STUDY OF SORPTION OF ALCOHOLS
ON HIGH SILICA ZSM-35

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Approval of the Graduate School of Natural and Sciences

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ABSTRACT

STUDY OF SORPTION OF ALCOHOLS ON HIGH SILICA ZEOLITE

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This study investigated the equilibrium sorption capacities and rates of sorption of some alcohols on Na- and/or H- form of ZSM-35 at different temperatures by gravimetric method using an electrobalance. The alcohols studied were methanol, ethanol, propan-1-ol, propan-2-ol, n-butanol.

The ZSM-35 sample used in sorption experiments resulted from a study for synthesis of high silica ZSM-35 zeolite. This ZSM-35 sample was called as NaZSM-35. The influence of ion-exchange on the sorption capacity and kinetics was investigated by converting NaZSM-35 into H-form by the ion exchange method.

In this method, a sufficient amount of ZSM-35 sample (200-250 mg) was mixed with 25 ml of 1 N NH_4Cl solution for 24 hours at room temperature. This procedure was repeated until no Na^+ was detected by a Flame Photometer. After the ion exchange was completed , the sample was washed with deionized water, filtered, dried and recalcined for the removal of the ammonia and this sample was denoted as HZSM-35.

The highest sorption capacity (cm^3/g) was observed for methanol on HZSM-35; 0.1656 cm^3/g and the lowest sorption capacity was observed for propan-2-ol at NaZSM-35; 0.003 cm^3/g. Sorption of methanol and ethanol were very rapid. The sorption capacities of other three alcohols; propan-1-ol, propan-2-ol and n-butanol, were lower and they had slower rates of sorption.

HZSM-35 had greater limiting sorption capacity than NaZSM-35 for propan-1-ol, propan-2-ol and n-butanol at all temperatures.

Keywords : ZSM-35, Sorption Properties, Methanol, Ethanol, Propan-1-ol, Propan-2-ol, n-Butanol

ÖZ

YÜKSEK SİLİKA ZEOLİT ÜZERİNDE ALKOLLERİN SORPSİYONU ÇALIŞMASI

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Bu çalışmada Na- ve/veya H- formundaki ZSM-35'te , farklı alkollerin sorpsiyon kapasitesileri ve sorpsiyon hızları gravimetrik metodla elektroterazi kullanılarak farklı sıcaklıklarda incelenmiştir. Çalışılan alkoller; metanol, etanol, propan-1-ol, propan-2-ol, at all temperatures n-butanoldür.

Sorpsiyon deneylerinde kullanılan ZSM-35, yüksek silika ZSM-35 zeolit sentezi çalışması sonucu elde edilmiştir. Bu zeolit NaZSM-35 olarak adlandırılmıştır.

İyon değişiminin sorpsiyon kapasitesi ve kinetiği üzerindeki etkisi NaZSM-35'in iyon değişimi metoduyla H- formuna çevrilmesiyle incelenmiştir. Bu metotta, bir miktar ZSM-35 (200-250 mg) 25 ml, 1 N NH4Cl ile oda sıcaklığında 24 saat süre karıştırılmıştır. Bu uygulama alev fotometresi ile çözeltide Na^+ görülmeyene kadar tekrarlanmıştır. İyon değişimi tamamlandıktan sonra numune yıkanıp tekrar kalsine edilip ve HZSM-35 olarak adlandırılmıştır.

En yüksek sorpsiyon kapasitesi (cm^3/g) HZSM-35 üzerinde metanol için görülmüştür; 0.1656 cm^3/g ve en düşük sorpsiyon kapasitesi NaZSM-35 üzerinde propan-2-ol için görülmüştür; 0.003 cm^3/g. Metanol ve etanolün sorpsiyonları çok hızlıdır. Diğer üç alkolün; propan-1-ol, propan-2-ol ve n-butanol, sorpsiyon kapasiteleri düşük ve hızları yavaştır.

Tüm sıcaklıklarda, propan-1-ol, propan-2-ol ve n-butanol için HZSM-35 , NaZSM-35'ten daha yüksek sorpsiyon kapasitesine sahip olduğu tespit edilmiştir.

Anahtar Kelimeler : ZSM-35, Sorpsiyon Özellikleri, Metanol, Etanol, Propan-1-ol, Propan-2-ol, n-butanol

To My Parents

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FER : Ferrierite
ZSM : Zeolite Socony Mobil
MR : Membered-ring
SiO_2 : Silicon dioxide
Al_2O_3 : Aluminum oxide
ED : Ethylenediamine
Py : Pryrolidine
t : time, h, min or sec
T : Temperature
P : Pressure of sorbate, torr (mmHg)
$P_{f,0°C}$: Final pressure of the system at 0°C, mmHg
$P_{0,0°C}$: Vapor pressure of the adsorbate at 0°C, mmHg
ρ_L : Density of liquid sorbate at the temperature of adsorption, g/cm^3

CHAPTER 1

INTRODUCTION

There have been considerable studies carried out in the field of zeolite. The properties and uses of zeolites are being explored in many scientific areas: organic and inorganic chemistry, physical chemistry, mineralogy, surface chemistry, catalysis and in all types of chemical engineering process technology.

Zeolites are crystalline, hydrated aluminosilicates as formed in nature or synthesized. Their structure is a framework based on an infinitely extending three dimensional network of SiO_4 and AlO_4 tetrahedra linked to each other by sharing oxygen atoms. The framework contains channels or interconnected voids, which are in micropore range. These channels and voids are occupied by water molecules, and the cations; mainly alkali or alkaline earth metal ions, so as to balance the negative charge of the framework (Breck, 1974).

The ideal formula of a zeolite for the crystallographic unit cell is given as:

$$M_{x/n} (AlO_2)_x (SiO_2)_y \; w \, H_2O$$

where M is the exchangeable cation of valence n, w is the number of water molecules. The sum (x+y) is the total number of tetrahedra in the unit cell. M is generally a Group I an II ion, although other metal, non-metal and organic cations may also balance the negative charge created by the presence of Al in the structure. Aluminosilicate framework of zeolites is shown in Figure 1.1.

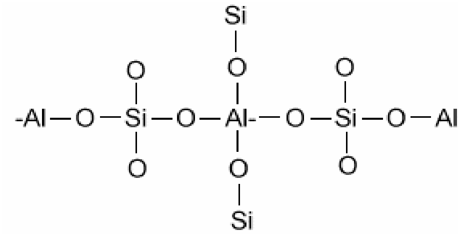


Figure 1.1. Aluminosilicate Framework of Zeolites

To activate the zeolite the intracrystalline zeolitic water can be removed reversibly by thermal treatment mostly below about 400 °C. For many zeolites the structure remains intact and the intracrystalline channels and voids become vacant except for the remaining cations. This leads to a highly crystalline, microporous adsorbent which has an internal structure which can be easily tailored to adsorb many number of species (Bhatia, 1990).

Zeolite was first discovered as a new type of mineral in 1756 by the Swedish mineralogist Cronstedt. The word "zeolite" derived from two Greek words "zeo" and "lithos". They mean "to boil" and a "stone" because when gently heated, the mineral loses water rapidly and thus seems to boil (Elvers and Hawkins, 1996).

Because of their unique porous properties, zeolites are used in a variety of applications. Major uses are in petrochemical cracking, ion-exchange (water softening and purification), and in the separation and removal of gases and solvents. They are often also referred to as *molecular sieves*.

All commercially useful zeolites owe their value to one or more of three properties: catalysis, adsorption, and ion exchange:

i. **Catalysis**

Zeolites have the ability to act as catalysts for chemical reactions which take place within the internal cavities. An important class of reactions is that catalysed by hydrogen-exchanged zeolites, whose framework-bound protons give rise to very high acidity. This is exploited in many organic reactions, including crude oil cracking, isomerisation and fuel synthesis.

Underpinning all these types of reaction is the unique microporous nature of zeolites, where the shape and size of a particular pore system exerts a steric influence on the reaction, controlling the access of reactants and products. Thus zeolites are often said to act as *shape-selective catalysts*.

ii. **Adsorption and Separation**

The shape-selective properties of zeolites are also the basis for their useage in molecular adsorption. The ability preferentially to adsorb certain molecules, while excluding others, has opened up a wide range of molecular sieving applications. Sometimes it is simply a matter of the size and shape of pores controlling access into the zeolite. In other cases different types of molecule enter the zeolite, but some diffuse through the channels more quickly, leaving others stuck behind, as in the purification of *para*-xylene by silicalite.

Cation-containing zeolites are extensively used as desiccants due to their high affinity for water, and also find application in gas separation, where molecules are differentiated on the basis of their electrostatic interactions with the metal ions. Conversely, hydrophobic silica zeolites preferentially absorb organic solvents. Zeolites can thus separate molecules based on differences of size, shape and polarity.

Adsorption based on molecular sieving, electrostatic fields, and polarizability are always reversible in theory and usually reversible in practice. This allows the zeolite to be reused many times, cycling between adsorption and desorption. This accounts for the considerable economic value of zeolite in adsorptive applications.

iii. **Ion Exchange**

The loosely-bound nature of extra-framework metal ions means that they are often readily exchanged for other types of metal when in aqueous solution. This is exploited in a major way in water softening, where alkali metals such as sodium or potassium prefer to exchange out of the zeolite, being replaced by the "hard" calcium and magnesium ions from the water. Many commercial washing powders thus contain substantial amounts of zeolite. Commercial waste water containing heavy metals can also be cleaned up using such zeolites.

Zeolites are a large group of some 40 to 50 different natural minerals and numerous synthetic forms. Since 1954, their introduction as a new class of commercial adsorbents zeolites, especially synthetic zeolites due to their high capacity and selectivity, have grown into a very important industry and have led to the reaction of a new branch of chemical technology (Bhatia, 1990).

Synthetic zeolites hold some key advantages over their natural analogs. The synthetics can, of course, be manufactured in a uniform, phase-pure state. It is also possible to manufacture desirable zeolite structures which do not appear in nature. Zeolite A is a well-known example. Since the principal raw materials used to manufacture zeolites are silica and alumina, which are among the most abundant mineral components on earth, the potential to supply zeolites is virtually unlimited. Finally, zeolite manufacturing processes engineered by man require significantly less time than the 50 to 50,000 years prescribed by nature.

Since synthetic zeolites were first used commercially, they have found many uses in adsorption seperation applications because of their unique physical structure. With today’s knowledge of zeolite properties and manufacturing processes, it is possible to tailor the structure of the zeolite for specific processes the development of synthetic zeolites for both adsorbent and catalytic applications has been truly outstanding and potential new processes based on zeolite appear to be equally important.

In this study, kinetic and equilibrium characteristics of ZSM-35, FER family member as a medium pore, high silica zeolite, for methanol, ethanol, propan-1-ol, propan-2-ol and n-butanol adsorption, the first important step of several important processes, have been considered and the effect of temperature on the equilibrium adsorption capacities and adsorption rates were determined by gravimetric method.

CHAPTER 2

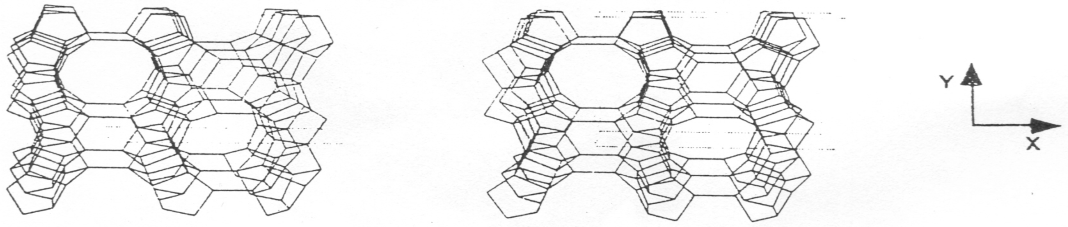
THEORETICAL BACKGROUND

2.1 The Synthetic Zeolite : ZSM-35

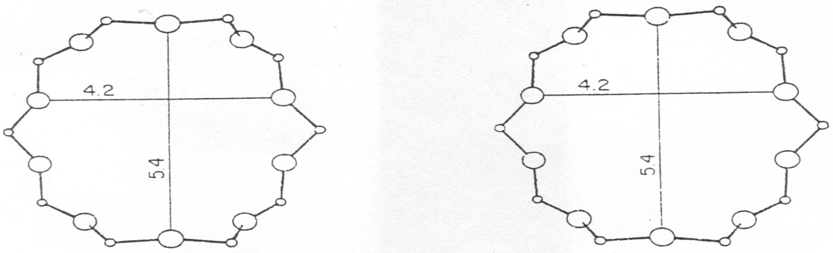
The evolution of synthetic zeolites is reciprocally developed with the novel zeolite materials and they fulfill the requirements in many industrial applications successfully.

