

Dielectric Behavior of the Catalyst Zeolite NaY

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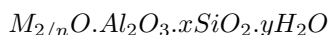
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Zeolites are crystalline hydrated aluminosilicates of alkaline and alkaline earth metals. The basic zeolite structure is an anionic frame of Si and Al T-atoms, which are tetrahedral and coordinated with oxygen atoms. The electrical properties of zeolites are of enormous technical importance due to their manifold applications as solid catalysts. Zeolite NaY was used in this investigation. Zeolite NaY is a synthetic zeolite and it has a faujasite structure. The electrical conductivity, dielectric permittivity, and loss factor of Na ion exchanged zeolite NaY was carried out in the 10^4 - 10^6 Hz frequency region at room temperature and different water contents using an HP 4194A LF Impedance Analyzer. The results of this investigation are given and explained to be used for further catalysis studies. Dielectric properties of zeolites have enormous importance because of their manifold applications as solid catalysts. Conductivity and dielectric permittivity studies are utilized in the investigation of the necessary conditions for catalytic activity.

Key Words: Zeolite, dielectric, conductivity, catalysis.

Introduction

Zeolites are porous crystalline, hydrated aluminosilicates of alkali and alkaline earth metal elements such as sodium, calcium, magnesium, and potassium. The empirical formula of a zeolite is



where M represents the exchangeable cation of valence n. Zeolite was discovered by a Swedish mineralogist, A.F. Cronstedt, in 1756. He found that zeolite loses water rapidly on heating and thus seems to boil. The name of zeolite comes from the Greek word *zeo* (to boil) and *lithos* (stone).¹⁻³

Zeolites can be naturally occurring or synthetic aluminosilicates of varying Si/Al ratio and channel structure.⁴ There are over 40 different kinds of natural zeolite found in various parts of the world and over 100 synthetic ones. They contain pores, channels, and cages of different dimensions,^{5,6} and are widely used in industry as ion exchangers, molecular sieves, and sorbents. In addition, they have found wide application in oil refining, petrochemistry, chemistry, and in the production of fine chemicals. They

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are commercially important solid acid catalysts for hydrocarbon conversion processes such as cracking, hydrocracking, isomerization, and alkylation.^{7–12}

In the late 1950s and early 1960s, certain zeolites were found to be excellent catalysts for catalytic cracking. They were observed to improve yields to gasoline, and in the early 1960s the Mobil Corporation introduced the first zeolite based, fluidized bed catalytic cracking process. Virtually all refineries in the world use some variation of this theme for catalytic cracking. It has been claimed that the improved efficiency of cracking with zeolite catalysts has provided the United States of America with a saving of greater than 400 million barrels of oil per year.²

Zeolite NaY, which is used in this study, is a synthetic zeolite and it is a member of the FCC zeolite group. FCC zeolites are zeolite Y, zeolite X, and ZSM-5.¹³ Zeolite NaX and zeolite NaY are Na⁺ ion exchanged forms of zeolite X and Y. The difference between NaX and NaY is the ratio of Si to Al: NaX \approx 1.1, NaY \approx 2.4.² To understand the function of zeolite NaY in a catalytic reaction, it is necessary to first describe the crystal chemistry of its framework. It consists of a 3D network of 12 Si or Al atoms that form circular channels 7.4 Å in diameter and it follows that silicon atoms generally prefer bonds with 4 neighboring atoms in tetrahedral geometry from the valency of silicon. If a SiO₄ entity could be isolated, its formal charge would be -4 since silicon is +4 and each oxygen anion is -2. However, a defect-free, pure SiO₂ framework will not contain any charge since an oxygen atom bridges 2 silicon atoms and shares electron density with each. If aluminum is tetrahedrally coordinated to 4 oxygen atoms in a framework, the net formal charge is -1 since aluminum carries a +3 valency. When tetrahedra containing silicon and aluminum are connected to form an aluminosilicate framework, there is a negative charge associated with each aluminum atom and it is balanced by a positive ion to give electrical neutrality. Typical cations are alkali metals, alkaline earth metals, and the proton H⁺. Figure 1 illustrates an example of a common cage structure known as sodalite and how it is constructed of silicon, aluminum, and oxygen atoms. Each line in the Figure 1 represents a bridging oxygen atom while the intersection is located at a silicon or aluminum atom. Zeolite Y is a principal component of cracking catalysts because of properties such as its high thermal stability and large internal surface area with easily accessible active sites.^{1,2,7–9,12}

