

FTIR SPECTROSCOPY OF METHANE ADSORPTION ON ZEOLITES

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ABSTRACT

Adsorption of gases onto zeolites studied by various methods revealed the important of zeolite physical and structural properties such as pore network system, pore size, and surface area. The effect of zeolite properties on methane adsorption was investigated using ZSM-5, mordenite, ferrierite, zeolite beta, and faujasite-type zeolites (NaX, NaY, and NaYS18) as adsorbents. The adsorbed methane was detected in the region between 3200 – 1200 cm⁻¹ using Fourier Transform Infrared (FTIR) spectrometer. The experimental results show that surface area is not the only factor that determines methane adsorption, in fact, the type of pore network system of the adsorbent also affects the adsorption of methane on zeolite. It also suggests that zeolites such as NaX and NaY are potential methane adsorbents.

Key Words : Zeolite, Adsorbent, Microporous, Adsorption, Structural framework

1.0 INTRODUCTION

Zeolites are crystalline alumino-silicate porous material of group IA and IIA elements such as sodium, potassium, magnesium and calcium [1]. It forms a large family with a framework based on an extensive three dimensional structures formed by TO₄ tetrahedra (T = Si or Al), and each T- atom is connected by oxygen to four other T-atoms to create well-defined pores and channels [2-4]. This alumino-silicate structure is negatively charged that attracts the positive cations resides within [5]. It is widely used due to the fact that it has a wide range of structures having different chemical composition and physicochemical properties [1, 5, 6] that potential to be used in gas storage [7-9], gas and chemical sensors [10 – 11], and semiconductor that involves metal-doped zeolites [12]. The applications of zeolites as adsorbents and catalysts are related to the exceptional extension of their solid-liquid interface, accessible through a perfectly defined pore structure [13].

The potential applications of zeolite as adsorbents leads to extensive adsorption study on various types of zeolites such as zeolite A, NaX, NaY, ZSM-5, zeolite beta, and mordenite, which mainly involves carbon dioxide, methane, or nitrogen as adsorbates. The study indicated that either surface properties, chemical composition, or pore size influence the behavior of adsorption [14 –17]. However, it reported also reported that structural differences did not give major differences in adsorption [18]. In addition, it has been reported that zeolites with parallel channels are more susceptible to

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blocking by cracking products than are those with two- or three-dimensional channel system [5].

In order to elucidate the effect of structurally different zeolite on gas adsorption, several types of zeolite were selected representing a system of uniform channel called channel type zeolite (ZSM-5, mordenite, ferrierite and zeolite beta) and an internal pore system of interconnected cage-like void is called cage type zeolite (NaX, NaY, and NaYS18). It is our interest to examine the potential application of zeolite as an adsorbent used in adsorptive methane storage. The application of FTIR spectroscopy will provide an insight on the effect of structural and physical properties of zeolites on methane adsorption. Methane is a very weak base and its interaction with zeolite cations and protons of acidic sites does not lead to a strong perturbation of adsorbed molecules. In addition, the small size and high symmetry of methane molecule IR spectra that are easy to interpret. The interaction of adsorbed methane with cations leads to the appearance of a band from fully symmetric C-H stretching vibration (ν_1), which is forbidden for methane [19].

2.0 EXPERIMENTAL

2.1 Materials

A powdered form of zeolite NaY, NaX, ZSM-5, mordenite, ferrierite and zeolite beta (Zeolyst Intl.) and, NaX (Aldrich Chemical) was used as methane adsorbents. NaYS18 was synthesized according to procedure described elsewhere [20]. NaOH (MERCK), sodium aluminate anhydrous (Riedel-de Haën), colloidal silica-(Aldrich Chemical) and double distilled water were used in the synthesis of the zeolite. Methane gas (99.9 %) used in the adsorption study were obtained from Southern Industrial Gas (M) Sdn. Bhd. and used without any further treatment.

2.2 Zeolite Characterization

The structural properties of the synthesized zeolite was determined using Bruker diffractometer with $\text{CuK}\alpha_1$ radiation of $\lambda = 1.5418\text{\AA}$ at 40 kV and 20mA in the range of $2\theta = 5^\circ - 50^\circ$ at scanning speed of 0.05° per second. The porosity of the samples was determined by measuring nitrogen adsorption at 77K by using Micromeritics analyzer (ASAP Model 2000). The total surface area was calculated using BET method, while the external surface area and micropore volume were calculated using the t-plot method.

Gas adsorption isotherms at 298 K were measured at various pressures using gas adsorption analyzer (Micromeritics, ASAP 2000). Initially, 10 – 20 mg of zeolite was heated at 673 K for 2 hours to remove water and other sorbed materials in the pore or channel. The sample was then cooled at room temperature before the methane gas was introduced initially at low pressure and gradually increased until it reached 101.3 kPa.