The results of research by using the organic cations during zeolite synthesis led to the discovery of many new zeolites. The most commercially interesting of these is the ZSM type (Zeolite Socony Mobil) developed by Mobil Oil Corp, scientists. ZSM-5 was discovered by Argauer and Landolt (1972), subsequently, ZSM-11 (Chu,1973), ZSM-12 (Rosinski and Rubin,1974), ZSM-21 (1977) and ZSM-34 (Rubin et al., 1978) were described.

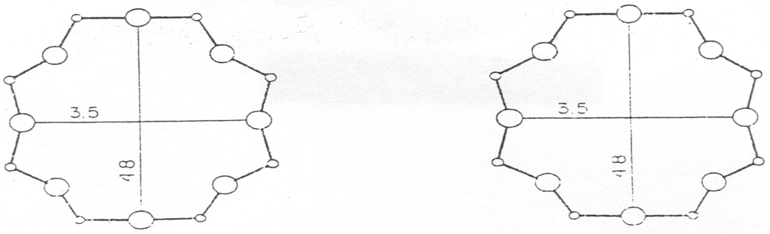
The zeolite *ZSM-35* was first synthesized by Planck, Rosinski and Rubin in 1977 at the Mobil R&D Laboratory in a system containing hexamethylenediamine as an organic template. *ZSM-35* is described as a medium pore zeolite with FER (ferrierite) topology, is composed of 5-, 8-, 10-rings. It has a two-dimensional channel system. The 10MR channels running paralel to the (001) direction are 5.4 × 4.2 Å in diameter and the 8MR channels running paralel to (010) direction are 4.8 × 3.5 Å in diameter (Borade & Clearfield, 1994 , Kıvanç, 1992) (Figure 2.1, 2.2) .



framework viewed along [001]



10-ring viewed along [001]



8-ring viewed along [010]

Figure 2.1 Two-dimensional Channel Structure of Ferrierite
(Borade & Clearfield, 1994)

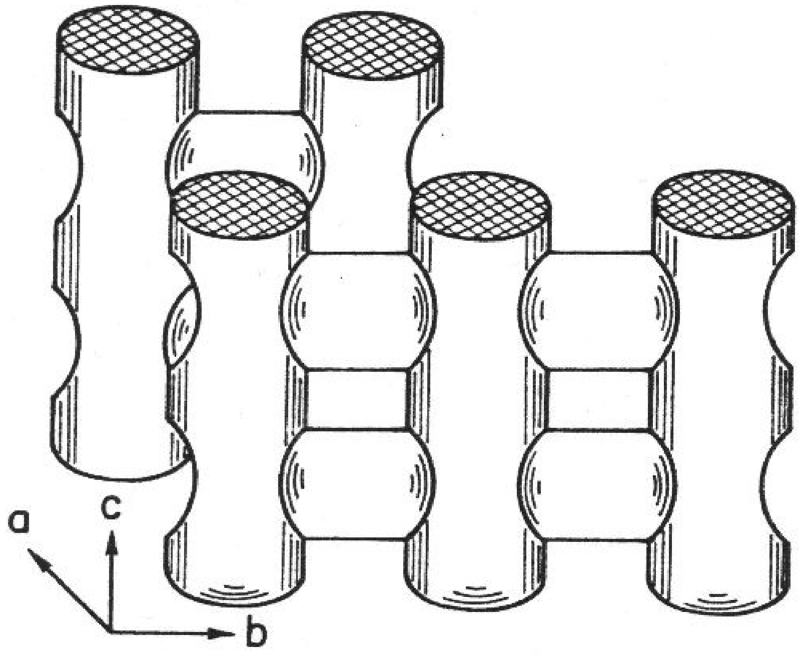


Figure 2.2 Three-dimensional Channel Structure of Ferrierite
(Borade & Clearfield, 1994)

The structure and properties of the molecular sieve product are highly dependent on the physical and chemical nature of the reactants used in preparing the reaction mixture and their pretreatment; the way in which the reactant is made and pretreated and its overall chemical composition; homogeneity or heterogeneity of the mixture; pH of the mixture; low temperature aging of gel; seeding; addition of special additives and temperature, pressure and duration of the hydrothermal treatment.

The pore structure varies greatly from one zeolite to another. In all zeolites, pore diameters are determined by the free aperture resulting from 4, 6, 8, 10 or 12 member rings of oxygen atoms.

The Si/Al ratio is one of the important factors defining the physical and chemical properties of zeolites. If the Si/Al ratio is around 1, this type of zeolites has the highest cation capacity and due to this property they have hydrophilic innersurface. This situation is because of the high electrostatic field gradient of cations placed in the aluminum silicate structure. Hydrophobic properties are observed at Si/Al ratio ≥10.

The zeolite ZSM-35 has Si/Al ratios between 12 and 60 as synthesized and having Na as cation in structure (Borade & Clearfield, 1994; Jacobs & Martens, 1987).

In Table 2.1 Some examples of zeolites with different Si/Al ratios were shown.

Table 2.1. Samples of Zeolites Regarding Si/Al ratios.

Zeolite	**Si / Al Ratio**
Natural Zeolites	
Chabazite	1.6-3
Erionite	2.9-3.7
Clinoptilolite	4.25-5.25
Synthetic Zeolites	
KA	1
NaA	1
CaA	1
X	1-1.5
Y	1.5-3
ZSM-5	>10
ZSM-35	>10

2.2 Adsorption Seperation

The process of adsorption involves separation of a substance from one phase accompanied by its accumulation or concentration at the surface of another. The adsorbing phase is the adsorbent and the material concentrated or adsorbed at the surface of that phase is the adsorbate. Adsorption is thus different from absorption; a process in which material transferred from one phase to another (e.g. liquid) interpenetrates the second phase to form a "solution". The term sorption is a general expression encompassing both processes.

Physical adsorption is caused mainly by van der Waals forces and electrostatic forces between adsorbate molecules and the atoms which compose the adsorbent surface. Thus adsorbents are characterized first by surface properties such as surface area and polarity.

A large specific surface area is preferable for providing large adsorption capacity, but the creation of a large internal surface area in a limited volume inevitably gives rise to large numbers of small pores between adsorption surfaces. The size of the micropores determines the accesibility of adsorbate molecules to the internal adsorption surface, so the pore size distribution of micropores is another important property for characterizing adsorptivity of adsorbents. Especially materials such as zeolite and carbon molecular sieves can be specifically engineered with precise pore size distributions and hence tuned for a particular separation.

2.2.1 Sorption with zeolites

There are two types of adsorption separation with zeolites; regarding pore size of the zeolite (molecular sieving) and selectivity of the surface such as the separation of polar molecules by hydrophilic (low silica) zeolites and less polar molecules by hydrophobic (high silica) zeolites.

Zeolites have uniform pore diameter distribution and these pore diameters may change from 3 to 10 Å. Figure 2.3 shows some zeolite pore sizes versus dimensions of molecules.

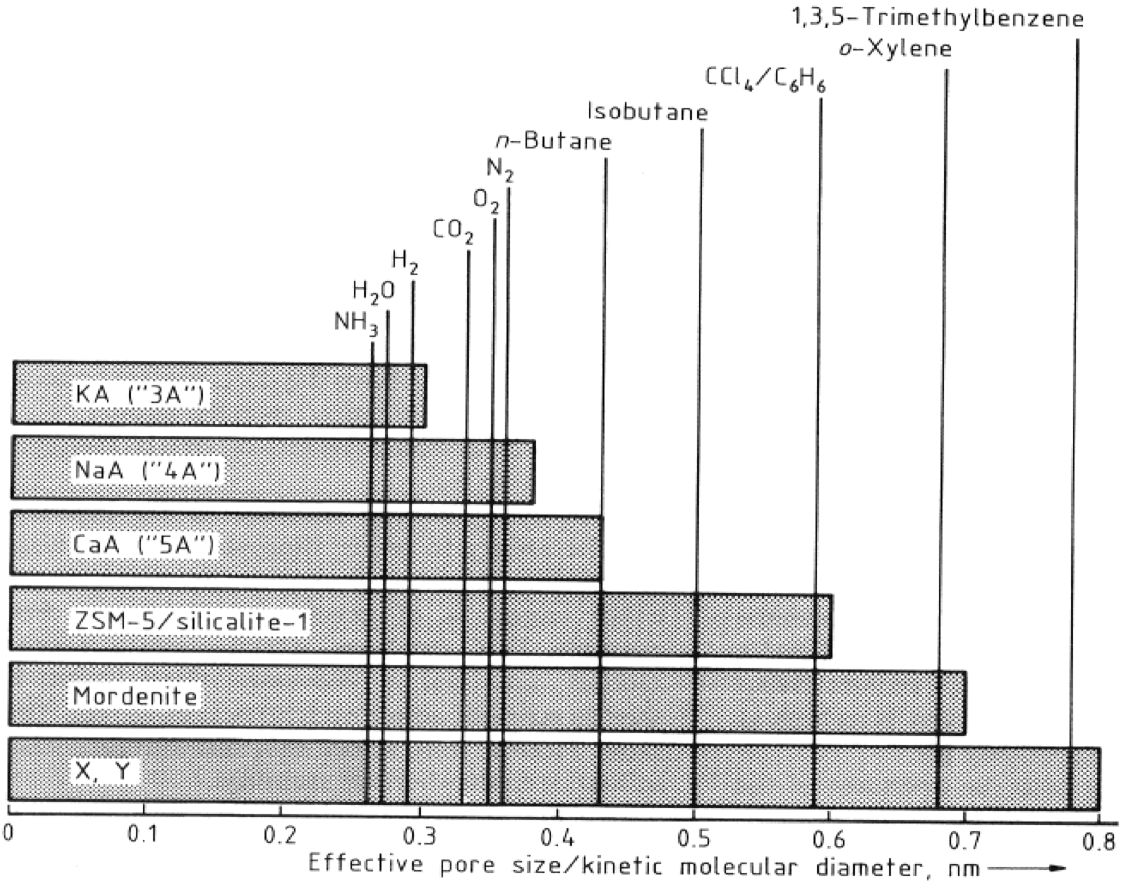


Figure 2.3 Correlation between the effective pore size of industrially important zeolites and the kinetic molecular diameter of selected compounds

at room temperature (Ullmann,1996).

Molecules which are too large to diffuse into the pores are excluded, whereas molecules which have a kinetic diameter smaller than the pore size, diffuse into the pores, adsorb and under certain conditions are capable of undergoing catalytic reactions. This property is called as sieve effect. Bulk separation depends on molecular sieving. For example normal hexane with a kinetic molecular diameter of about 5.1 Å can pass through a 10 ring or larger, whereas cyclohexane with a kinetic molecular diameter of 6.9 Å would be hard pressed to pass through a 10 ring. Thus all other things being equal, a 10-ring zeolite could be used to separate mixtures of normal hexane and cyclohexane (Kokotailo & Meier, 1979; Bhatia, 1990).

Purification separation depends on the surface selectivity. Surface polarity corresponds to affinity with polar substances. Polar adsorbents are thus called "hydrophillic" and aluminosilicates such as zeolites, porous alumina, silica gel or silica-alumina are examples of adsorbents of this type. Low silica zeolites have a high affinity for molecules such as water, ammonia and carbon monoxide and for molecules such as nitrogen and carbon dioxide which have large quadrupole moments. This is because of the ionic structure of the crystal giving rise to a highly non-uniform electrostatic field within the micropores. Molecules which have the ability to interact with this field are therefore adsorbed more strongly then non-polar molecules.

On the other hand, non-polar adsorbents are generally "hydrophobic" carbonaceous adsorbents, polymer adsorbents and silicalite are typical non-polar adsorbents. These adsorbents have more affinity to oil or hydrocarbons than water.

CHAPTER 3

LITERATURE SURVEY

ZSM-35 which is a high silica zeolite with ferrierite topology was first synthesized by Planck, Rosinski and Rubin in 1977 at the Mobil R & D Laboratories in a system containing organic template ethylenediamine or pyrrolidine.