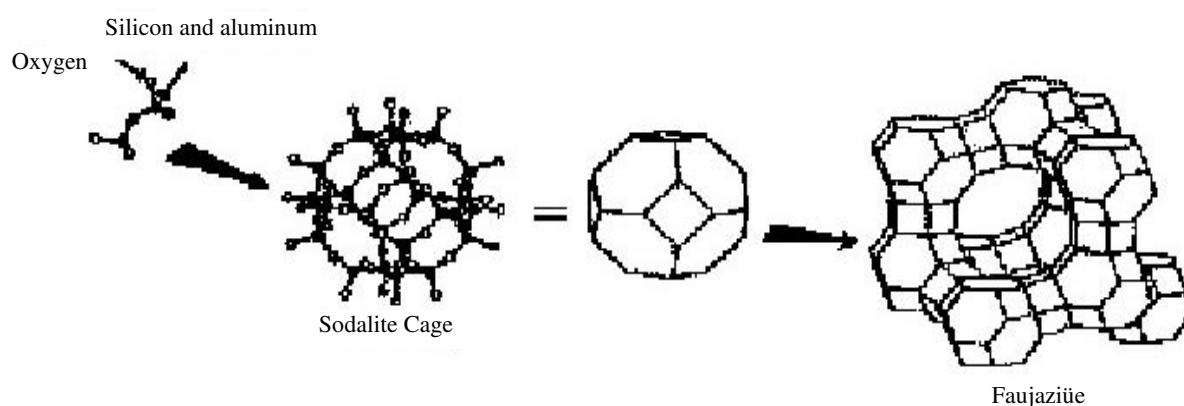


Figure 1. Schematic of zeolite frameworks.⁴

Zeolites are dielectric materials. A material is classified as dielectric if it has the ability to store energy when an external electric field is applied. The complex electrical properties of zeolites have been the subject of intense studies for more than 3 decades.^{14–17}

When a material body is exposed to an electric field (E), free electrons are displaced by electric forces until the field in the material body vanishes. Charges in equilibrium when displaced will form an electric field. This phenomenon is called displacement polarization (electronic or ionic polarization). Due to the polarization process, an image charge Q occurs on the metal electrodes, adding to the displacement charge that is present in vacuum. The charge per unit area deposited on the electrodes is called the electric displacement (D). It can be separated into the vacuum contribution and material contribution:

$$D = \varepsilon_0 \varepsilon_r E \quad (1)$$

where ε_0 is the permittivity of free space and ε_r is the relative permittivity of the material. ε_r is a complex number defined as

$$\varepsilon_r = \varepsilon' - j\varepsilon'' \quad (2)$$

where ε' is only the real part of the relative permittivity. It is usually called the permittivity and is a measure of the energy stored in the oscillations of the dipolar units. ε'' is called the dielectric loss or loss factor, because it is related to the energy dissipation in the material due to internal friction. The loss factor includes the effects of both dielectric loss and conductivity. The losses in the material can be represented as a conductance (G) in parallel with a capacitor (C). The dielectric losses represent the portion of the electric field energy dissipated to heat in the ceramic body. The admittance is given by

$$Y = j(\varepsilon' - j\varepsilon'')\omega C_0 = G + jB. \quad (3)$$

Equating the imaginary part of admittance gives conductance

$$G = \varepsilon''\omega C_0 \quad (4)$$

and the real part of it gives susceptance.

$$B = \varepsilon'\omega C_0 \quad (5)$$

where the cell constant for a parallel plate capacitor is the capacitance C_0 of an empty capacitor with no material between the plates:

$$C_0 = \varepsilon_0 A/d \quad (6)$$

where A is the surface area of the plates (m^2), d is the distance between the plates (m), and ε_0 is the permittivity of a vacuum ($= 8.85 \times 10^{-12}$ F/m). Related properties are the tangent of the loss angle, δ , commonly called the loss tangent or dissipation factor,

$$\tan \delta = \varepsilon''/\varepsilon' \quad (7)$$

and the a.c. conductivity,

$$\sigma_{ac} = \omega \varepsilon_0 \varepsilon'' \quad (8)$$

where ω is the angular frequency, $2\pi f$, and ε_0 is the permittivity of the free space, 8.85×10^{-12} F/m. f is called frequency. The losses in the material can be represented as a conductance (G) in parallel with a capacitor (C).¹⁸⁻²⁵

