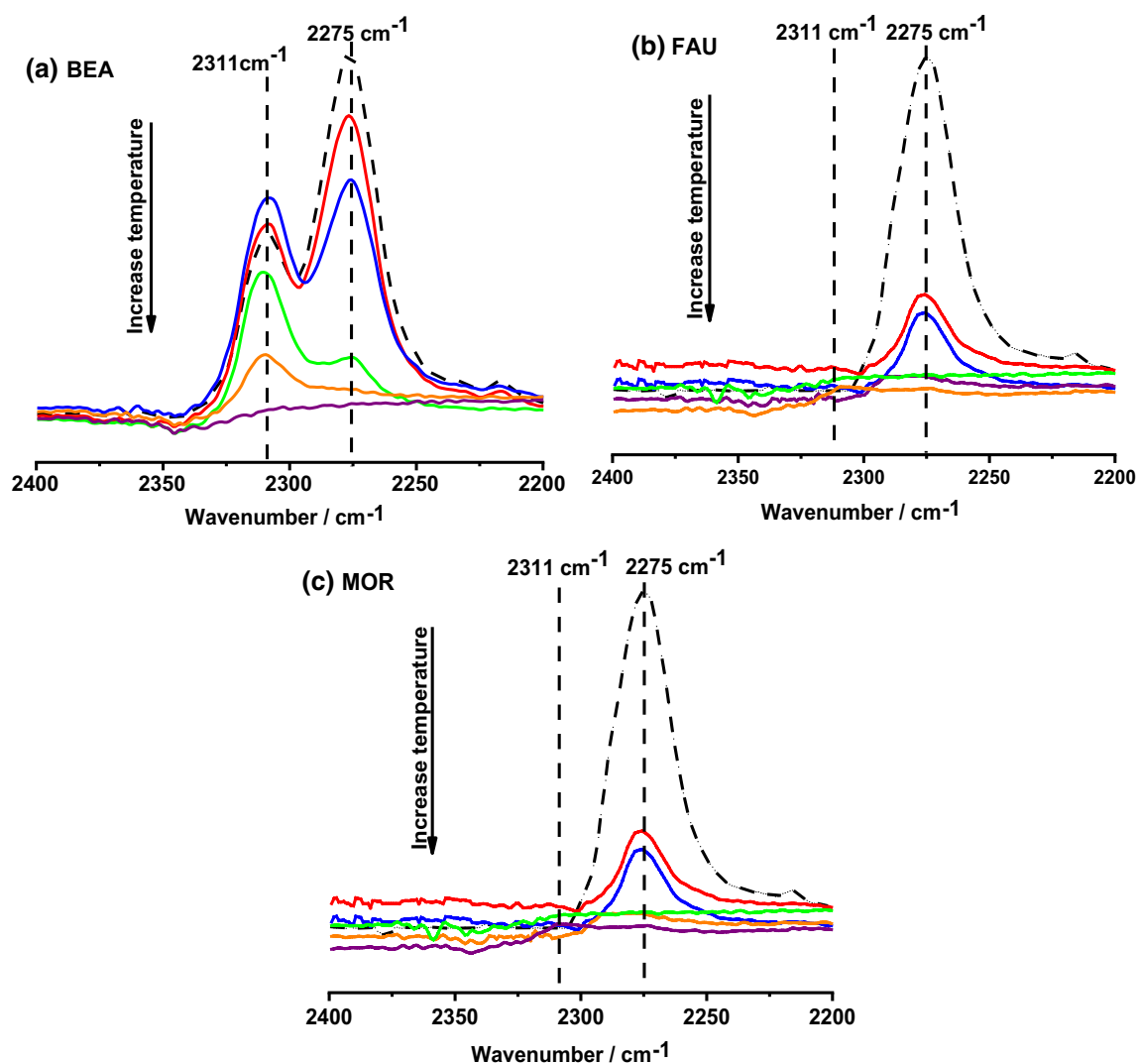


Fig. 5 DRIFT spectra of Sn-(BEA, FUA and MOR), dashed curve 10-min treatment with CD_3CN at 25 °C. Different temperatures of desorption (25 °C (black), 50 °C (red), 100 °C (blue), 150 °C (green), 200 °C (orange) and 250 °C (purple)) are shown

Fig. 6. The signal of the octahedral Al atoms was not intrinsically influenced by the dealumination of FAU and MOR zeolites. This finding is in line with the results obtained from the ICP-OES (see Table 1), and this was also evidenced by Yi et al. [21].