Barrer and Lee (1969) investigated sorption properties of strontium ferrierite in the ion-exchanged crystals (Li, Na, K, Ca and H forms) for O_2, N_2, Ne, Ar, Kr, Xe, CH_4, CO_2, pyrrole, thiophene, benzene, and o-m-p-xylenes. They found that H form had the largest saturation capacities and the capacities of the other monovalent cationic forms decreased as the intracrystalline cations occupied greater volume. However, Sr-form had the greatest capacity and also as the sorbate molecules increased in size ($O_2<N_2<$, Ar<Kr<Xe, CH_4) irregularities appeared in some of the cationic forms. Besides cation size, cation position was an important factor affecting saturation sorption capacity. Also they pointed out that the aromatic hydrocarbons could be unable to penetrate the narrow channels. When CO_2 was the sorbate, a high affinity as shown arising in part from interacting with the large quadrupole of

CO_2.

Kibby et al. (1974) prepared synthetic sodium and sodium-tetramethylammonium ferrierites under hydrothermal conditions at 300-325 °C to investigate the composition, sorption and catalytic properties of these synthetic ferrierites. They concluded that treatment of Na-ferrierite with mineral acids or ammonium ion exchange of calcined Na-TMA-ferrierites produced hydrogen ferrierites with relatively high n-paraffin sorption capacities and cracking activities; the sorption capacities of isoparaffins and aromatics were low in hydrogen ferrierite, and the cracking rates for these compounds could be reduced to low levels by pretreating hydrogen ferrierite at 400-500 °C with toluene. They also found that the cracking activity of hydrogen ferrierite could be greatly reduced by steaming at 750 °C, but this treatment did not significantly alter the sorption selectivities or capacities for n-paraffins: the structure remained intact. In their study, sorption capacities were 0.05-0.09 cm^3/g for light n-paraffins, and 0.002 -0.01 cm^3/g for isoparaffins and aromatics.

Malashevich et al. , in 1981, described the hydrothermal synthesis of ferrierite having a higher silicon-to-aluminum ratio than native ferrierite and presented data on its physicochemical and adsorption properties in relation to the conditions of preliminary thermal and chemical treatment. They calcined the sample at 550 °C. The starting template for synthesis was N-methylpyridium iodine and they carried out an ion exchange in hot HCl solution with 0.5 N HCl and NH_4Cl solution following a recalcination at 550 °C. The sorption properties of ferrierite species with respect to water, hexane and benzene were studied in a vacuum apparatus. They obtained isotherms for water, n-hexane and benzene. The sorption capacities were, 0.09 and 0.05 cm3/g for hexane and water respectively and low for benzene.

Harrison et al. (1987) compared the shape-selective properties of ferrierite, ZSM-5 and ZSM-11 and examined the effect of mixed zeolitic phases on the properties of the resulting catalysts. Characterization of the pore structures of these zeolites was performed by measuring the rates and extents of adsorption of molecules of different kinetic diameters. The results were consistent with the reported pore dimensions of the three zeolites. Molecules with kinetic diameters less than the zeolite pore dimensions are readily adsorbed. In contrast, the sorption of molecules with dimensions similar to those of the channel openings is subject to diffusion control. Molecules with dimensions greater than the pore openings were effectively excluded from the intracrystalline pore structure of zeolite. The sorption data recorded for ferrierite revealed that water and methanol are more rapidly adsorbed than the hydrocarbon species. This was attributed in part to the decreased hydrophobicity of ferrierite relative to ZSM-5 and ZSM-1, but moreover from the ability of the water and methanol molecules to diffuse into both 8- and 10-membered ring channels, while only the 10-membered ring channels are accessible to the larger hydrocarbon species. Molecules with dimension greater than 0.5 nm are effectively excluded from the intracyrstalline pore structure, in agreement with the reported pore dimensions of ferrierite.

Karslı in 1990, worked on H-forms of synthetic ferrierite by using water, propane, hexane, o-m-p-xylenes and methanol as sorbents. He obtained isotherms for mentioned liquid vapors and gases at 25 °C. He observed that the sorption rates of propane, hexane, o-m-p-xylenes were very slow as compared to those of water and methanol and added that the sorption capacities of o-m-p-xylenes are very low. He furthermore mentioned that although the hexane molecules has the same kinetic diameter as propane, the diffusion of hexane is faster than that of propane.

Shashikala et al., in 1991, synthesized zeolite ZSM-35 with ferrierite structure having silica:alumina ratio of 22.5 hydrothermally using pyrrolidine as the template. As-synthesized samples are characterized with X-ray diffraction, IR spectroscopy and SEM methods. They calcined samples at 600 °C for 12 h followed by ion exchange with ammonium nitrate and recalcination. The catalytic experiments were carried out in a quartz reactor. They concluded that, the acid form, HZSM-35, showed exceptionally high para selectivity in ethylbenzene disproportionation , but deactivated rapidly due to coking. A mixture of HZSM-35 with 10% HZSM-5 showed much better stability while retaining high para selectivity. Isomerization of m-xylene yielded p-xylene with high selectivity. The unique pore structure of ZSM-35 is responsible not only for its high para selectivity, but also for rapid coking, leading to deactivation.

Kıvanç, in 1992, investigated the sorption properties of synthetic and natural ferrierite and their H-forms for water, methanol, ethanol, hexane and toluene. He measured the sorption isotherms and uptake curves of these sorbates at room temperature. He observed that the cations present in ferrierite samples influence the sorption capacity and rate of sorption. For synthetic ferrierite, replacing the original cations potassium and sodium by hydrogen increase the sorption capacity of all sorbates studied but to different extents. He concluded that ferrierite samples have the highest capacity for water and methanol which are sorbed very rapidly; for ethanol, hexane and toluene the rates of sorption are considerably slower. He also concluded that water and methanol diffuse into both of the 8- and 10-membered ring channels wheras ethanol and toluene are essentially excluded from the smaller 8-membered ring channels.

Öztin (1997) worked on the sorption of ZSM-35 (Na- and H-form) for methanol, water, hexane, benzene, ethylbenzene, o-, m-, p-xylene . ZSM-35 samples had the highest sorption capacity for water and methanol that were sorbed very rapid. The methanol sorption capacity of NaZSM-35 was 0.1218 cm^3/g corresponding to 78 % the total pore volume at 25 ºC and $P/P_0=0.5$.

Tütüncü (2003) worked on the sorption of Na and H ZSM-35 for methanol and ethanol at four different temperatures (0 ºC, 23 ºC, 40 ºC, 60 ºC). Na form of ZSM-35 showed higher sorption capacity than H form. Also, the sorption capacity of ZSM-35 for ethanol was observed to be higher than for methanol. 73.7 % of the total pore volume was filled with methanol at $P/P_0=0.5$.

Coşkun (2003) worked on the sorption of Na ZSM-35 for methanol. The methanol sorption capacity of NaZSM-35 was 0.1380 cm^3/g corresponding to 88.4 % the total pore volume at 25 ºC and $P/P_0=0.5$.

CHAPTER 4

EXPERIMENTAL

4.1 Materials

The ZSM-35 sample used in sorption experiments resulted from a particular batch obtained in a previous study by Coşkun (2003) at METU Chemical Engineering Department. The procedure was decribed briefly below:

Coşkun's (2003) study on crystallization field of ZSM-35 was carried out for the purpose of synthesizing pure and highly crystalline ZSM-35 products from an aqueous gel composition of 1.85 $Na_2O.Al_2O_3.x\ SiO_2.592\ H_2O$. 19.7 R, where $10<x<25$ and R is pryrolidine (Py) or ethylenediamine (ED). The temperature range of crystallization was from 150 to 225 °C and the crystallization period was in the range of 0 to 480 hours. The basis of these conditions for that particular batch were $x= 15.2$, $T=177$ °C and $t= 240$ hours and the template was ethylenediamine. The raw materials used in Coşkun's (2003) study for the synthesis were collodial silica (LUDOX AS-30, 30 wt. % SiO_2, Aldrich, lot no: 02302DO), sodium hydroxide (pure pellets, Merck, lot no: B102362 802), aluminum hydroxide (pure powder, Merck, lot no: K24826491 817), pyrrolidine (99 %, Aldrich, lot no: S055094-061) and ethylenediamine (99.5 %, Aldrich, lot no: 01746DI-081).

ZSM-35 with SiO_2/Al_2O_3 ratio 19 was identified by XRD pattern and SEM micrographs by Coşkun (Coşkun , 2003).

The sorbates were used without any purification step. Sorbates used in these analyses were methanol (J.T. Baker, 99.8+%, lot no: 0417640002), ethanol (absolute, Gurup Deltalar, 99.5%, lot no: ASO 55-L 50), propan-1-ol (anhydrous, Acros, 99.8+%, lot no: A019329501), propan-2-ol (anhydrous, Acros, 99.8+%, lot no: A019329501), n-butanol (J.T. Baker, 99.4%, lot no: 0216510014). Vapor pressures and liquid densities of sorbates are given in Table A-1 and A-2, respectively. Also the kinetic diameters of probe molecules are given in Appendix B.

4.2 Conversion to H form

Some of the calcined sample (NaZSM-35) was converted into H-form by the ion exchange method:

A sufficient amount of ZSM-35 sample (200-250 mg) was placed in a test tube and 25 ml of 1 N NH_4Cl solution was added. After mixing for 24 hours at room temperature the centrifuged effluent solution was analyzed for Na^+ by a Flame Photometer (Jenway PFP7). This procedure was repeated until no Na^+ was detected. After the ion exchange was completed , the sample was washed with deionized water, filtered, dried and recalcined for the removal of the ammonia and this sample was denoted as

HZSM-35, and calcined, as-synthesized ZSM-35 was denoted as NaZSM-35.

4.3 Apparatus for Sorption Measurements

The adsorption isotherm is generally determined by one of two methods:

The first method, the volumetric method, determines the quantity of gas present in the system by measuring the pressure, volume and temperature. After exposing the activated adsorbent to a quantity of gas in the closed system, the adsorbed quantity is determined from the pressure, temperature and volume when the equilibrium is reached.

The second method, the gravimetric method, measures the amount of gas or vapor adsorbed by weighing the sample in a closed system on a balance (Barrer, 1978).

For the measurement of equilibrium sorption capacities and rates of sorption, the weight change as a function of time was measured for methanol, ethanol, propan-1-ol, propan-2-ol and n-butanol on zeolite ZSM-35 with an electrobalance.

4.3.1 Apparatus

The expertimental apparatus comprised of recording microbalance enclosed in a vacuum chamber, a combined rotary and diffusion high vacuum pump unit (Edwards) was used as high vacuum pump unit, an electronic manometer

(Datametrics), two doser chambers, a liquid sorbate tube, a thermostat (Grant), temperature monitor (Comark). The measurements performed at -20 °C, 0 °C, 25 °C and 50 °C in a conventional gravimetric adsorption system which was used in the study of Öztin (1997) is shown in Figure 4.1.

The microbalance was Cahn R.G. automatic recording electrobalance. The ultimate sensitivity of the balance is 10^{-4} mg. The time constant changes from 0.068 to 0.5 second depending on the filter setting. The output of the electrobalance was fed to a strip chart recorder (BBC Goerz).

