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Review of Processes Concerning Zeolite Activation And Modification

Zeolitin Aktive ve Modifiye Edilmesi Süreçleri Hakkinda Bir Derleme

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Abstract:

Zeolite is mainly used in several processes such removal of metals from wastewater, adsorption of desired material from aqueous solutions. Before apply it to any solution, it is better to activate zeolite and then, if needed, to modify with any chemical material. In this manuscript, acid and thermal activation of zeolite were explained according to their usage in literature. And also, in some cases, the reason for modification of zeolite and how it is used in literature were mentioned.

Keywords: Acid activation, thermal activation, dealumination, modification, calcination.

Öz:

Zeolit, metallerin atıksudan uzaklaştırılması, istenen malzemenin sulu çözeltilerden adsorpsiyonu gibi çeşitli işlemlerde kullanılır. Herhangi bir çözeltiye uygulamadan önce, zeolitin aktif hale getirilmesi ve daha sonra gerekirse herhangi bir kimyasal madde ile modifiye edilmesi daha iyidir. Bu makalede, zeolitin asit ve termal aktivasyonu, literatürdeki kullanımlarına göre açıklanmıştır. Ayrıca, bazı durumlarda, zeolitin modifikasyon nedeninden ve literatürde nasıl kullanıldığından bahsedilmiştir.

Anahtar sözcükler: Asit aktivasyonu, termal aktivasyon, dealuminasyon, modifikasyon, kalsinasyon.

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Introduction

Natural zeolite ores are being used in chemical processes after they are saved from impurities by using several processes. Beside impurities inside, natural zeolites are pretreated to replace exchangeable cations (Na^+, K^+, Ca^{2+}, Mg^{2+}, etc.) in the channels to only one kind of cation (Ates and Hardacre, 2012; de Barros et al., 1997). These pretreatment methods are sole or combined treatments of thermal and acid activations (with HCl or HNO_3) and modifications with simple inorganic salts and alkali bases (Ates and Hardacre, 2012; Wang et al., 2012). Pretreated zeolitic materials have improved surface area, higher porosity and cation exchange capacity, and better adsorption properties. In this text, all pretreatment techniques will be mentioned.

Zeolites as crystalline aluminosilicates are based on tetrahedral units of silicon–oxygen (SiO_4) and aluminum–oxygen (AlO_4) containing interchangeable alkaline cations of earths (Fig. 1). Na^+, K^+, Ca^{2+} and Mg^{2+} ions keep a natural charge on zeolite structure (Villa et al., 2010). de Barros et al (1997) improves the zeolite exchange capacity by using NaCl to convert zeolite structure in monovalent exchangeable cations. And also, they used different size of zeolite particles which has an effect on exchange capacity of zeolite. In smaller size of zeolite, it has greater exchange with Na^+ ions.

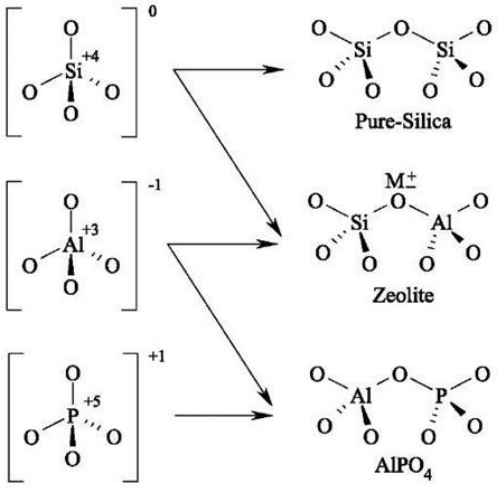

Figure 1. Zeolite structure

Acid Treatment for activation

Zeolite treated with an acid has an excess negative charge formed by being exchangeable cations (Na, K, Ca, Mg) moved away from the structure substituted with oxygen. In this case, the positively charged ions in the zeolite will be incorporated into the medium with weak dipole -dipole interaction (Fig. 2).