3.3 Catalytic Performance: Transfer Hydrogenation

Transfer hydrogenation is an essential chemical reaction to constitute a pair of H_2 atoms of hydrocarbon molecules with the aid of catalysis. In this study, the catalytic activity of the prepared 2 wt% Sn-(BEA, FAU, MOR) zeolites catalysts was evaluated by determining the transfer hydrogenation of a carbonyl structure, cyclohexanone (CyO) via the Meerwein-Ponndorf-Verley (MPV) reduction at a reaction time up to 120 min.

Figure 7 shows the activity of all zeolitic catalysts in the reaction condition of catalysis/CyO molar ratio is 1. It can be clearly seen that 2 wt% Sn-BEA has a superior catalytic activity in transferring hydrogenation of cyclohexanone to cyclohexanol compared to other zeolitic catalysts. This is apparently for presence of Lewis acid site, Sn (IV) in the BEA zeolite framework. Similarly, the Sn-Beta was an excellent catalyst for the MPV conversion of aldehydes and ketones and Oppenauer's oxidation of alcohols for its Lewis acidic properties that revealed a high stereoselectivity with alkylcyclohexanones and produced the right polarization of the carbonyl compound [22]. Furthermore, Ferdov et al. [23] stated the physicochemical characteristics of any mesoporous zeolites mainly depend on the Si/Al molar ratio and its distribution in the dealuminated zeolites.