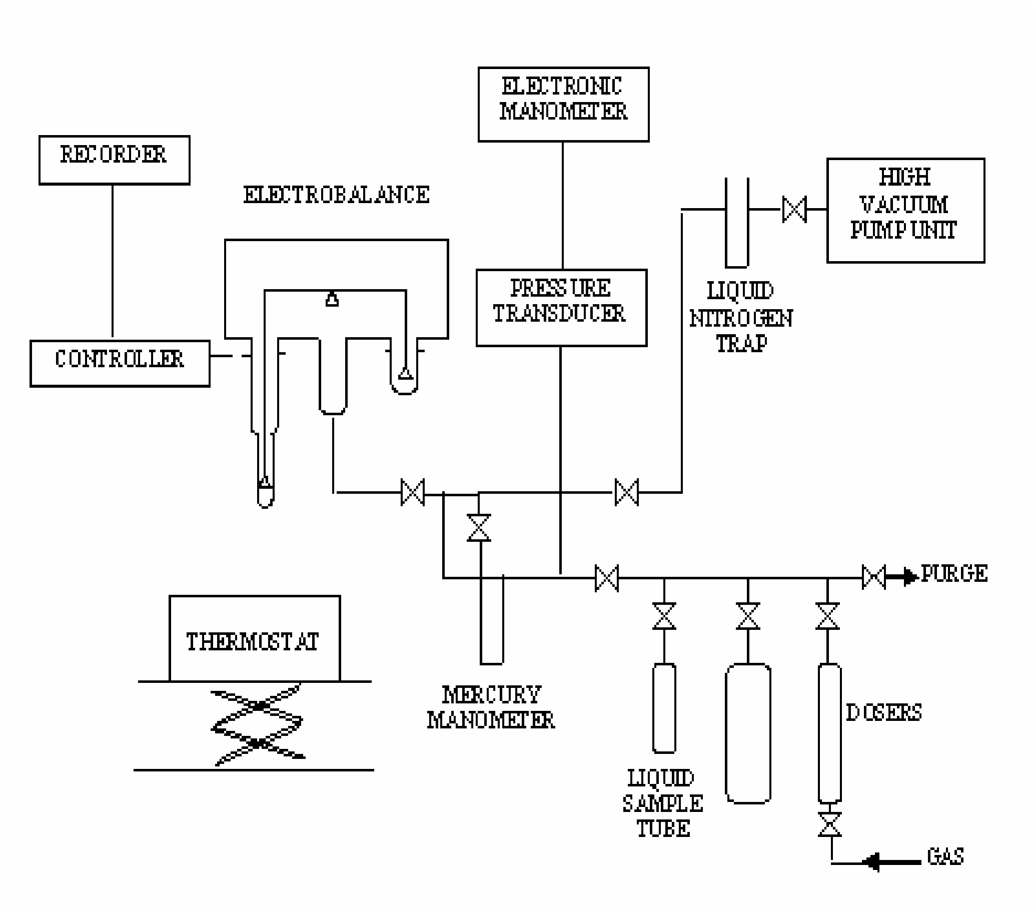


Figure 4.1 Schematic Diagram of Sorption Apparatus

1 - 4 mg sensitivity for the recorder range (100 divisions) was used in the experiments. The chart speed of the recorder could be varied between 3 cm/hr and 60 cm/min. For the step change of sorbate pressure, the rapid chart speed values were used to observe kinetics of the sorption on the zeolite sample.

The vacuum chamber contained the beam of the balance with a volume of nearly 3 liters. The sample pan was attached vertically to the beam of the electrobalance by a nichrome wire in a hangdown tube about 60 cm long and 2 cm in diameter. By this way, the zeolite sample could be immersed in a thermostat for the sorption experiments to fix the temperature or in a furnace for the regeneration of the fresh and used zeolite samples.

A liquid nitrogen trap was also used to prevent back diffusion of pump oil vapor into the sorption chamber, and by this way the intensive coke deposition on the zeolite could be reduced during regeneration.

Apiezon M and Silicone High Vacuum Grease (Edwards) were used to seal the glass stopcocks and all glass joints. These greases were recommended because of their low vapor pressures 10^{-8} and 10^{-7} torr at 25^0C, respectively (Cahn Electrobalance &Weighing Unit Manual#6).

4.3.2 Regeneration of Zeolite Samples

The rates of sorption in zeolites are strongly influenced by traces of moisture, or other adsorbed species. Since the regeneration procedure and purity of sorbates are very critical for obtaining reliable and reproducible rate measurements, before each sorption experiment the zeolite samples were degassed. For regeneration the sample, a Furnace (Ventron Outgassing, Model 330), Temperature Programmer (Cahn, Model 3600) was used. A digital Thermometer (Comark 6600 Microprocessor Scanning) was used to observe the temperature of the furnace during the regeneration process.

In order to regenerate the sample, the tube enclosing the ZSM-35 was inserted into the outgassing furnace and by the temperature programmer heating was started. During regeneration, the temperature of the zeolite was increased up to 430 °C under vacuum. The rate of heating was not constant but varied between 1-6 ^{0}C/min.

4.3.3 Experimental Procedure for Sorption Experiments

The sorption capacities and the sorption rates of zeolite ZSM-35 for probe molecules methanol, ethanol, propan-1-ol, propan-2-ol and n-butanol have been determined by using gravimetric method with an electrobalance system as described before.

It was necessary to give a step change to sorbate pressure in a relatively short time. The sorbate pressure was increased by opening the valve to the doser chamber containing the sorbate. Sorption proceeded in a closed system where the pressure remained essentially constant since the amount of vapor sorbed by the sample was small compared to the amount in sorption chamber. For some runs the sorbate pressure was increased in a stepwise manner for the purpose of obtaining equilibrium data with liquid sorbates. The sorbate was put the liquid sample tube and the space above the liquid was evacuated to remove air over the liquid sample.

At first, the electrobalance was calibrated according to procedure given in Cahn Electrobalance & Weighing Unit Manual #6.

About 30 mg zeolite sample was put in the aluminum sample pan attached to the weighing arm of the electrobalance. System was evacuated by using rotary pump up to the lowest value 10^{-2} torr and 10^{-3} torr. When the system reached the possible lowest pressure heating of the sample was started. When it reached about 430 ^{0}C, diffusion pump is started. The initial degassing took almost a day to reach vacuum at the lowest value about 10^{-5} torr. It was usually sufficient to wait 5 or 6 hours for subsequent regeneration processes. Before heating, the sample tube was immersed in the furnace. After completion of regeneration almost at about 430 ^{0}C, the furnace was isolated and the sample was cooled to room temperature. After 20 or 25 minutes, the sample was immersed into thermostat to keep the sample at adsorption temperature. Four different temperatures (-20 ^{0}C, 0 ^{0}C, 25 ^{0}C, 50 ^{0}C) were used in these experiments.

The sorbate was introduced to the sorption chamber quickly by means of the stopcock. When the sorbate pressure reached to the desired value the doser chamber was isolated by means of the stopcocks.

At the same time when the sorbate was loaded to the system, the recorder was started and the weight change of the zeolite sample was recorded as a function of time with suitable chart speed and recorder range. When the line on the recorder chart observed as constant, it indicated that the equilibrium was reached at that pressure and temperature.

The regeneration procedure was followed before each adsorption experiment.

CHAPTER 5

RESULTS AND DISCUSSIONS

5.1 Sorption on ZSM-35

The adsorption properties of zeolites may be influenced by the type and number of cations present in the framework structure. It is known that sorption capacities of ferrierite type zeolites containing exchangeable cations can be improved by replacing the cations by hydrogen ions. This replacement can be achieved by acid treatment or by exchange with ammonium ion followed by calcination to remove ammonia (Karslı, 1990). With this idea, ZSM-35, a high-silica zeolite belonging to the ferrierite family was ion-exchanged, and that made it possible to do some sorption experiments both with hydrogen and sodium forms of ZSM-35.

The uptake curves and equilibrium sorption capacities for propan-1-ol, propan-2-ol and butanol on both sodium (Na) and hydrogen (H) forms of ZSM-35 were measured at 0°C, 25°C and 50°C. The uptake curves and equilibrium sorption capacities for methanol and ethanol on hydrogen (H) form of ZSM-35 were measured at -20°C, 0°C, 25°C and 50°C.

5.1.1 Methanol and Ethanol Sorption on HZSM-35

As mentioned in section 2.1, Ferrierite contains two channel systems. 10 membered ring channel system paralel to the (001) direction with dimensions 5.4 × 4.2 Å in diameter is reported to have a volume of 0.1000 cm^3/g. The other channel system; 8 membered ring paralel to the (010) direction with dimensions 4.8 × 3.5 Å in diameter is reported to have a volume of 0.056 cm^3/g (Jacobs and Marten; 1987).

It would be desirable to know the relative occupancies of the channel systems for the sorbates studied. Volumetric sorption capacities of alcohols are given in Table 5.1 where the percent volume filling is also shown in order to assess the ability of the molecules to occupy the channels of *ZSM-35.* The volumetric capacity was calculated by the following way: The difference of the weight over the zeolite comes from the sorbed alcohol. This weight converted to volume by using the density of the normal liquid alcohol at the temperature of adsorption.

If the sorbed volume of sorbate is close to the total pore volume of *ZSM-35,* it indicates that the molecule can diffuse and are sorbed into both 10 and 8 membered ring channels of *ZSM-35.*

Table 5.1 Limiting Equilibrium Sorption Capacities of HZSM-35 for Methanol and Ethanol.

Zeolite	Temperature (°C)	Methanol Adsorption			Ethanol Adsorption		
		Adsorbed volume of sorbate (cm^3/g)	% filling of total volume	% filling of 10 MR volume	Adsorbed volume of Sorbate (cm^3/g)	% filling of total volume	% filling of 10 MR volume
HZSM-35	-20	0.1656	105	164	0.1248	80	125
	0	0.1568	101	157	0.1572	101	158
	25	0.1462	94	148	0.1544	99	154
	50	0.1273	82	128	0.1507	97	151

As seen from Table 5.1 the highest methanol sorption capacity was found as 0.1656 cm^3/g at -20°C and for ethanol the highest sorption capacity was found as 0.1572 cm^3/g at 0°C. These capacities are greater than the volume of total capacity of the zeolite showing that both methanol and ethanol fills 10 membered ring channels and 8 membered ring channels.

The sorption capacities (in cm^3/g) decrease while the temperature increase for HZSM-35 for both methanol and ethanol sorption except at -20°C for ethanol.

For the other experimental temperatures, again it was observed that sorption capacities are greater than the volume of 10 membered rings, these results show that both methanol and ethanol fills 10 membered ring channels and 8 membered ring channels partially.

Uptake curves of methanol and ethanol sorption on HZSM-35 at different temperatures are given in Figures 5.1 and 5.2, respectively. These curves (Figures 5.1 and 5.2) give mg sorbate / g sorbent as a function of time.

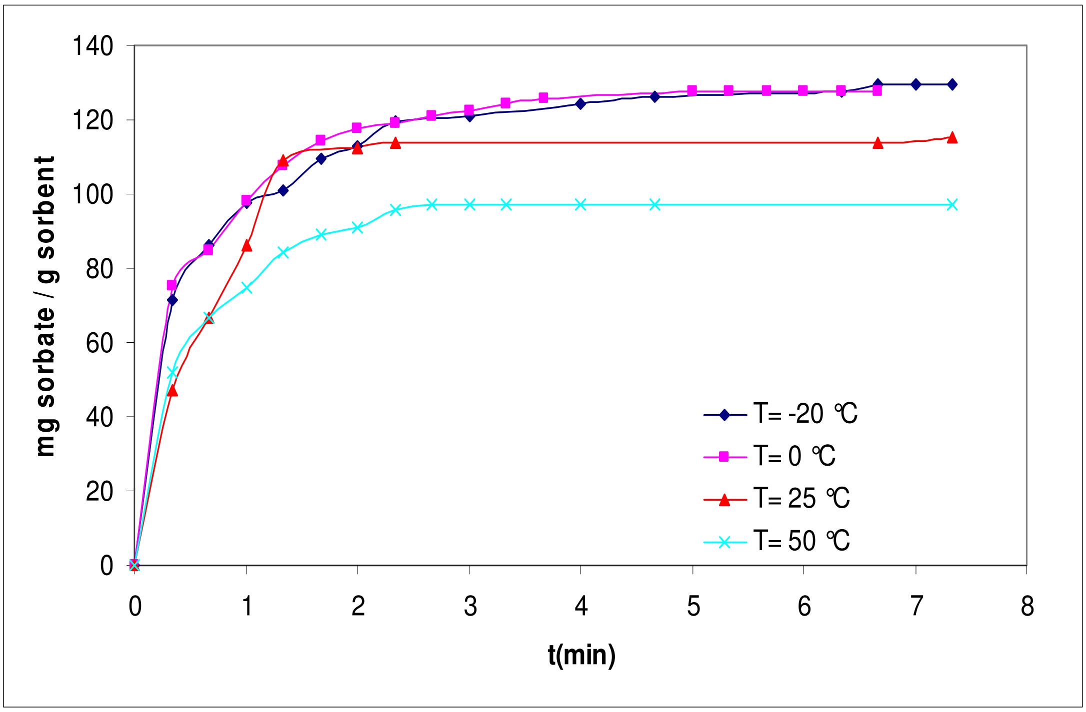


Figure 5.1 Methanol Uptake Curves in HZSM-35 at different temperatures

($P_{f,-20°C} = P_{o,-20°C} / 2$, $P_{f,0°C} = P_{o,0°C} / 2$, $P_{f,25°C,\ ,50°C} = P_{o,25°C} / 2$)