New physical properties of aluminosilicates such as their electrical and dielectric properties are studied together in an attempt to correlate these properties with their catalytic activity, with special reference to an electronic theory of catalysis that has developed over the last 3 decades.^{26,27} Although there have been some studies on the dielectric properties of the zeolite NaY,^{3,17,28,29} no detailed work of the effects of firing temperatures on the permittivity and loss tangent at different frequencies has been carried out. In particular, little has been reported on the catalytic effects of different zeolite materials or their catalytic mechanisms.³⁰

Experimental

The zeolite sample used in this work is a commercial product. It was obtained from Aldrich Ltd. The sample was compacted to pellets with a diameter of 6.5 mm and thickness of 1.28 ± 0.02 mm, under a pressure of 5 t. They were placed on a ceramic plate and fired at different temperatures for 1 h and afterwards they cooled to room temperature.

Electric contacts are deposited by sputtering a platinum film on their surface. The conductance (G) and susceptance (B) of these pellets were measured in the frequency range 10^4 to 10^6 Hz at room temperature using an HP 4194A LF Impedance Analyzer. The permittivity (ϵ'), loss tangent ($\tan\delta$), and a.c. conductivity (σ_{ac}) of them were calculated at these measuring results. ϵ' , $\tan\delta$, and σ_{ac} versus frequencies between 10^4 and 10^6 Hz and temperatures between 100 and 500 °C and Cole-Cole plots were plotted and commented on.

Results and Discussion

The main objective of this work was to investigate the effects of the permittivity, loss tangent, a.c. conductivity, and Cole-Cole plots on the firing temperature.

In Figure 2, the permittivity (ϵ') of zeolite NaY for different firing temperatures was found to decrease with an increase in frequency. Characteristic is the low frequency increase of the permittivity. At 500 °C, the permittivity value is higher than at other temperatures. The increase seems to disappear when the sample is fired. Actually, the motion of the charge carriers increases with increasing temperature and higher values of permittivity are observed.³¹ The low dielectric constant of zeolites (ϵ approximate to 1.6) suggests, however, that such processes in the zeolite channels should involve concerted action rather than strong charge separation, thus resembling gas phase reactions.¹⁰

Figure 3 shows the values of loss tangent, $\tan\delta$, as a function of frequency at room temperature, at different firing temperatures. Variations in the loss tangent with frequency show a good contrast with that of the permittivity. According to Figure 3, the loss tangent of zeolite NaY increased with an increase in frequency at 100, 400, and 500 °C, which were the firing temperatures. The loss tangent is a useful indicator of the potential of a material to extract energy from an electromagnetic field. The increase in permittivity and loss tangent, observed at all temperatures as frequency decreases, can be ascribed to the mobility enhancement of the ionic charge carriers. The heating ability of a material depends on its magnetic and/or dielectric loss to absorb energy from the electromagnetic field and so to reach and maintain the reaction temperature. Catalysts for use at RF fields must have sufficient magnetic and/or dielectric loss to absorb energy from the electromagnetic field.¹³ In addition, treatment of the discharging currents did not disclose relaxation processes of the Maxwell Wagner type deriving from the charge carriers' accumulation at the boundaries between the different phases, even at the lowest frequency investigated.

According to the reported results, obtaining high temperature insulating materials requires optimization of zeolites, composition, thermal treatment, and sintering technology.³²