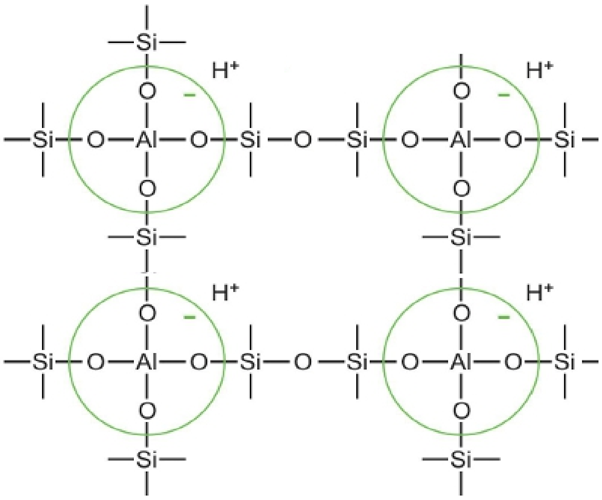

Figure 2. Conversion of zeolite to H-form

By acid treatment, protons in strong acids with high acid concentration cause in high temperatures (500°C) broken Al-O bonds which lead to skeletal cavities and defects called dealumination of zeolites (Wang et al., 2012; Guzman et al., 2006) (see Fig.3). Besides, dealumination leads to loss of crystallinity in particularly at low Si/Al ratios. The achieved spaces in the structure enlarge the pore size of the zeolite, increase the surface area and adsorption ability. On the other hand, using acids with lower concentration for acid treatment lead to remove impurities, such as iron oxide, resulting with higher aluminosilicate concentration (Koshy and Singh, 2016).

HCl and HNO_3 are the most commonly preferred acids for acid treatment (Ates and Hardacre, 2012). In literature, acid solutions are prepared from the solution of 0.1M, 1M to 12M for HCl and from 0.1M, 3M to 15.8M for HNO_3 (Ates and Hardacre, 2012; Burris and Juenger, 2016; Nasser et al., 2016). Besides, sulphuric and acetic acid are used in activation process of zeolites.

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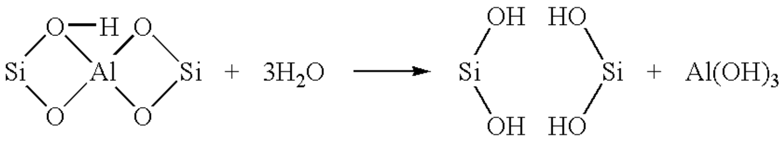

Figure 3. Dealumination process (Breck, 1974)

Nasser et al (2016) have used nitric acid for dealumination process. They also found that acid treatment time factor has a noticeable effect on the degree of porosity. With increasing treatment time from 3 to 6 h the silica content increased and the alumina concentration decreased from 81.56 to 82.63 wt.% and 9.22 to 8.88 wt %, respectively. In other words, the

Si/Al ratio showed a raise from 5.53 to 8.85 and 9.31 after the 3 and 6h of treatments, respectively. Increasing Si/Al ratio reduces strongly active acidic sites.

Thermal Treatment for activation

Thermal effect on zeolite leads to loose of water associated with zeolite and causes excessive negative charges that provide better conditions of higher adsorption capacity. Thermal treatment is used for both activation of zeolite by losing water from the structure and calcination process leading to dealumination. Different types of zeolitic water can be removed from the zeolite molecules in different time periods, therefore, thermal treatment should be extended to chosen time intervals. While heat exposure level changes 400°C to 700°C with heating rate of changing from 1°K/min to 2°C/min, exposure time lasts from 2h to 12h (Dyballa et al, 2016; Emdadi et al, 2016; Guesh et al, 2016; Nasser et al, 2016; Martinez and Peris, 2016; Yang et al, 2016). Guzman et al (2006) found optimum thermal activation at 270°C.

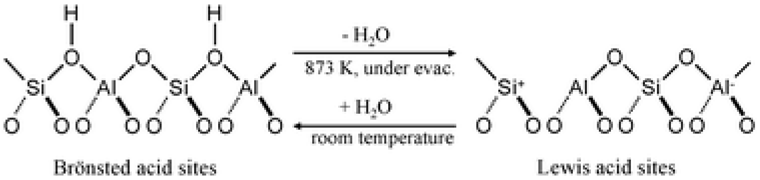

Figure 4. The cycle of Bronsted-Lewis acid sites on zeolite

The time period in which zeolite stays at the temperature is significant as much as chosen heating rate and calcination occuring temperature. Thermal activation is achieved under air atmosphere. After thermal activation, zeolite has a proton form which is ready for the following modification or adsorption processes (Chen et al, 2016; Vieira et al, 2016; Wei et al, 2015). However, thermal activation is also used after modification in order to achieve formation of bridging hydroxyl groups in the zeolite framework (Guzman et al, 2006).