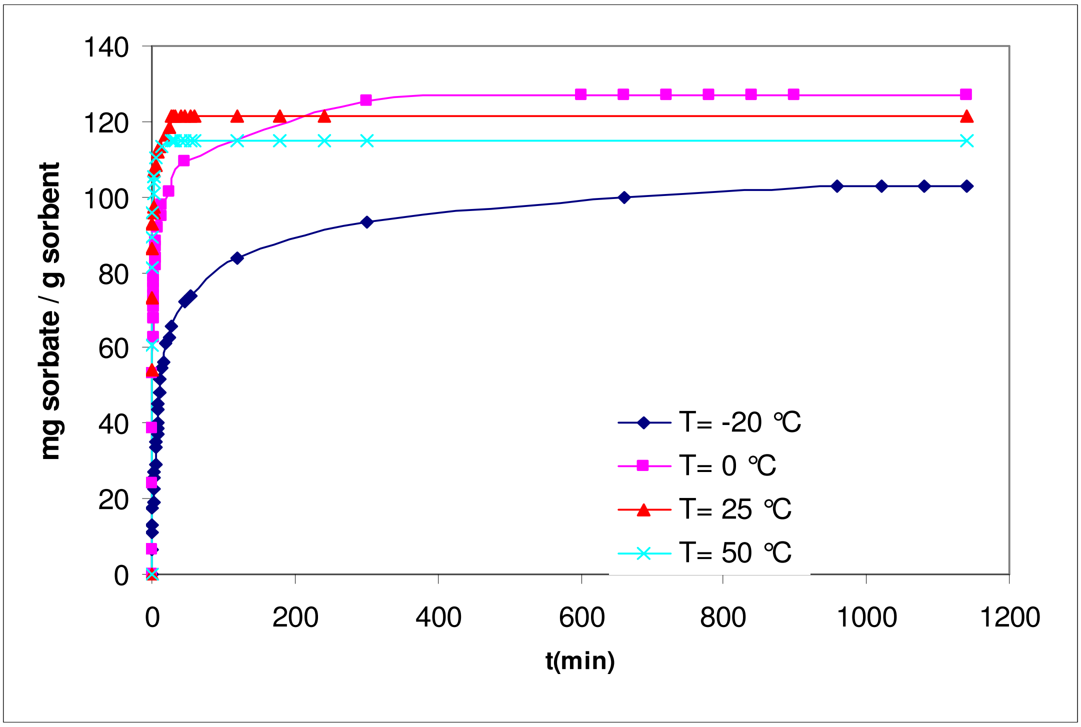


Figure 5.2. Ethanol Uptake Curves in HZSM-35 at different temperatures

($P_{f,-20°C} = P_{o,-20°C} / 2$, $P_{f,0°C} = P_{o,0°C} / 2$, $P_{f,25°C,\ ,50°C} = P_{o,25°C} / 2$)

Figure 5.1 indicate that at all temperatures, in about 5 min methanol - HZSM-35 system reached equilibrium.

On the other hand at -20°C & 0 °C ethanol - HZSM-35 system reached its equilibrium sorption capacities after 16 h and 10 h respectively. At 25 °C & 50 °C ethanol-H ZSM-35 system reached its equilibrium sorption capacities after 26 min. It is seen that the sorption rate of ethanol- H ZSM-35 system become faster while the temperature increase.

At the same temperatures, the methanol sorption rate is faster than ethanol on HZSM-35. The lowest rate of adsorption was obtained for ethanol on HZSM-35 at -20°C. It took about 16 h to reach equilibrium and the fastest rate of adsorption was obtained for methanol on HZSM-35 at 25°C. It took about 2.3 min to reach equilibrium.

Methanol and ethanol adsorption capacity of HZSM-35 (0.1462 and 0.1544 cm^3/g) at 25°C and $P/P_o=0.5$ can be compared with some previous studies for ZSM-35 and its analogs like ferrierite. These similar studies in the literature are shown in Table 5.2.

Table 5.2 Selected Sorption Studies on Ferrierite Type Zeolites

Study by	Experimental Conditions	Sorbent	Sorbate	Equilibrium capacity
Harrison et al., 1987	23°C and $P/P_0=0.5$	Synthetic H-Ferrierite	methanol	0.1357
Kıvanç, 1992	25°C and $P/P_0=0.5$	Natural H-Ferrierite	methanol	0.0757
			ethanol	0.0536
	25°C and $P/P_0=0.5$	Synthetic H-Ferrierite	methanol	0.1268
			ethanol	0.0789
Karslı, 1990	25°C and $P/P_0=0.5$	Synthetic H-Ferrierite	methanol	0.1200
Öztin, 1997	25°C and $P/P_0=0.5$	HZSM-35	methanol	0.1186
Tütüncü, 2003	23°C and $P/P_0=0.5$	HZSM-35	methanol	0.0906
			ethanol	0.0963
Coşkun, 2003	25°C and $P/P_0=0.5$	NaZSM35	methanol	0.1380
This study	25°C and $P/P_0=0.5$	HZSM-35	methanol	0.1462
			ethanol	0.1544

Study of Long et aL. (2000) showed that the adsorption capacities of H ferrierites obtained by different acid treatment and/or calcination for methanol at P/P_0 =0.6 and 30°C varies in the range between 0.072 and 0.088 cm^3/g. They claimed that they determined the microporous volume of samples with the adsorption of nitrogen at 77 K and it changes from 0.115 to 0.138 cm^3/g. From their adsorption isotherms of methanol for P/P_0 =0.5 at 30°C the adsorption capacity was nearly the same as P/P_0 =0.6.

In our study and Coşkun's study, the same sample of ZSM-35 were investigated , but in Coşkun's study NaZSM-35 was investigated that it helps us in a way to compare the methanol sorption capacity on Na and H forms of ZSM-35. It can be seen that there are some differences. The methanol adsorption capacity on NaZSM-35 was 0.1380 cm^3/g at 25 ºC, in Coşkun's study; and the methanol adsorption capacity on HZSM-35 was 0.1462 cm^3/g at 25 ºC, in this study. It is seen that whether the cation content of ZSM-35 is Na or H the sorption capacity of methanol is greater than the volume of 10 MR of the zeolite at 25 ºC. The differerence between the sorption capacities come from the different cation type.

Harrison et al., (1987) showed that methanol sorption capacity on synthetic ferrierite at 23°C and P/P_0 =0.5 was 0.1357 cm^3/g and in Kıvanç's study (1992) the H form of synthetic ferrierite had capacity for methanol at about 0.1268 cm^3/g. On the same sample which was used in Kıvanç's study, Karslı found methanol limiting sorption capacity for H form of synthetic ferrierite as 0.1200 cm^3/g. In this study, the value for methanol adsorption capacity was found for ZSM-35 as *0.1462* cm^3/g at 25° C which is greater than the studies mentioned before. The differences between the studies may be explained by the differences of the structure of the zeolite due to the source of silica and alumina used in the synthesis and Si/Al ratios of zeolite samples. Si/Al ratios are 18.9 for Harrison's study, 8.82 for Kıvanç's study.

Also, Öztin (1997) studied methanol sorption capacity on HZSM-35 at 25°C and P/P_0 =0.5 which was found as 0.1186 cm^3/g. In Tütüncü's (2003) study, the HZSM-35 had capacity for methanol and ethanol at 23°C and P/P_0 =0.5 as 0.0906 cm^3/g and 0.0963 cm^3/g respectively.

There may be some reasons for the differences between literature values and our results at room temeperature. The nature and locations of the cations in the zeolite channels, and also treatments to exchange cations are not same. This makes the structure-based differences (Breck, 1974).

One of the important point is the synthesis process and the preparation of the synthesis mixture. A variation occurred in process parameters changes the product properties, moreover the product. Therefore, the composition and the homogeneity of the synthesis mixture, chemical nature of the reactants, crystallization temperature, crystallization period, crystallization, the template molecule, and pH of the system are the main factors affecting the zeolite product where all those differences may affect the sorption capacities (Breck, 1974).

During the regeneration step there may be coke deposition which may occur irreversible changes on structure of zeolite that this may effect the sorption properties of zeolite for sorbates.

5.1.2 Propan-1-ol, Propan-2-ol, n-Butanol Sorption on ZSM-35

There were several studies of sorption of methanol and ethanol on ferrierite type zeolites but it would be interesting to observe the effects of chain length on the sorption rate and equilibrium behaviour of much longer chain and more branched type of alcohols on Ferrierite type of zeolite, ZSM-35.

The probe alcohol molecules used were propan-1-ol, propan-2-ol, n-butanol. The uptake curves and equilibrium sorption capacities for propan-1-ol, propan-2-ol and butanol on sodium (Na) and hydrogen (H) forms of ZSM-35 were measured at 0°C, 25°C and 50°C.

In Table 5.3 and 5.4 the percent volume filling is also shown in order to assess the ability of the molecules to occupy the channels of *ZSM-35.* If the sorbed volume of sorbate is greater than the total pore volume of *ZSM-35,* it indicates that the molecule can diffuse and are sorbed into both 10 and 8 membered ring channels of *ZSM-35.*

Table 5.3 Limiting Equilibrium Sorption Capacities of NaZSM-35 for Propan-1-ol, Propan-2-ol, n-Butanol.

	Temperature (°C)	Propan-1-ol Adsorption			Propan-2-ol Adsorption			n-Butanol Adsorption		
		Adsorbed volume of sorbate *cm^3/g*	% filling of total volume	% filling of 10 MR volume	Adsorbed volume of sorbate *cm^3/g*	% filling of total volume	% filling of 10 MR volume	Adsorbed volume of sorbate *cm^3/g*	% filling of total volume	% filling of 10 MR volume
Na form of ZSM-35	0	0.046	29	46	0.012	8	12	0.031	20	31
	25	0.043	28	43	0.006	4	6	0.027	17	27
	50	0.034	22	34	0.003	2	3	0.024	15	24

Table 5.4 Limiting Equilibrium Sorption Capacities of HZSM-35 for Propan-1-ol, Propan-2-ol, n-Butanol.

	Temperature (°C)	Propan-1-ol Adsorption			Propan-2-ol Adsorption			n-Butanol Adsorption		
		Adsorbed volume of sorbate *cm^3/g*	% filling of total volume	% filling of 10 MR volume	Adsorbed volume of sorbate *cm^3/g*	% filling of total volume	% filling of 10 MR volume	Adsorbed volume of sorbate *cm^3/g*	% filling of total volume	% filling of 10 MR volume
H form of ZSM-35	0	0.102	65	102	0.026	17	26	0.045	29	45
	25	0.100	64	100	0.021	13	21	0.090	58	90
	50	0.099	63	99	0.068	43	68	0.041	26	41

As seen from Table 5.3 and 5.4, among the probe molecules, propan-1-ol, propan-2-ol, n-butanol, the highest equilibrium sorption capacities on HZSM-35 and NaZSM-35 were found for propan-1-ol. The highest equilibrium sorption capacities of propan-1-ol were 0.1020 cm^3/g and 0.055 cm^3/g on H- and Na-form of ZSM-35 respectively.

The results of this experimental study indicated that limiting sorption capacities decreased as temperature increased for NaZSM-35 and HZSM-35 for propan-1-ol.

Also for propan-2-ol & NaZSM-35 system, limiting sorption capacities decreased as temperature increased but there is an exceptional case at 50°C for propan-2-ol & HZSM-35 system.

When these capacities are compared with the volume of 10 membered rings, these results show that only propan-1-ol fills 10 membered ring channels completely.

It was observed that the sorption capacity of HZSM-35 were somewhat greater at all temperatures for all probe molecules, propan-1-ol, propan-2-ol and n-butanol (Table 5.3 and Figure 5.3 - Figure 5.14). Uptake curves of propan-1-ol, propan-2-ol and n-butanol sorption on NaZSM-35 and HZSM-35 at different temperatures are given in Figure 5.3 - Figure 5.11, respectively.

