

# Determination Of The Surface Properties Of Zsm-5 Zeolite By Inverse Gas Chromatography

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**Abstract** Inverse gas chromatography (IGC) has been used to measure the surface adsorption of some probes (n-alkanes on a series (n-C6 to n-C9) on ZSM-5 zeolite. The adsorption thermodynamic parameters (the standard enthalpy ( $\Delta H^0$ ), entropy ( $\Delta S^0$ ) and free energy of adsorption ( $\Delta G^0$ ) and the dispersive component of the surface energy ( $\gamma_s^d$ ), of zeolite surface were estimated by using the retention time of different non-polar probes at infinite dilution region. Dispersive component of the surface energy of zeolite was calculated between 290 and 320 °C. It was observed that,  $\gamma_s^d$  values decrease with increasing temperature.

**Keywords:** Inverse gas chromatography, Adsorption thermodynamic parameters, Surface energy, ZSM-5 zeolite

## INTRODUCTION

Zeolites are a large group of minerals that belongs to the class of silicates and have different chemical composition, framework and properties. The term “zeolite” was introduced in 1765 by Swedish mineralogist Axel Frederik Cronstedt. The name comes from Greek and means “boiling stones”. Zeolites have the ability to accumulate so-called “zeolite water” in the internal channels. This water can be removed as a result of heating and then re-absorbed or replaced by other substances (Piaskowski, K. and Anielak A.M., 2000; Karge, *et al.*, 1982). Zeolites are microporous, crystalline aluminosilicate minerals. They are divided into natural (e.g. mordenite, clinoptilolite, chabazite, analcime) and synthetic. There are known more than 40 natural zeolites, and synthesize more than 100. The most popular synthetic zeolites are zeolite type A, X, Y (Ruren, *et al.*, 2007). Zeolites are crystalline aluminosilicates containing pores and cavities of molecular dimension. The primary structural units of zeolites are the tetrahedral of silicon and aluminum. The framework contains well organized and regular system of channels and cages. Inside these voids are water molecules and small cations which compensate the negative framework charge and can be easily exchanged by other ions. In these solids dominate adsorption of molecules that fit snugly inside the pores and exclude molecules that are too large. Thus, zeolites act as sieves on a molecular scale and belong to the family of molecular sieves (Van Bekkum, *et al.*, 2001). They are very good matrices for hosting nano-sized particles because of large variety of crystalline

structures with different pore sizes and shapes. Zeolites can absorb large amounts of molecules both in the gas and in liquid phases. Moreover, they are nontoxic and have good thermal and chemical stability. Due to this, they became very popular in different areas of chemical research and are widely used in industrial, agricultural, environmental and biological technology. They are applied for water purification, gas drying, and separation of mixtures of different compounds. ZSM-5 is one of the more important zeolites due to its high number of industrial applications, mainly in the field of acid catalysis (Chen, 1989; Satterfield, 1991). It is a synthetic zeolite of medium pore size, and its structure and properties have been widely studied and are well known. The crystalline structure consists of two sets of channels: a set of straight channels (elliptical cross-section of about 5.7x5.1 Å) and another set of sinusoidal channels (circular cross-section of about 5.4 Å diameter) (Dwyer, 1989).

Inverse Gas Chromatography (IGC) was applied for the examination of surface properties of the aluminosilicates at the different conditions (humidity). IGC is the extension of conventional gas chromatography (Voelkel, A., 2004; Belgacem and Gandini, 1999; Schreiber, H.P. and Lloyd, D.R., 1989). The word “inverse” means that the examined material is placed in the chromatographic column and its properties are determined based on the retention behaviour of carefully selected test compounds. Dispersive properties of the surface may be studied by means of IGC. Reversed-flow GC (or time-resolved GC) introduced by Katsanos and Karaiskakis is sophisticated version of IGC technique (Katsanos and Karaiskakis, 2004). Time-resolved IGC can be used in examination of such properties as adsorption energies (Katsanos, *et al.*, 1999) local monolayer capacities, local isotherms, energy distribution functions, adsorption rates with lateral molecular interactions (Katsanos, *et al.*, 2002), mass transfer coefficients (Karaiskakis, *et al.*, 1986), surface diffusion coefficients, activity coefficients (Katsanos *et al.*, 1985) and other (Katsanos and Karaiskakis, 2004; Thielmann, *et al.*, 2001; Bogillo *et al.*, 1998; Schultz, *et al.*, 1987).