According to Guzman et al, during heat treatment, some of the bridging hydroxyl groups in zeolite can be converted into Lewis acid sites by dehydroxylation, and the degree of this process depends on the heating conditions. Al^{3+} as a T-atom in a silicate framework causes a negative framework charge, which has to be balanced by a proton (forming a hydroxy group, Bronsted acid site) or by a metal cation (forming a Lewis acid site) (Fig. 4). If the dehydroxylated zeolite is contacted with water, Lewis acid sites are reconverted to Bronsted acid sites. In that sense, the acidity of the activated or rehydrated zeolite could differ significantly. Addition of water to magnesium and calcium X zeolites leads to the formation of Bronsted acid sites which could be eliminated by subsequent evacuation at elevated temperature. However, during rehydration, water may be not only chemisorbed to restore the Bronsted acidity, but it is also physically adsorbed on the zeolite surface blocking or modifying acid and base sites. Figure 5 shows loss of water from zeolite structure in IR graph.

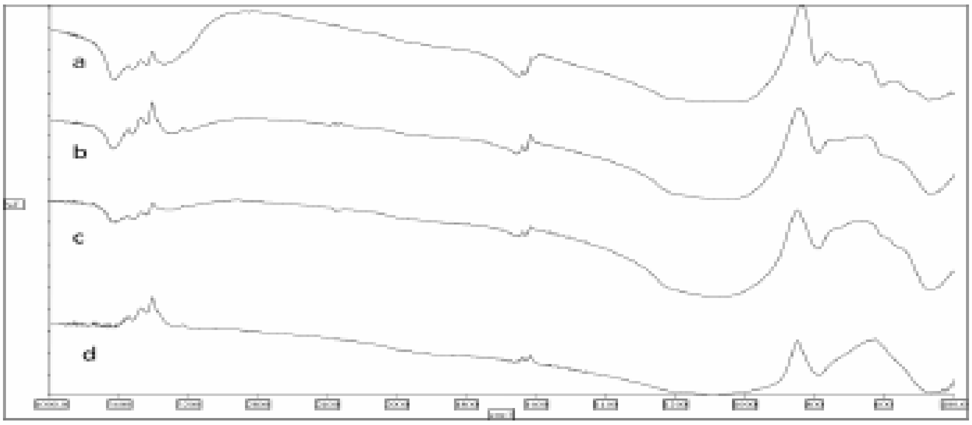

Figure 5. Thermal behavior of Natural zeolite at different temperatures in FT- IR spektra; a) 400°C, b) 600°C, c) 800°C, d) 950°C (Çanlı, 2013)

Modification of zeolite

Every AlO_2 unit carries a negative charge in zeolite because of trivalent charge of aluminum. A positive charge associated with a cation that determines the ion-exchange capacity of a zeolite is needed to balance formal charge (Kühl, 1999). With low SiO_2/Al_2O_3 ratio, a higher ion-exchange capacity can be achieved in zeolites. In addition, the specific ion-exchange capacity of zeolite varies with its structure and the exchanged cation.

Turning zeolite into the monovalent form such as Na, K form increases the modification efficiency with the desired ions or compounds. Especially, Na form of zeolite is obtained using NaCl or NaOH solutions (Jin et al, 2015; Koshy and Singh, 2016; Sun et al, 2015; Visa, 2016). For example, Mirzaei et al (2016) practiced one molar solution of sodium chloride salt to saturate the exchange sites with sodium ions, before modifying the surface of zeolites with surfactant. Therefore, Na-form of zeolite was exposed to a dosage of 100g/L of zeolites for 48h. For other cations, the compounds with nitrate, oxide, or chloride are usually preferred in modification process.

Contact time of zeolite with the cations varies from 4h to 24h to get modified form of zeolite. After washing and filtrating the solutions for removing excessive cations, new zeolite forms are dried at 100°C in an oven and calcined in high temperatures.

Using NH_4^+ for modification (Meusinger and Corma, 1995), converting zeolite into monovalent form or later on dealumination process are also commonly used in literature (Chen et al, 2016; Dyballa et al, 2016; Emdadi et al, 2016; Giroux et al, 2016; Jin et al, 2015; Vieira et al, 2016). Both Rodriguesa et al (2015) and Nasser et al (2016) converted zeolite into the H-form by

NH_4NO_3 solution at ambient temperature for 2-3h and subsequent calcination at 500-550°C under air atmosphere.

Xu et al (2016) practiced organosilane to obtained OS form of zeolite, and carried out the experiments in anhydrous conditions to avoid the reaction between organosilane and H_2O.