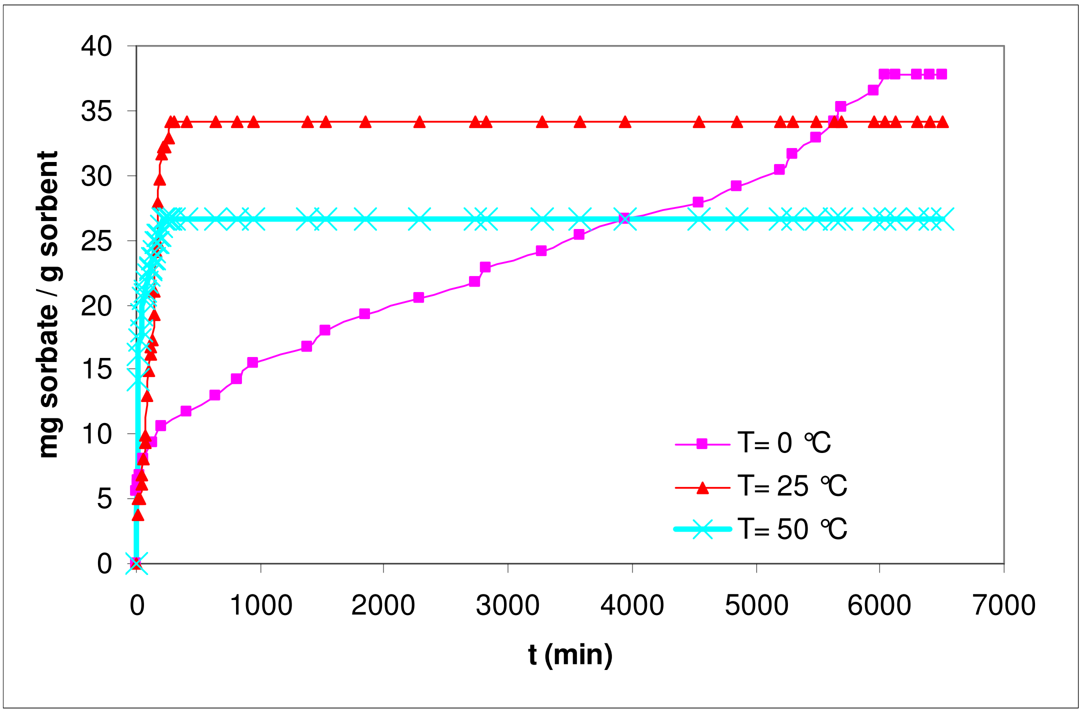


Figure 5.3 Propan-1-ol Uptake Curves in NaZSM-35 at different temperatures ($P_{f,0°C} = P_{o,0°C} / 2$, $P_{f,25°C,\ ,50°C} = P_{o,25°C} / 2$)

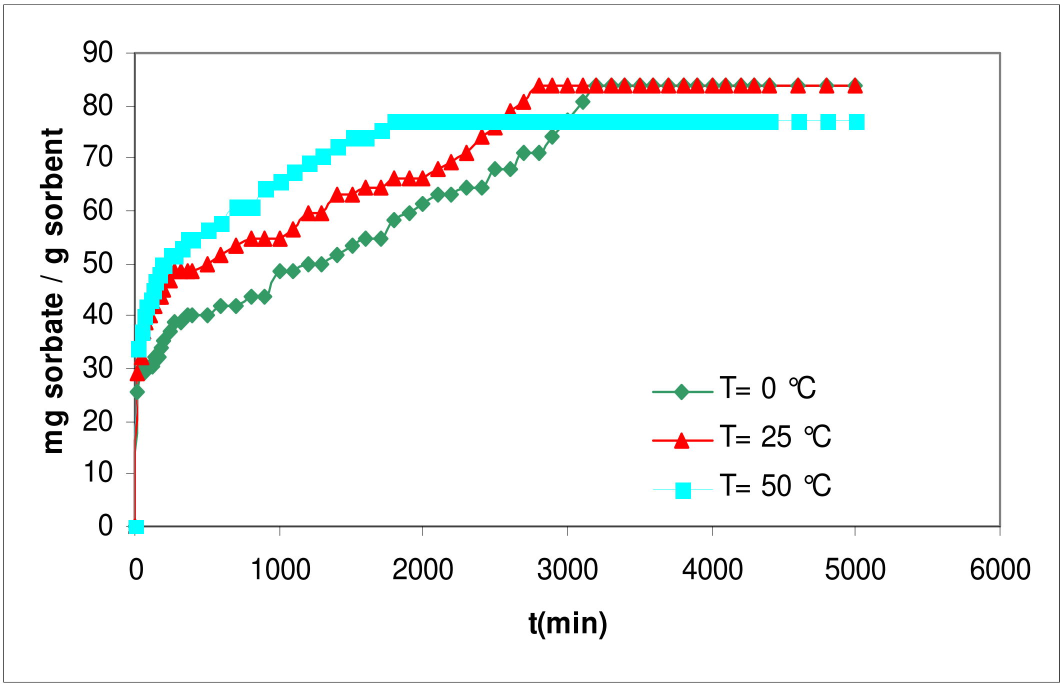


Figure 5.4 Propan-1-ol Uptake Curves in HZSM-35 at different temperatures ($P_{f,0°C} = P_{o,0°C} / 2$, $P_{f,25°C,\ ,50°C} = P_{o,25°C} / 2$)

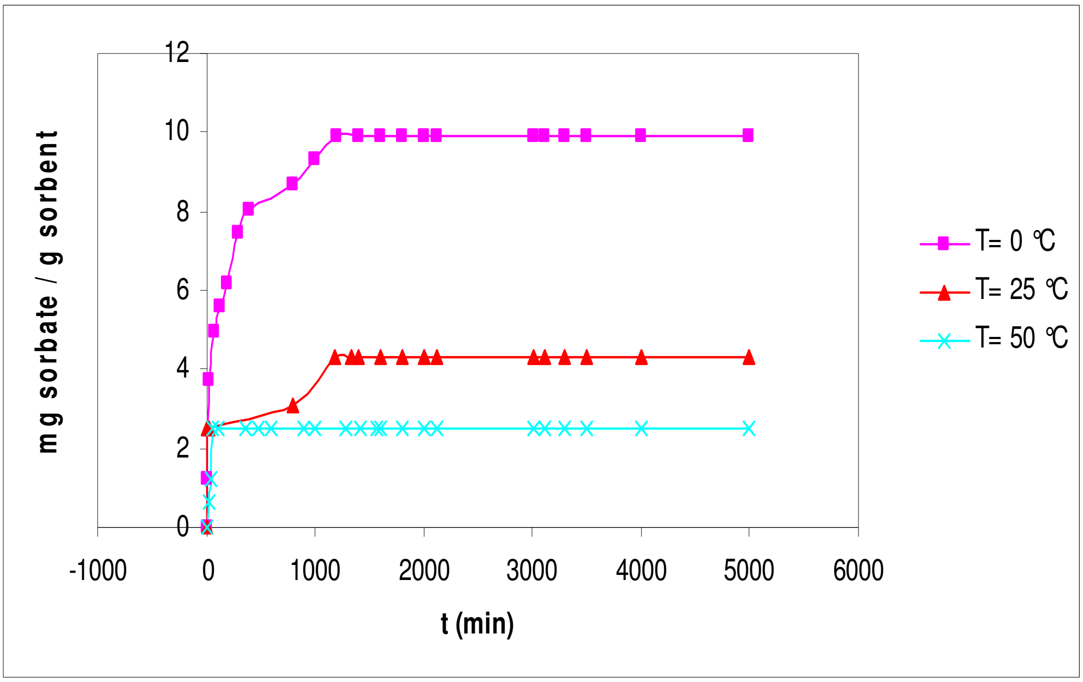


Figure 5.5 Propan-2-ol Uptake Curves in NaZSM-35 at different temperatures ($P_{f,0°C} = P_{o,0°C} / 2$, $P_{f,25°C, ,50°C} = P_{o,25°C} / 2$)

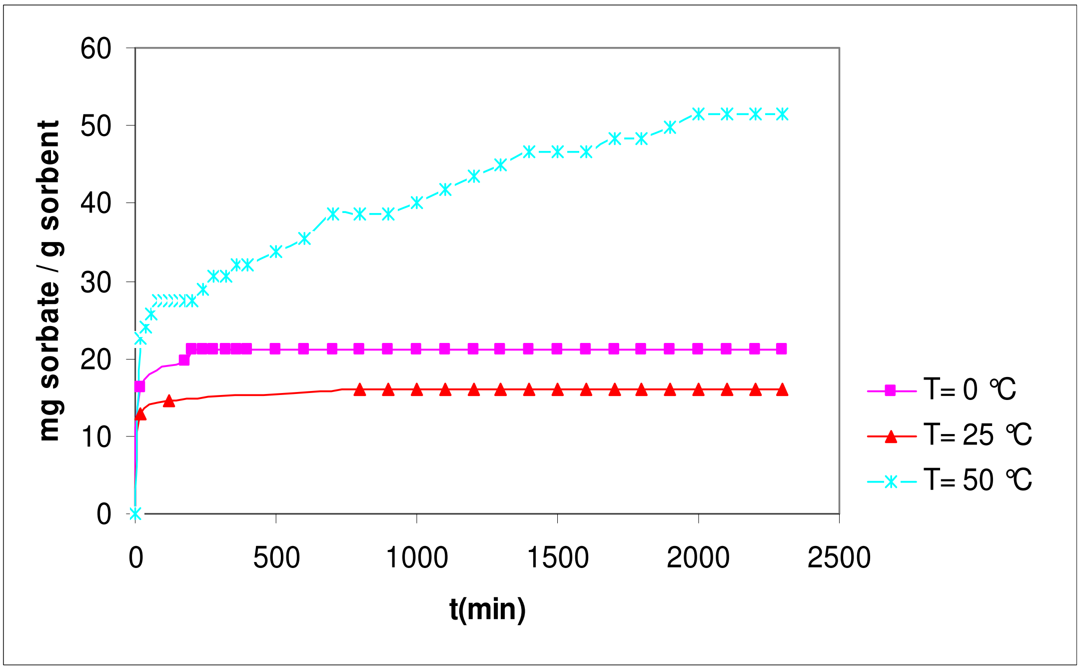


Figure 5.6 Propan-2-ol Uptake Curves in HZSM-35 at different temperatures ($P_{f,0°C} = P_{o,0°C} / 2$, $P_{f,25°C, ,50°C} = P_{o,25°C} / 2$)

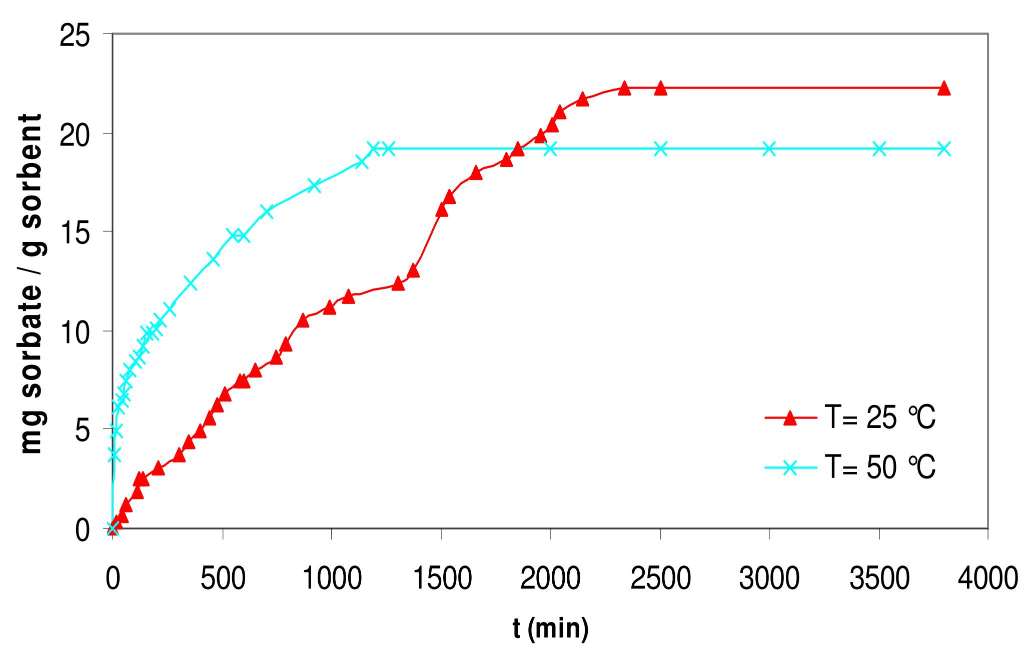


Figure 5.7 n-butanol Uptake Curves in NaZSM-35 at different temperatures
($P_{f,0°C} = P_{o,0°C} / 2$, $P_{f,25°C, ,50°C} = P_{o,25°C} / 2$)

