

Determination of Surface Energy of Natural Zeolite by Inverse Gas Chromatography

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Abstract. In this study, surface energy of natural zeolite was investigated using inverse gas chromatography (IGC). Purified zeolite was prepared from natural zeolite applying decantation and centrifugation process together. For IGC studies, retention time of *n*-octane, *n*-nonane and *n*-decane were measured at infinite dilution conditions, between 250 and 280 °C. Dispersive component of the surface energy (γ_s^d) of purified zeolite was calculated. γ_s^d values calculated using Schultz et al methods decrease with temperature.

1. Introduction

Zeolites are a large group of minerals that belongs to the class of silicates and have different chemical composition, framework and properties. They belong to the class of minerals known as “tectosilicates.” Most common natural zeolites are formed by alteration of glass-rich volcanic rocks (tuff) with fresh water in playa lakes or by seawater Badillo-Almaraz et al. [1]. The zeolite framework is arranged as such to form a microporous structure with large cages (diameters of less than 2 nm) connected into channels. They possess special properties, such as ion exchange, molecular sieves, a large surface area, and catalytic activity, which make them a preferable material for tremendous industrial applications in industries such as domestic and commercial water purification, applications in adsorption, catalysis, building industry, agriculture, soil remediation, softening, sorbents and ion exchangers in petroleum refining, nuclear industry, biogas industry, heating and refrigeration, detergents, medicine, agriculture Bish and Ming, [2] Tsitsishvili et al. [3] Zorpas et al. [4] .



Naturally occurring zeolites are rarely pure and are contaminated to varying degrees by other minerals, metals, quartz, or other zeolites. At least 41 types of natural zeolites are known to exist, and many others have been synthesized. Clinoptilolite, mordenite, thomsonite, gismondine and gonnardite are the commonly known natural zeolites. Clinoptilolite, one of the most commonly observed natural zeolite mineral, is a member of the heulandite group. Its typical unit cell formula is given either by $\text{Na}_6[(\text{AlO}_2)_6(\text{SiO}_2)_{30}] \cdot 24\text{H}_2\text{O}$ or $(\text{Na}_2, \text{K}_2, \text{Ca}, \text{Mg})_3[(\text{AlO}_2)_6(\text{SiO}_2)_{30}] \cdot 24\text{H}_2\text{O}$ Haggerty et al.[5]. Clinoptilolite has some ion exchangeable cations such as Na, K, Ca and Mg in channels. Such cations give a high cation exchange capability to clinoptilolite, hence it can be exchanged with organic and inorganic cations Mortier and Pearce [6], Ames, [7], Barrer et al. [8], Turan et al. [9]. Its framework structure consists of three channels. Composition of the zeolite framework (Si/Al ratio) has a significant effect on the sorptive properties of the adsorbent. Beside this, natural zeolites, mining of which is easier and cheaper than other mines, are found in large reserves. Turkey currently has ~345 million tons of reserves of clinoptilolite as recorded by General Directorate of Mineral Research and Exploration in 2013. They are associated with clay minerals, borates, carbonates and soda minerals similar to many other parts of the world. They are also found in close association with lignite bearing lacustrine rocks and evaporate Birsoy, [10].

Gas–solid chromatography (GSC), when applied to the investigation of solid surface properties, is usually called inverse gas chromatography (IGC). This method is based on the study of physical adsorption of appropriate molecular probes by means of chromatographic (dynamic) experiments. In contrast to static methods, dynamic systems utilize a flowing gas system. The most common flow methods are IGC, gravimetric instruments, and permeability measurement systems. The principle of dynamic gravimetric systems is the measurement of the amount of solute adsorbed from a flowing gas stream using a microbalance Buckton and Darcy [11].

In the present study, we applied IGC method at infinite dilution to the investigation of surface properties of natural zeolite. The objectives of this study were, (i) to purify the natural zeolite (clinoptilolite) of Gördes–Manisa (in Western Anatolia of Turkey) via decantation process, (ii) to estimate the dispersive (London) component of the surface energy, (iii) to demonstrate whether or not the IGC technique provides an efficient and successful way in determining the surface properties of zeolite minerals.

2. Materials and methods

2.1. Materials and zeolite purification

The natural zeolite (clinoptilolite) of Gördes–Manisa (in Western Anatolia of Turkey) used in this work was supplied from Rota Mining Corporation. Because it was received as it was taken out of the ground, without having been processed, it contained many impurities. In order to purify it's a decantation and centrifugation process was applied. About fifty grams of raw zeolite were agitated for 60 min in 1 L of distilled water. The obtained clay was stirred until it was fully dissolved. It was continuously stirred by a magnetic stirrer for 2 h and then it was heated over two days. Colloidal solution is formed in the upper and middle parts of the bottles. The separated colloidal solution is taken to another container

and stored for two days. The same process was repeated ten times on the successive settled solid fraction. The clay in the colloidal solution from the most recent transaction was poured into 50 mL polyethylene centrifuge bottles, closed with screw-on caps, and then centrifuged for 20 min. The clay in the bottom of the tube was taken by a spatula was collected in a petri dish. It was dried overnight at 80 °C in an oven and then ground to fine powder.