In the IGC the molecular sieve zeolite to be characterized is used as the stationary phase, and a solute with well-known properties is injected as a probe. Several thermodynamic quantities, including surface energy, can thus be derived from the retention volume of probe passing

through the column filled with zeolites. This work was thus undertaken in order to investigate how IGC could be applied in estimating dispersive components of surface energies of ZSM-5 zeolite. Another purpose was to determine the variation in adsorption thermodynamic parameters of some hydrocarbons on zeolite minerals.

## 2. MATERIALS AND METHODS

### 2.1. Materials

ZSM-5 zeolite (CBV28014) was directly supplied in the ammonium form by Zeolyst International. For the IGC analysis, the polar probes used were *n*-hexane, *n*-heptane, *n*-octane, *n*-nonane. Properties were taken from literature of the probes (Cordeiro *et al.*, 2011). These probes are commonly used for solid surface characterizations by IGC method. 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 and 60 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 two ends of the column were plugged with silane-treated glass wool. Measurements were carried out in the temperature range of 290–320 °C. The column was stabilized overnight in stream of nitrogen at 350 °C. The dead volumes of the columns were determined by injecting methane. At least three replicate determinations were used in averaging the net retention volume ( $V_N$ ).

### 2.2. Calculations

IGC is used to study the surface free energy and acid–base properties of solids; the study is generally performed in the area of infinite dilution where the interactions between the adsorbed probe molecules are negligible. The basic value in IGC is the net retention volume. The net retention volume is the volume of carrier gas required to elute a given probe. The net retention volume ( $V_N$ ) is calculated using the following equation:

$$V_N = (t_R - t_m) \cdot F_a \cdot \frac{T}{T_a} \cdot j \quad (1)$$

where  $t_R$  is the probe retention time,  $t_m$  is the retention time of the mobile phase (holdup time, dead-time), determined by methane,  $F_a$  is volumetric flow rate measured at column outlet and at ambient temperature,  $T_a$  is ambient temperature (K),  $T$  is the column temperature (K) and  $j$  is James-Martin gas compressibility correction factor.

When adsorption takes place in the Henry's law region, the standard free energy of adsorption ( $\Delta G^0$ ), as a function of  $V_N$ , can be determined from:

$$\Delta G^0 = -RT \ln \left( \frac{V_N P_0}{m S \pi_0} \right) \quad (2)$$

where  $R$  is the ideal gas constant,  $m$  is the mass of adsorbent in the column,  $S$  is the specific surface area of adsorbent,  $P_0$  is the adsorbate vapor pressure in the gaseous standard state having a value of 101.3 kN/m<sup>2</sup> (1 atm) and  $\pi_0$  is the reference two-dimensional surface pressure whose standard state is arbitrary. The standard reference state was taken as  $\pi_0 = 0.338$  mJ/m<sup>2</sup> proposed by de Boer (Boer, 1953).

Therefore,  $\Delta G^0$  can be written as:

$$\Delta G^0 = -RT \ln V_N + C \quad (3)$$

At zero surface coverage  $\Delta H^0$  is the differential heat of adsorption of the probe and it is estimated from the changes in  $V_N$  with temperature, i.e.:

$$\Delta H^0 = -R \frac{d \ln V_N}{d(1/T)} \quad (4)$$

The standard entropy change of adsorption of the probe at zero coverage,  $\Delta S^0$ , can be calculated the following equation:

$$\Delta S^0 = \frac{\Delta H^0 - \Delta G^0}{T} \quad (5)$$

Provided that  $\Delta H^0$  is temperature independent in the investigated temperature range, Eq. (5) predicts a linear relationship between  $\Delta G^0$  and  $\Delta H^0$  (Vidal *et al.*, 1987, Rodriguez *et al.*, 1997, Chappell and Williams, 1989)