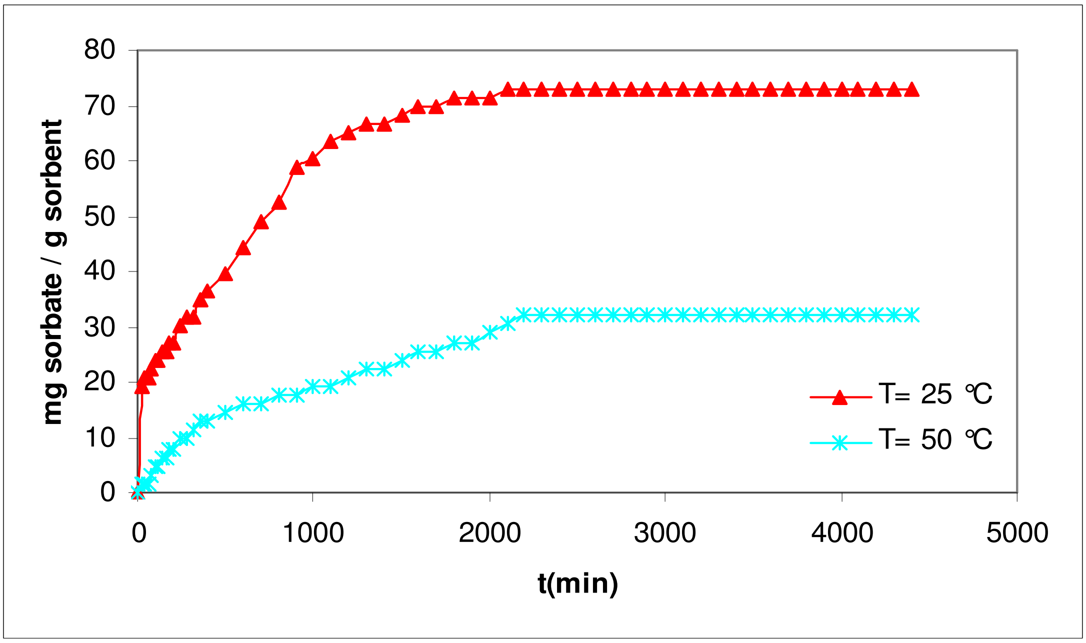


Figure 5.8 n-butanol Uptake Curves in HZSM-35 at different temperatures
($P_{f,0°C} = P_{o,0°C} / 2$, $P_{f,25°C, ,50°C} = P_{o,25°C} / 2$)

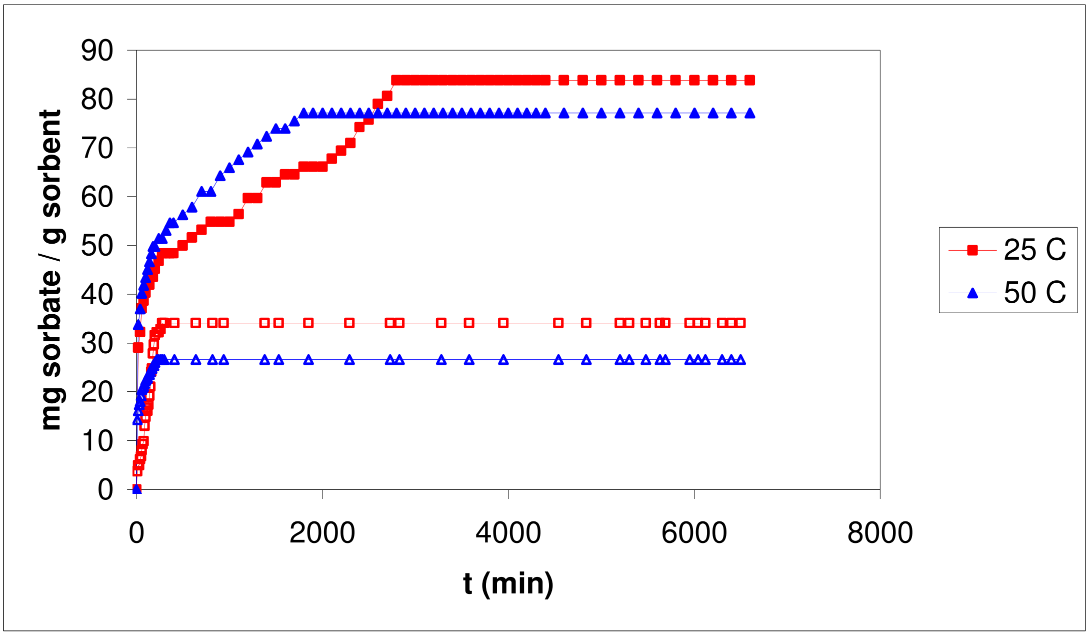


Figure 5.9 Propan-1-ol Uptake Curves in NaZSM-35 and HZSM-35 at T=25°C and T=50°C $P_f=P_{o,25°C}$ / 2 (Filled symbols denote H-ZSM35 and empty symbols denote Na-ZSM35)

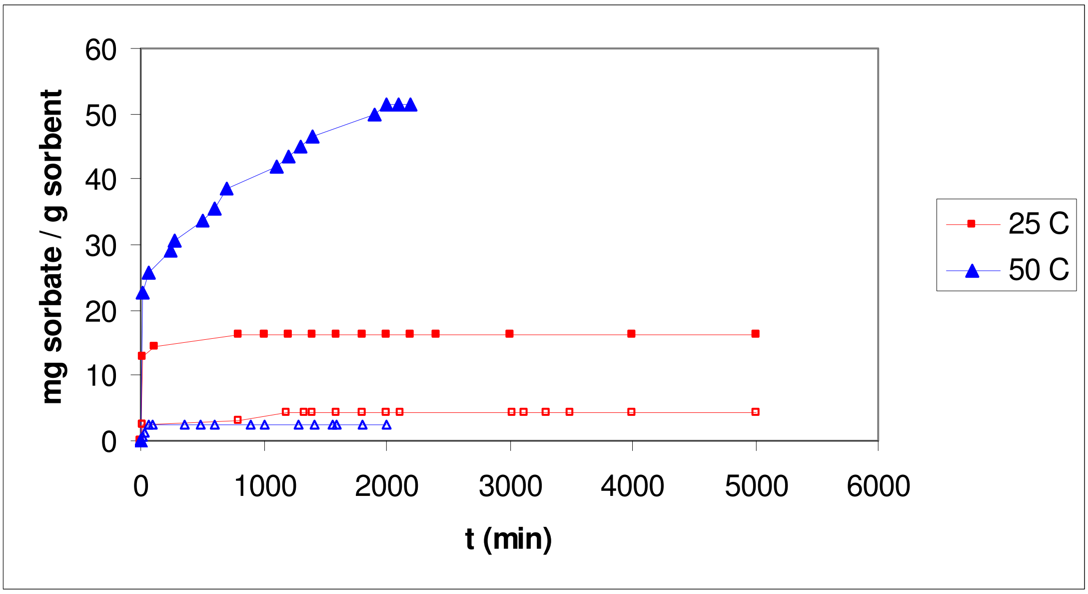


Figure 5.10 Propan-2-ol Uptake Curves in NaZSM-35 and HZSM-35 at T=25°C and T=50°C $P_f=P_{o,25°C}$ / 2 (Filled symbols denote H-ZSM35 and empty symbols denote Na-ZSM35)

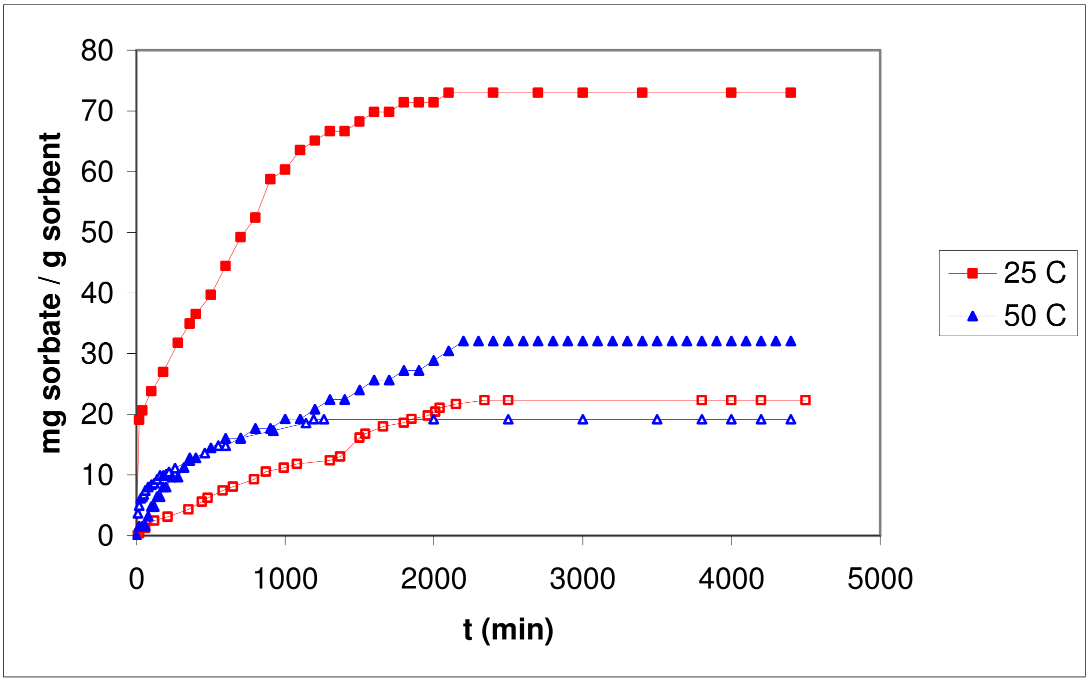


Figure 5.11 n-butanol Uptake Curves in NaZSM-35 and HZSM-35 at T=25°C and T=50°C $P_f=P_{o,25°C}$ / 2 (Filled symbols denote H-ZSM35 and empty symbols denote Na-ZSM35)

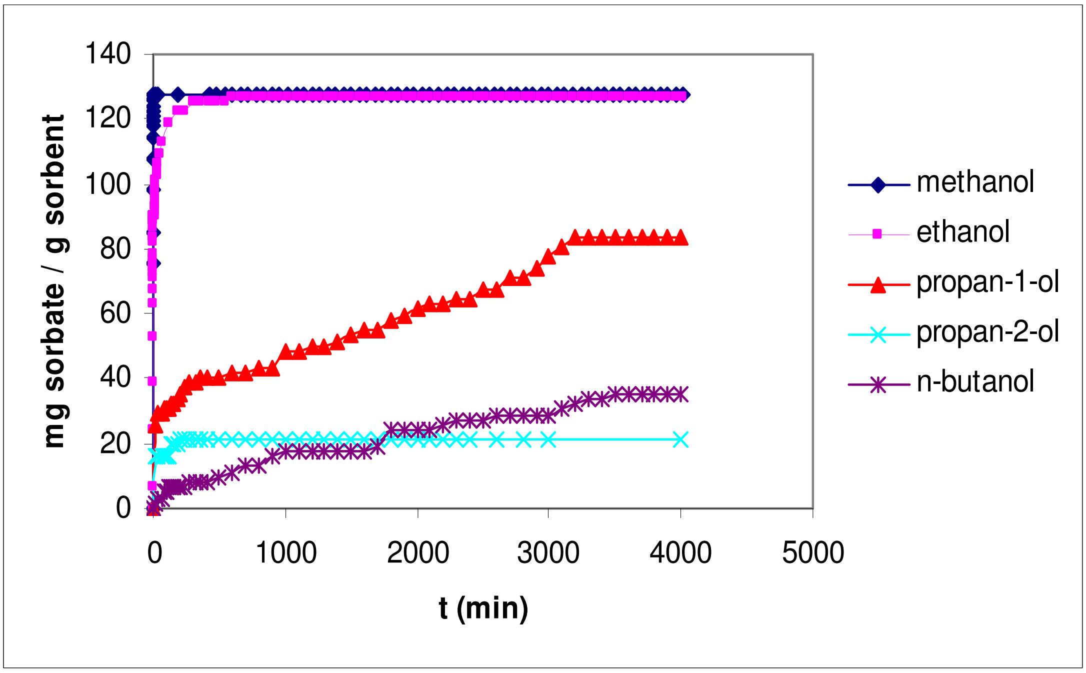


Figure 5.12 HZSM-35 Methanol, Ethanol, Propan-1-ol, Propan-2-ol and n-butanol Uptake Curves Comparison at T=0°C and $P_f=P_{o,0°C}$ / 2