Sun et al (2016) treated NaY zeolites with $Ce(NO_3)_4$ solution at 353°K for 20 h under stirring. CeO_2 weight loading on NaY zeolites was found as 5%. Jablonska et al (2015) also used zeolite NaY as catalytic supports for palladium deposition. Time for removal of all Pd^{2+} ions from the solution was determined 24h by using aqueous solution of $PdCl_2$ (2.23×10^{-3} M).

Forming Na-, NH_4- or H-form of zeolite, and then using them for modification is very popular in zeolite studies (Chakarova et al, 2016). Gora-Marek et al (2015) substituted monovalent forms with using ion-exchange procedure with a 0.05M $Fe(NO_3)_3$ solution (1 g of zeolite per 100 ml of solution) performed at 60°C for 1h.

Srebowata et al (2016) applied both 0.2 M NaOH solution and then 0.5 M NH_4NO_3 at 60°C to obtain NH_4-form of zeolites. After activation with Na and NH_4, the zeolite was modified with the use of aqueous solution of 2.5×10^{-3}M $PdCl_2$, completion time for adsorption of Pd^{2+}ions was 36 h.

Completeness of cation adsorption was determined by chloride ions left from cations with colorimetric monitored via the reaction with thiourea (Jablonska et al, 2015; Srebowata et al, 2016**)**. The wash waste solution was analyzed for the presence of chloride ion using the argentometric titration method in order to ensure the removal of chloride ions (Mirzaei et al, 2016).

Similar to others, Yamasaki et al (2016) treated zeolite with NH_4^+ by carrying out dealumination involving a combination of steaming at 700°C and H_2SO_4 (0.40-0.75 M) treatment at 30 °C for 16 h. Then, the Na form was obtained from dealuminated zeolite. Finally, the zeolite was treated with an aqueous solution of NH_4NO_3 (1.0 M) at 60 °C for 6 h, and then, NH_4 form was calcined at 450 °C for 6 h, yielding the H-form. And also, Wei et al (2015) generated NH_4-form after applying ion-exchange to Na-form zeolite, and finally activated to H-form by a thermal treatment at about 500°C. They found that NH_4 and H-form were much more active than Na-form explained by the difference of their acidity.

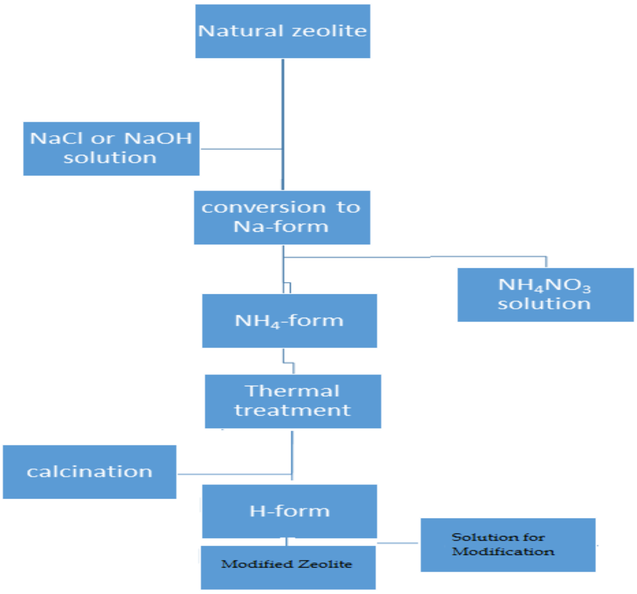

Figure 6. Modification process of zeolite

Ates and Hardacre (2012) improved natural zeolites with containing Na^+ , K^+ , Ca^{2+} and H_2O, as well as traces of Mg^{2+}, Ti^{4+}, Pd^{2+}, K^+, and Ba^{2+} ions by various methods such as steaming and high temperature calcination. Among these cations, Na^+ , K^+ , Ca^{2+}, and Mg^{2+} are exchangeable with NH_4^+ ions that type and density of the exchangeable cations determine the stability of the pores and the thermal behavior of a zeolite (Fig. 6). While Ates and Hardacre (2012) find out that high Si/Al ratios and the presence of K^+ ions increase the stability of the crystal structure upon heating, Jiang et al (2010) claims that lanthanum species in zeolite are very stable in modified zeolites even at the temperature of 650°K. Guzman et al (2006) also used lanthanum nitrate to produce a lanthanum-exchanged X zeolite at 353°K for 2h, and investigated its performance during alkylation of isobutane with 2-butene.

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