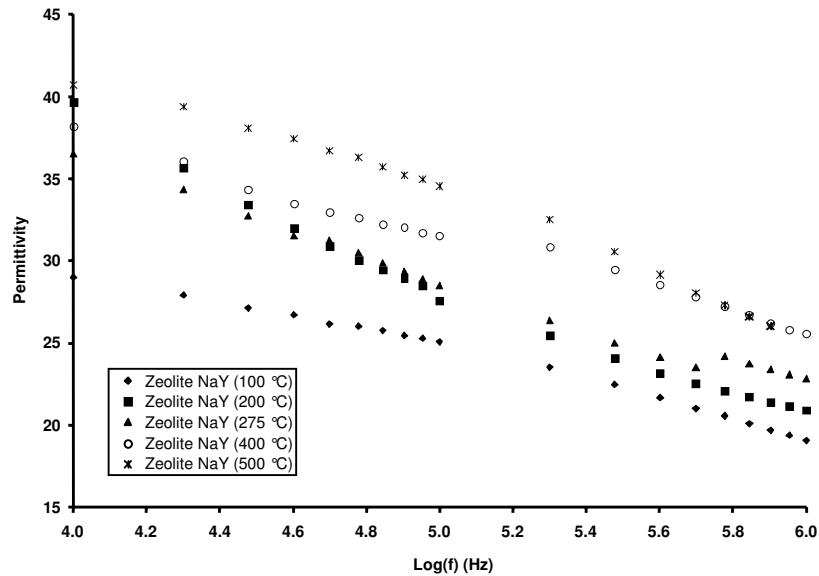


Figure 2. Plot of the permittivity versus the logarithm of measuring frequency for zeolite NaY at room temperature, for different firing temperatures.

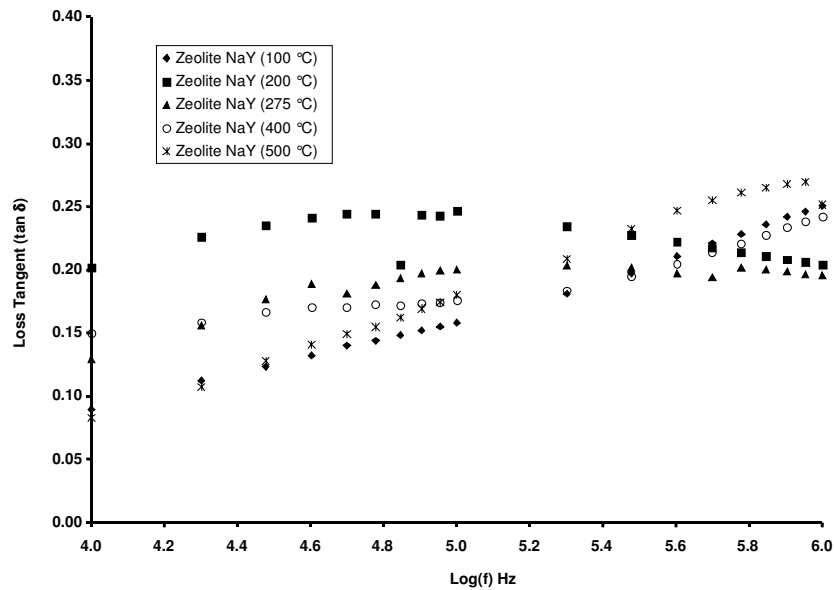


Figure 3. Dependence of the loss tangent on frequency of zeolite NaY at room temperatures, for different firing temperatures.

Figure 4 shows the values of a.c. conductivity, σ_{ac} , as a function of frequency at room temperature, at different firing temperatures. Variations in the a.c. conductivity with frequency show a good contrast with that of the permittivity. Consistent with the variation in the dielectric relaxation, the conductivity increases with frequency. The minimum conductivity for zeolite NaY is at 100 °C. It is attributed to a transition of the conduction from low temperature thermally enhanced mechanisms.⁴

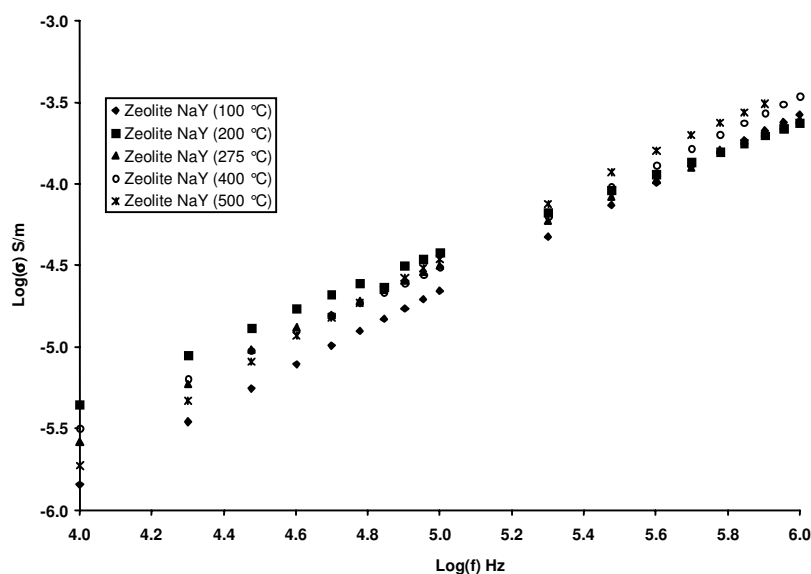


Figure 4. Conductivity versus frequency of zeolite NaY at room temperature, for different firing temperatures.