Chemical and physical properties of natural zeolite were supplied by the producer. The crystalline phase composition of the natural zeolite used in this work was almost 95% clinoptilolite and the remainder was heulandite. Cation exchange capacity and bulk density of are 1.5–2.1 meq/g and 0.6–0.8 g/m³, respectively. Chemical composition of the clinoptilolite sample is as follows (in %wt): SiO₂: 71.00, Al₂O₃: 11.80, Fe₂O₃: 1.70, MgO: 1.40, CaO: 3.40, Na₂O: 0.40, K₂O: 2.40, TiO₂: 0.01, P₂O₅: 0.01, SO₃: 0.12.

2.2. Chromatographic experiments

The chromatographic experiments were performed with Agilent 7890 gas chromatography equipped with a flame ionization detector (FID). A vacuum pump was used for packing the solids into the columns. High purity nitrogen was used as the carrier gas with a flow rate of about 40 mL/min. The flow rate of carrier gas was corrected for pressure drop and temperature change in the column using James-Martin gas compressibility factor. A stainless steel column (2.00 m long, 5.35 mm I.D.) previously washed with methanol and acetone was packed with zeolite powders. The dead volumes of the columns were determined by injecting methane. At least three replicate determinations were used in averaging the net retention volume (V_N). For the IGC analysis, the polar probes used were *n*-octane, *n*-nonane, *n*-decane. All of these chemicals were analytical reagent grade and used without further purification. Properties were taken from literature of the probes Cordeiro et al. [12]. These probes are commonly used for solid surface characterizations by IGC method.

The net retention volume (V_N) is calculated using the equation below Cordeiro et al. [12].

$$V_N = F_o \cdot \frac{T}{T_o} \cdot \frac{3}{2} \left[\frac{\left(\frac{P_g}{P_g} \right)^2 - 1}{\left(\frac{P_g}{P_g} \right)^3 - 1} \right] \cdot (t_A - t_0) \quad (1)$$

The retention time of a series of homologous *n*-alkanes is used to determine the dispersive surface energy (γ_s^d) of Al-pillared sepiolite, which is obtained by the following equation Lavielle and Schultz [13].

$$RT \cdot \ln(V_N) = 2N \cdot a \cdot \sqrt{\gamma_s^d} \cdot \sqrt{\gamma_L^d} + C' \quad (2)$$

3. Results and Discussions

The dispersive component of the surface energy was determined by injection of a homologous series of *n*-alkanes having between 8 and 10 carbon atoms. One of the most

commonly measured parameters for the description of the energy situation on the surface of a solid is the surface energy. The surface energy can affect, e.g. catalytic activity or the strength of particle-particle interaction Thielmann [14]. The dispersive components of zeolite at experimental temperatures were calculated from Eq. (2). It was observed that the values decreased with temperature. The obtained values for zeolite were compared to the corresponding values of different clay types reported by various authors and listed in Table 1.

High values of layered clays may result from retention of the alkane probes in structural heterogeneities of molecular size (nanorugosities), formed by the irregular stacking of the layers, on the lateral sides of the clay. These nanorugosities would then allow a partial insertion of the alkane probes. Hence, the alkane probe would be submitted to a higher force field generated by the two silicate layers than to the one resulting from a simple adsorption on a flat layer. It would consequently be more strongly retained, thus inducing a notable increase in the apparent values Rodriguez et al. [15].

Table 1. Comparison of the present and reported dispersive component of surface energy

T [°C]	γ_s^d (mJ/m ²)								
	Zeolite 13X from Diaz et al. [16]	Zeolite NaY from Aşkın, and Bilgiç [17]	Zeolite 5A from Diaz et al. [16]	Alumina from Diaz et al. [16]	Activated carbon from Diaz et al. [16].	Sepiolite from Lazarević et al. [18]	Kaolinite from Kubilay et al. [19].	Bentonite from Hamdi et al. [20]	Natural Zeolite This Study
200	155		242	59.3	230.3		15.39		
210						149.9			
220						143.6			
225							10.85		
230	153		241	56.7	224.5	136			
240		52.6				130.4			
250	152	51.8	232.6	50.1	218.7		6.38		84.1
260		47.4							80.7
270	150	47.3	227	44.6	210.1				76.3
275							6.99		
280								155	73
350								145	
400								140	

4. Conclusions

Dynamic measurements give less accurate results when compared with static methods because they rely on measuring a small difference between quantities at different temperatures. However, for heats at zero coverage, infinite dilution gas chromatography is a more reliable method because it requires no extrapolation of data over a region where the heat can be very sensitive to small changes in coverage. In this study, purified zeolite was

prepared by decantation and centrifugation process. The high value of the dispersive component of free energy of adsorption related to structural heterogeneities on the lateral surfaces, as well as to the channels and pores present at 250–280 °C. γ_s^d values calculated using Schultz et al methods decrease with temperature.

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