2.3 Methane adsorption measurement

An adsorption cell having CaF_2 as infrared window integrated to the FTIR instrument was used to study methane adsorption on different zeolites (Figure 1). The cell could stand pressures in the range of 0.001 to 1013.5 kPa. A thin self-supported sample wafer was prepared, placed inside the adsorption cell, and outgassed (activated) in a dynamic

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vacuum (residual pressure $< 2 \times 10^{-3}$ kPa) for 2 hours at about 700 K to remove the moisture and other components, if any, adsorbed on the zeolite. The adsorption cell was then isolated by closing the valves, allowed to cool to room temperature (298 K), followed by recording of the FTIR spectrum using spectroscopic instrument (Spectrum One-Perkin Elmer). This FTIR spectrum was designated as the background spectrum of the zeolite wafer. The methane was then introduced at 137 kPa, allowing the gas to adsorb on the zeolite sample at 300 K for 2 hours which is sufficient to achieve the adsorption equilibrium. The valve was closed and the FTIR spectrum was again measured using the same FTIR instrument. The FTIR spectra obtained were compared against the background spectrum of zeolite wafer. The ZSM-5 zeolites were synthesized by hydrothermal crystallization at 160°C for five days from mixtures containing sodium silicate, aluminium sulfate, tetrapropylammonium bromide, based on method described by Plank *et al.* [9]. The crystalline white solid product was filtered, washed thoroughly with deionized water, dried at 12 °C for 12 hours. The resultant material was calcined at 550 °C for five hours to remove the organic material and to obtain sodium form of the ZSM-5. The Na-form so obtained was converted into the NH₄-form by ion exchanging it with 1M solution of ammonium nitrate. The procedure was repeated three times. Finally the catalyst is dried and calcined at 550°C and marked as HZSM-5. BZSM-5 were prepared according to the above method except that boric acid was used to replace aluminium sulfate.

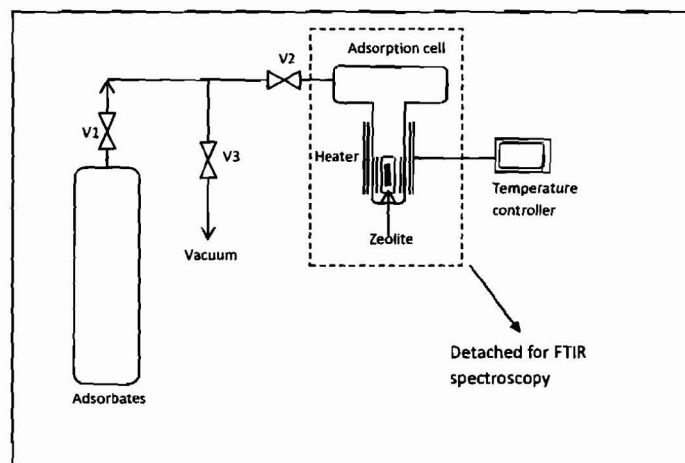


Figure 1 A schematic diagram of gas - zeolite interaction adsorption cell.

3.0 RESULTS AND DISCUSSION

3.1 FTIR adsorption spectra

FTIR spectra of adsorbed methane could be observed in the region between 3200 – 1200 cm^{-1} . In the case of methane, it is a very weak base and its interaction with zeolite cations and protons of acidic sites does not lead to a strong perturbation of adsorbed molecules. Due to this fact and the small size and high symmetry of methane, its IR spectra are easy to interpret. The interaction of adsorbed methane with cations leads to the appearance of a band from fully symmetric C-H stretching vibration (ν_1), which is forbidden for methane molecules [19]. Two peaks appeared in the region around 3020 cm^{-1} and 1306 cm^{-1} are assigned to asymmetric band (ν_3) and symmetric band (ν_4), respectively [21]. However, a

weaker band around 2900 cm^{-1} assigned to ν_1 (symmetric) band could only be observed at temperature lower than 273K [22].

3.2 Adsorption on channel type zeolites

Figure 2 shows the FTIR spectra of methane adsorbed on channel-type zeolites. Peak assigned to the ν_3 (antisymmetric) of adsorbed CH_4 was observed in the region around 3015 cm^{-1} . It is a result of free rotation of the adsorbed molecules around a single axis normal to the adsorbent surface [22]. There is another band in the region around 1300 cm^{-1} that is assigned to ν_4 band. The appearance of ν_4 band is induced by the interaction of adsorbed molecules with the sites creating an electrical field at the surface. Except for zeolite beta, the peaks could not be clearly distinguished from other peaks appeared in that region. It suggests that only weak interaction exists between the adsorbate and the channel type zeolites.