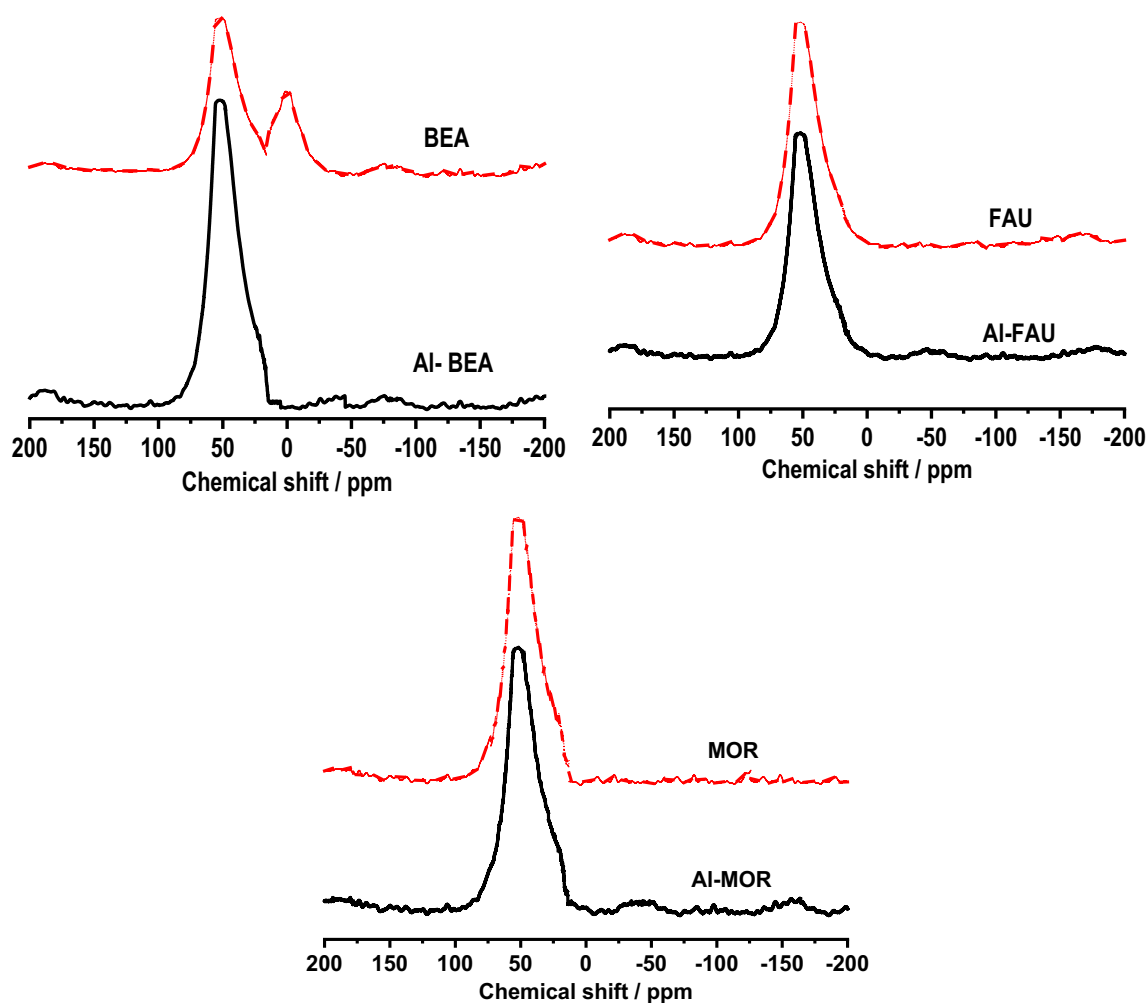


Fig. 6 The ^{27}Al MAS NMR spectra of the untreated (black line) and acid-treated (red dashed line) zeolites

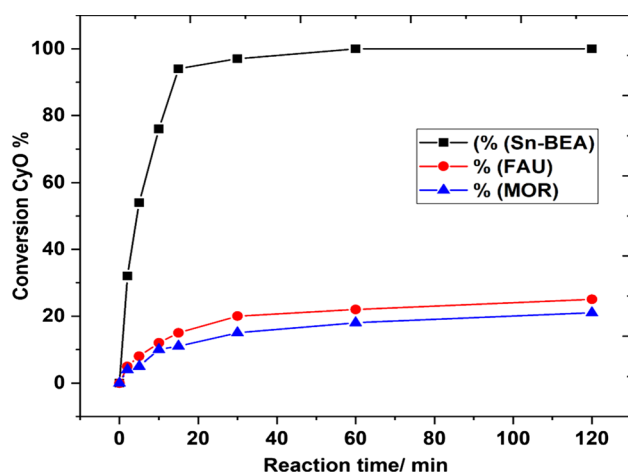


Fig. 7 The MPV hydrogenation of cyclohexanone (CyO) with 2-butanol at reaction conditions of 100 °C, 2 h, 10 mL CyO in 2-butanol (0.2 M), Sn/CyO molar ratio of 1%

The long-range order of Lewis acid, Sn-O_4 (Fig. 1C) is an essential parameter for a better catalytic activity of the Sn-BEA zeolite. However, the lower catalytic activity of 2 wt% Sn-(FAU, MOR) reaction is attributed to the presence a small number of silanol nest and absence of Lewis acid metal after the incorporation of heteroatoms Sn (IV). It is important to mention here that the ultra-thermodynamic stability of FAU and MOR zeolites besides their extra-framework Si structure ($\text{Si}/\text{Al} \geq 30$) tend to poor dealumination even with leaching by strong nitric acid (13 M). This consequently resulted in poor Al–O bonds broken, limited free Al metal (Brønsted acid) and poor catalytic activity. In fact, it was stated in the literature that some types of zeolites with relatively lower Si/Al ratios, for example, FAU-type (Y zeolite) with a Si/Al ratio of 3.3, can be properly dealuminated for creation of more isolated Brønsted acid sites [2], or dealuminated and postsynthesis of Lewis acidic tetrahedrally Sn metal for better catalytic performance in Baeyer–Villiger oxidation of 2-adamantanone [24].

4 Conclusions

In this study, the possibility of removing Al metal (dealumination) from three zeolitic frameworks whose close and higher Si/Al ratios ≥ 30 , i.e., Al-BEA, Al-FAU-type Y and Al-MOR, was attempted by nitric acid (13 M). Later, the SSI method was utilized for Lewis acid Sn-activation. Based on the structural characteristics and the catalytic activity test of all catalysts, it can be concluded that the dealumination and Lewis acid incorporation were successfully carried out for the Al-BEA and numerous vacant tetrahedral sites with a siliceous-rich framework attained. The dealumination of Al-BEA has effectively extracted the 4-ring Al Brønsted acid sites and silanol nests that required for effectively completing the SSI-Sn-incorporation has created. The dealumination, however was shown to be inefficient and inadequate for Lewis acidic sites obtained for the other Al zeolites due to their ultra-stable structures even with strong acid leaching. As a result, the catalytic performance of the Sn-BEA zeolite in hydrogenation conversion of cyclohexanone to cyclohexanol by the MPV was significant where it reached 95% in 10 min reaction, while it was about 10% for the other FAU and MOR zeolites under the same conditions.

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