Generally, surface free energy of a solid ( $\gamma_s$ ) can be split into two components: the dispersive component ( $\gamma_s^d$ ), and the specific component ( $\gamma_s^{sp}$ ). The dispersive component depends on the van der Waals dispersion forces which are relatively weak, while the specific component contains all the polar forces (Milonjic, 1999, Ansari and Price, 2004).

$$\gamma_s = \gamma_s^d + \gamma_s^{sp} \quad (6)$$

There are various methods for calculating the dispersive component of the surface free energy using IGC, but two of these are the most widely used. These are the Dorris–Gray and Schultz methods. In both these methods, when calculating  $\gamma_s^d$ , a homologue alkane series in extremely small concentrations (infinite dilution) and in isothermal conditions is injected into the column in sequence. A single numerical  $\gamma_s^d$  value is calculated from the acquired alkane series retention time data at studied column temperature (Ylä-Mäihäniemi *et al.*, 2008). The calculation of  $\gamma_s^d$  according to the Schultz method, using infinite dilution measurements, is done using the following equation (Shi *et al.*, 2011).

$$RTL \ln V_N = 2N \cdot (\gamma_s^d)^{1/2} \cdot a \cdot (\gamma_L^d)^{1/2} + C \quad (7)$$

where  $V_N$  is the net retention volume of the *n*-alkane probe,  $R$  is the gas constant,  $T$  is the absolute column temperature (K),  $a$  is the molecular surface area coated with a kind of adsorbed alkane,  $N$  is Avogadro's number, and  $C$  is the constant. In this equation,  $\gamma_s^d$  is the dispersive component of the surface free energy of the solid phase,

and  $\gamma_L^d$  is the dispersive component of the surface free energy of the probe. The plot of  $(RT \ln V_N)$  versus  $a(\gamma_L^d)^{1/2}$  can be useful. Such a plot is linear and the slope of the lines gives dispersive free energy of the solid phase. The values of  $a(\gamma_L^d)^{1/2}$  are necessary for the calculations and can be easily found in the literature.

### 3. RESULTS AND DISCUSSION

The chromatographic peaks were symmetric and had maxima that were independent of the amount injected. It is assumed that the adsorption occurs in the Henry's law region (at zero surface coverage) where lateral interactions between the adsorbates at the surface can be neglected. The net retention volumes,  $V_N$ , were obtained from the maxima of the chromatographic peaks and the dead time volume.

In this study, thermodynamic parameters for adsorption of polar probes on zeolite were determined in the infinite dilution region. Standard free energies changes of adsorption ( $\Delta G^0$ ) were calculated by Eq. (2). Differential heats of adsorption ( $\Delta H^0$ ) were calculated from plots of  $\ln V_N$  against  $1/T$ . The slopes of the lines are  $[-(\Delta H^0/R)]$  according to Eq. (4). Standard entropies of adsorption ( $\Delta S^0$ ) were calculated by Eq. (5). Thermodynamic parameters (average values) are given in Table 1. The values of  $\Delta H^0$ ,  $\Delta S^0$  and  $\Delta G^0$  increase with increasing carbon number and the linear increase was obtained for the n-alkanes. This is due to the increase in the boiling points of n-alkanes and to the stronger interaction between the solute and adsorbent surface. The more negative the heat of adsorption, the greater the interaction between the adsorbate and the adsorbents.