Zeolites contain mobile cations, which are exchangeable cations. In the zeolites, exchangeable cations more weakly bond to the adjacent atoms than the framework ions do and thus are more mobile.^{14,15,33,34} The catalytic properties of zeolites are strongly influenced by the guest materials and ions.³⁵ Their ionic conductivity and a number of dielectric relaxation phenomena are strongly affected by the presence of various molecular and ionic species.³⁶ The electrical conductivity of zeolites is a function of the number of current carriers and their mobilities.^{26,27,37} A knowledge of the conduction mechanism may be useful in view of their potential in electrochemical applications.³⁸ Water supports the ionic conductivity up to a temperature of 200-375 °C, depending on the type of zeolite. Above this the water is removed and the ionic conductivity is no longer dependent on the water absorbed.^{6,16,39,40} In the results, zeolites have poor conductivity unless quenched with fairly strong bases like ammonia and other amine derivatives.⁴

Figure 5 shows the Cole-Cole plots for these dispersions with a step rise of ϵ'' , which is usually attributed to conductivity loss.⁴¹ The Cole-Cole circular arc plot proves very successful in separating the loss process from the conductivity. The loss factor for conductivity generally increases as the frequency falls so that the Cole-Cole plot usually distinguishes between them, but the procedure is effective only when the dielectric loss process is not too small relative to the conduction process over a significant frequency range.⁴²

The electrical properties of zeolites are of enormous technical importance due to their manifold applications as solid catalysts or in gas separation.⁴³ The appearance of charged particles can markedly affect the catalytic properties of the system because some reactions such as chlorohydrocarbon include electron transfer from the catalyst to the reactant molecule, and they are sensitive to the charge state of a catalyst. The charging increases with the growth of both temperature and the dielectric permittivity of a solvent.⁴⁴

On the other hand, shapes and their surface are negatively charge-balanced with exchangeable cations. The negative charge of the alumina tetrahedra is balanced by interchangeable metal cations, which are present inside the channels and cavities.^{5,6}

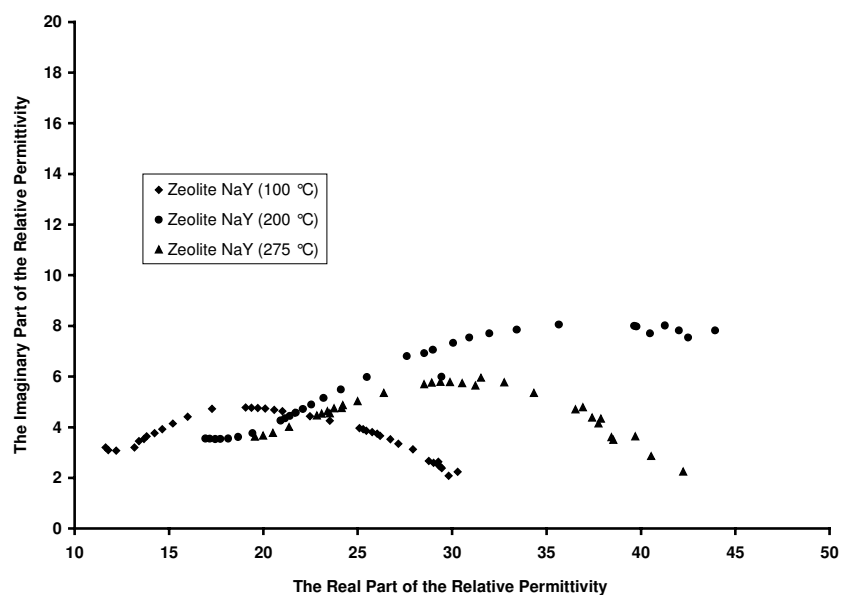


Figure 5. The Cole-Cole plots of zeolite NaY at room temperatures, for different firing temperatures.

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