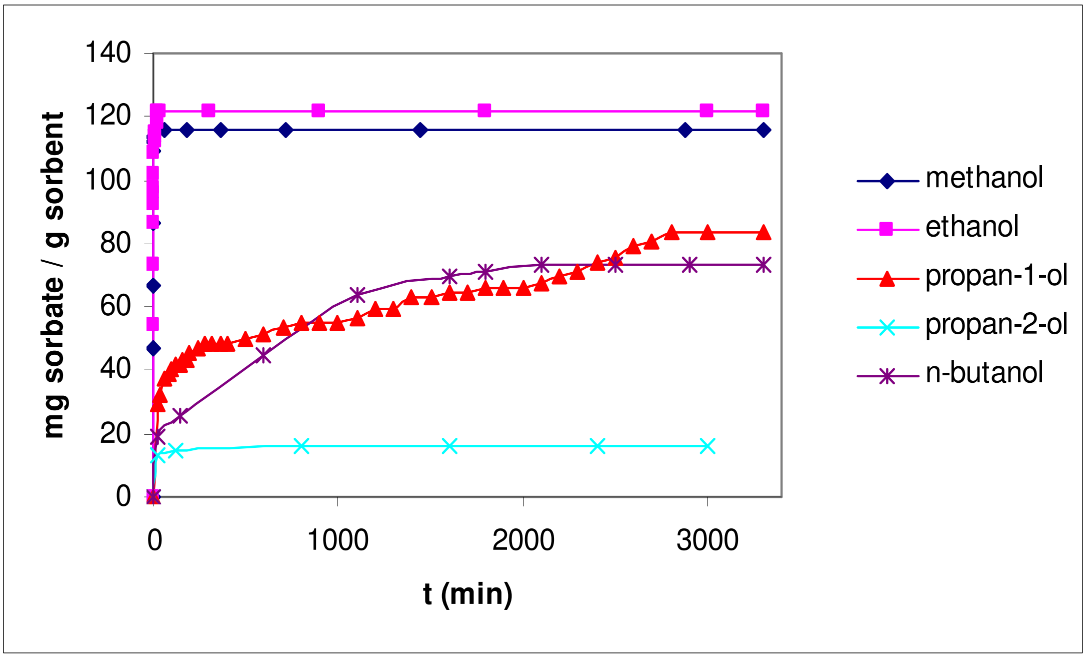


Figure 5.13 HZSM-35 Methanol, Ethanol, Propan-1-ol, Propan-2-ol and n-butanol Uptake Curves Comparison at T=25°C and $P_f=P_{o,25°C}$ / 2

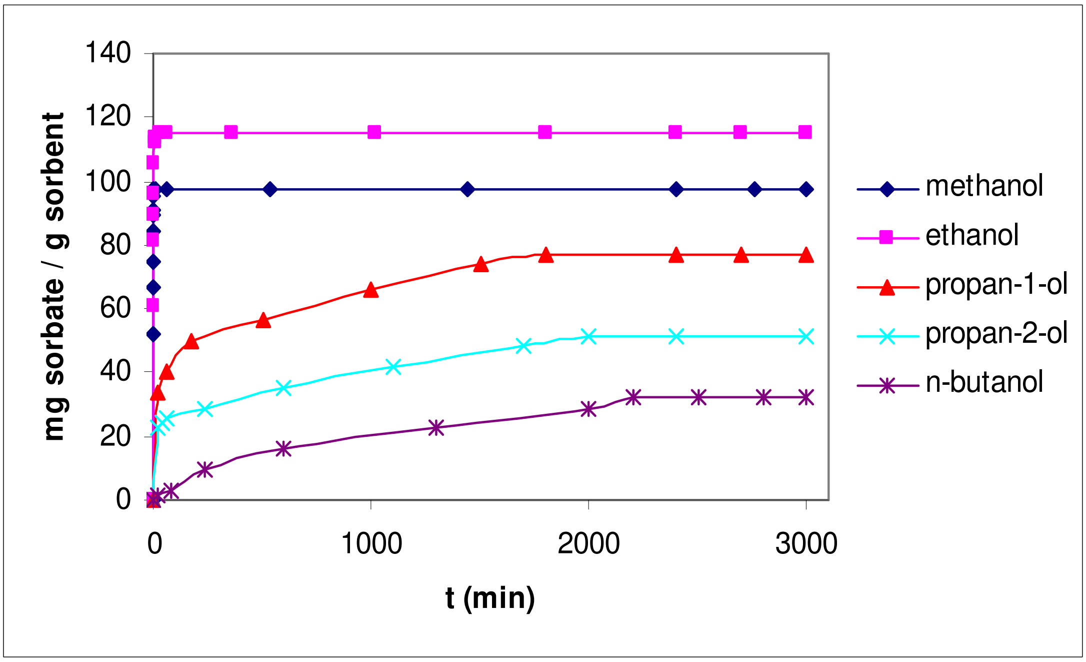


Figure 5.14 HZSM-35 Methanol, Ethanol, Propan-1-ol, Propan-2-ol and n-butanol Uptake Curves Comparison at T=50°C and $P_f=P_{o,25°C}$ / 2

Comparing the sorption experiments of five alcohols on Na- and H- form of ZSM-35 gave the following results;

It has shown that both methanol and ethanol can penetrate both 10 and 8 MR channels of both the Na- and H- form of ZSM-35. Also, Propan-1-ol can almost penetrate 10 MR channels of H- form of ZSM-35 where total sorption volume of ZSM-35 was reported as 0.1561 cm^3/g of which 0.1000 cm^3/g is the pore volume of 10 MR.

The volumetric sorption capacities calculated at lower temperatures are higher than those calculated at higher temperatures under comparable relative pressures. This is probably due to more favorable packing of molecules in the channels of ZSM-35 at the lower temperatures.

The equilibrium sorption capacities at 25 ºC for methanol on HZSM-35 is 0.1462 cm^3/g in this study. Öztin (1997), showed that the sorption capacity of methanol on HZSM-35 as 0.1186 cm^3/g and Tütüncü (2003) as 0.0906 cm^3/g (Table 5.2).

It was observed that the sorption capacities of HZSM-35 were greater than that of NaZSM-35 at all temperatures for propan-1-ol, propan-2-ol and n-butanol (Figure 5.9 - 5.11).

It was observed that the sorption capacity of HZSM-35 for propan-1-ol is about 2-3 times more than NaZSM-35 at all experimental temperatures (Table 5.3 - 5.4).

As shown in Figures 5.1 – 5.14 the kinetics of methanol are characterized by a very rapid initial uptake. Methanol sorption is relatively faster than other alcohols. Methanol- HZSM-35 system reached its equilibrium sorption capacities after 2 min to 26 min.

From uptake curves, it was seen that methanol had the highest sorption rate than the other alcohols (Table 5.5 – 5.6). Time to reach equilibrium for methanol and ethanol sorption on HZSM-35 is shown on Table 5.5. As it is seen on Table 5.5, methanol reaches its equilibrium faster than ethanol for all temperatures. Time to reach equilibrium for Propan-1-ol, Propan-2-ol, n-Butanol sorption on ZSM-35 is shown on Table 5.6 and as it is seen on Table 5.6 , propan-1-ol reaches its equilibrium on NaZSM-35 faster than HZSM-35.

It can be attributed to configuration of the adsorbate since methanol has the shortest chain. However, equilibrium adsorption capacities of ethanol were greater than that of methanol probably due to more efficient packing effect.

Table 5.5 Limiting Equilibrium Sorption Time of Methanol, Ethanol on HZSM-35

Probe molecules	Time to reach equilibrium on HZSM-35			
	- 20 °C	0 °C	25 °C	50 °C
Methanol	6.6 min	5 min	7.3 min	2.6 min
Ethanol	960 min	600 min	26.6 min	26.6 min

Table 5.6 Limiting Equilibrium Sorption Time of Propan-1-ol, Propan-2-ol, n-Butanol on ZSM-35

Probe molecules	Time to reach equilibrium on HZSM-35		Time to reach equilibrium on NaZSM-35	
	25 °C	50 °C	25 °C	50 °C
Propan-1-ol	2800 min	1800 min	300 min	220 min
Propan-2-ol	800 min	2000 min	1180 min	60 min
n-butanol	2100 min	2200 min	2340 min	1190 min

The efficient packing effect was seen between the propan-2-ol and n-butanol where they both have the same kinetic size, equilibrium adsorption capacities of n-butanol were greater than that of propan-2-ol.

During the sorption experiments coke deposition on the zeolite sample was observed. The color of the sample which was white in the beginning turned into tones of gray-black which was one of the indication coke depositon. This case may cause changes on structure of zeolite that may effect the sorption properties of zeolite. In our study, sorption experiments were carried out at room temperatures but during the regeneration step the temperatures were over 400 ºC where Shashikila et al. (1991) described the coking of ZSM-35 at high temperatures in catalytic reactions.

CHAPTER 6

CONCLUSIONS AND RECOMMENDATIONS

The main purpose of this study was to investigate the adsorption properties of Na- and H- from of ZSM-35, a ferrierite family member, for probe molecules methanol, ethanol, propan-1-ol, propan-2-ol and n-butanol at different temperatures The adsorption of these alcohols on zeolites has been considered the first step of several industrially important processes for transformation to hydrocarbons.

Based on the experimental studies the following conclusions can be drawn:

The volumetric sorption capacities for methanol and ethanol at lower temperatures exceeded to the theoretical pore volume reported for ZSM-35.

The type of cations in the framework structure affects the adsorption properties of zeolites such as the sorption capacity. When the limiting equilibrium sorption capacities of Na- and H-form of ZSM-35 for propan-1-ol, propan-2-ol and n-butanol are compared, the sorption capacities of HZSM-35 have the greater value for all sorbates at all temperatures used in this study.

It is seen that the number of carbon molecules in the probe molecules effect the sorption capacity. Increasing the carbon number decrease the sorption capacity. For example at 0 °C the sorption capacities of methanol, ethanol, propan-1-ol and n-butanol on HZSM-35 are 0.1568 cm^3/g, 0.1572 cm^3/g, 0.1020 cm^3/g, 0.0450 cm^3/g respectively.

Methanol and ethanol molecules may occupy both 10 and 8 membered ring channels on HZSM-35 and propan-1-ol molecules occupied 10 membered ring channels on HZSM-35 and also at least partially diffused into 8 membered ring channels.

The sorption capacity of branched alcohols along the channels of the ZSM-35 was found to be lower while the sorption capacity of linear alcohols is higher.

The distribution of molecules in the channels may be different, where branching may make the molecules trapped at the intersection of the 10-ring and 8-ring channels. For linear alcohols, it shows better distribution in the channels.

Small chains may be preferably adsorbed in the 8-ring channels where it is difficult for larger chains to reside in the 8-ring channels that results the decreasing of sorption capacity.

The differences between the experimental results of this study and literature can be explained as the aperture size and shape of the zeolite sample may change during the dehydration due to the framework distortion and cation movement.

Based on the present study, for the future, some points can be recommended.

In this study, five types of alcohols were investigated. The adsorption behaviour of normal and branch-chain alcohols on ZSM-35 was observed and it was seen that the lenght of the alcohols affects the sorption capacity and sorption rate. It is suggested that for more information about the effects of chain length in the sorption rate on ferrierite type zeolites, much longer chain and more branched type of alcohols may be studied.

In many zeolite based catalytic applications, the temperature of reaction is very high. Sorption behavior of alcohols may be studied with higher temperatures to observe the temperature effect in these reactions.

The adsorption behaviour of ZSM-35 can further be extended by using different sorbates.

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APPENDIX A

PHYSICAL PROPERTIES OF SORBATES

Table A.1 Vapor Pressures of the Probe Molecules at Different Temperatures
(Perry and Green, 1999)

T (°C) P_0(torr)	-20	0	25	50
Methanol	3.24	29.32	112.75	414.49
Ethanol	2.06	11.85	52.45	220.49
Propanol	0.56	3.32	20.45	89.82
Isopropanol	1.62	8.33	45.03	178.82
N-Butanol	0.14	0.96	6.91	34.30

Table A.2 Liquid Densities of the Probe Molecules at Different Temperatures

(Perry and Green, 1999)

T (°C) ρ_L(g/cm^3)	-20	0	25	50
Methanol	0.83	0.82	0.79	0.77
Ethanol	0.83	0.81	0.79	0.76
Propanol	0.84	0.82	0.80	0.78
Isopropanol	0.82	0.80	0.78	0.76
N-Butanol	0.84	0.83	0.81	0.79

APPENDIX B

KINETIC DIAMETERS

Table B.1. Kinetic Diameters of probe molecules

Probe Molecules	**Kinetic Diameters**
Methanol	3.8 Å (Bowen et al., 2003)
Ethanol	4.3 Å (Bowen et al., 2003)
Propan-1-ol	4.7 Å (Bowen et al., 2003)
Propan-2-ol	4.7 Å (Bowen et al., 2003) 5.0 Å (Lewis et al., 1997)
n-butanol	5.0 Å (Bowen et al., 2003)