**Table 1.** Thermodynamic parameters for ZSM-5 zeolite

	$-\Delta H^0$ (kJ.mol <sup>-1</sup> )	$-\Delta S^0$ (kJ.mol <sup>-1</sup> K <sup>-1</sup> )	$-\Delta G^0$ (kJ.mol <sup>-1</sup> )
n-Hexane	78.506	105.03	17.77
n-Heptane	89.831	118.61	21.24
n-Octane	130.31	186.98	22.20
n-Nonane	105.94	138.16	26.05

The dispersive component of the surface free energy,  $\gamma_s^d$ , was determined by injection of a homologous series of n-alkanes having between 6 and 9 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. The dispersive components of zeolite at experimental temperatures were calculated from Eq. (7), (Fig. 1). The variation of  $\gamma_s^d$  calculated as a function of temperature. It

was observed that  $\gamma_s^d$  values decrease with temperature. The obtained  $\gamma_s^d$  values for zeolite were compared to the corresponding values of different clay types reported by various authors and listed in Table 2.

### 4. CONCLUSION

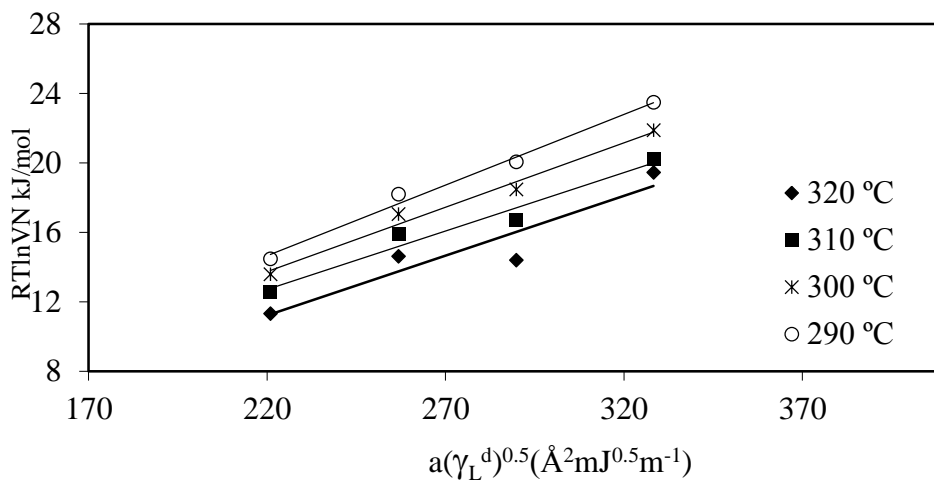
IGC method is based on the study of physical adsorption of appropriate molecular probes by means of chromatographic (dynamic) experiments. In contrast to static methods, dynamic systems utilize a flowing gas system. The most common flow methods are IGC, gravimetric instruments, and permeability measurement systems. The principle of dynamic gravimetric systems is the measurement of the amount of solute adsorbed from a flowing gas stream using a microbalance.

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, showed that IGC is a powerful analytical technique very useful for studying the surface properties of ZSM-5 zeolite and for monitoring adsorption processes. Thermodynamic information on adsorption was obtained from the temperature variation of the partition coefficients for probes at zero coverage. The high value of the dispersive component of free energy of adsorption  $\gamma_s^d$  probably was related to structural heterogeneities on the lateral surfaces, as well as to the channels and pores present at 290–320 °C.

**Table 2.** Comparison of the present and reported dispersive component of surface energy

T (°C)	$\gamma_s^d$ (mJ/m <sup>2</sup> )							
	Zeolite 13X	Zeolite NaY	Zeolite 5A	Alümina	Activated carbon	Sepiolite	Kaolinite	ZSM-5 Zeolite
	from (Diaz <i>et al.</i> ,2004)	from (Aşkın, and Bilgiç 2005)	from (Diaz <i>et al.</i> ,2004)	from (Diaz <i>et al.</i> ,2004)	from (Diaz <i>et al.</i> , 2004)	from (Lazarević <i>et al.</i> 2009)	from (Kubilay <i>et al.</i> 2006)	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	
260		47.4						
270	150	47.3	227	44.6	210.1			
275							6.99	
280								
290								45.79
300								38.03
310								31.40
320								32.63



**Figure 1.** The  $RT \ln(V_N) - a(\gamma_L^d)^{1/2}$  graphs for ZSM-5 Zeolite

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