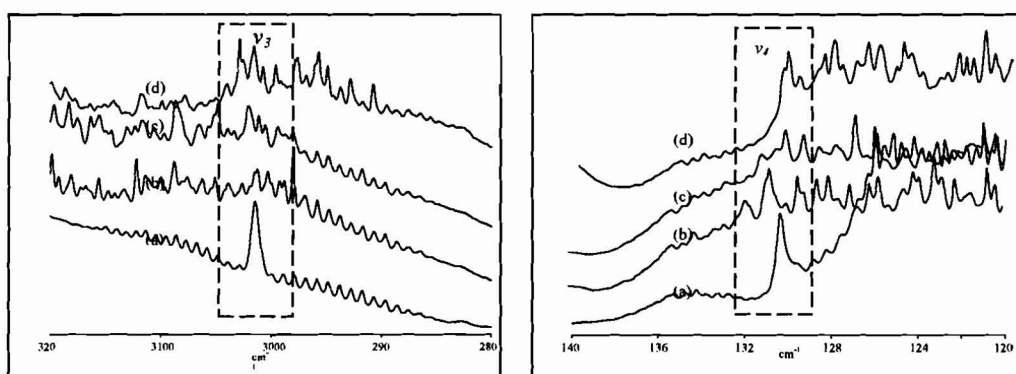


Figure 2 The FTIR spectra (ν_3) and (ν_4) of CH_4 adsorbed on zeolites at 293K and 137 kPa : (a) zeolite beta; (b) ZSM-5; (c) mordenite; and (d) ferrierite.

3.3 Adsorption on cage type zeolites

The FTIR spectra of adsorbed methane on cage-type zeolites are shown in Figure 3. The spectra show that the peak (ν_3 band) intensities for cage type zeolites are higher and sharper than channel type zeolites. The peak positions also shift to the low-frequency side of methane gas, in which indicate that the adsorbed molecules experience some perturbation. The presence of supercages within faujasite structures (NaX, NaY, and Na-SZ18) would allow the larger freedom for the adsorbed molecules to rotate and experience a symmetrical field from the pore wall of the zeolites. The FTIR spectra of ν_4 band for methane adsorbed in cage type zeolites are clearly shown in Figure 5.

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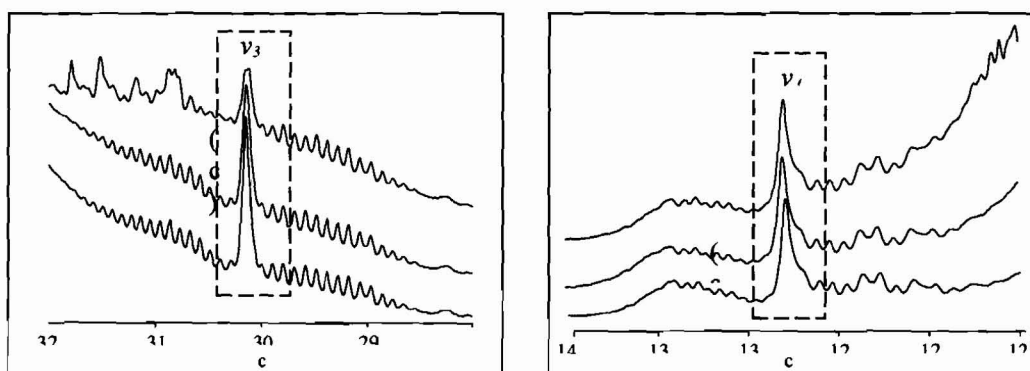


Figure 3 The FTIR spectra (ν_3) and (ν_1) of CH_4 adsorbed on zeolites at 293K and 137 kPa : (a) NaY; (b) NaY_{S18} ; and (c) NaX.

3.4 Adsorption mechanism

Depending on the structure of the adsorbent, several types of diffusion mechanisms become dominant and sometimes two or three of them compete or cooperate [24]. The dominant mechanism also depends on a combination of adsorbate and adsorbent, and adsorption conditions used such as pressure, temperature, and concentration range. In microporous adsorbent such as zeolites, macropores usually act as a path for the adsorbate molecules to reach the interior part of the particle. Based on the average pore diameter of the zeolites and the kinetic diameter of methane, diffusion inside zeolite's microchannel is likely Knudsen-type diffusion. The interaction between gas molecule and the wall of the micro-channel becomes more dominant.

FTIR spectra of adsorbed methane could be observed in the region between $3200 - 1200 \text{ cm}^{-1}$. In general, there are several possible interactions between methane and zeolite structures. The electrostatic forces of methane-zeolite might exist between C -- Na, H -- O, and Si -- C. The results of these interactions could be indicated in the FTIR spectra of asymmetric and symmetric bands of the adsorbates. Although unique identification of the adsorption spectra is difficult to performed, some peaks that attribute to specific interactions of the adsorbate on the adsorbent could be observed.

Peak assigned to the ν_3 - band of adsorbed CH_4 observed in the region around 3015 cm^{-1} is a result of free rotation of the adsorbed molecules around a single axis normal to the adsorbent surface [22]. For ZSM-5, mordenite and ferrierite, peaks in this region are relatively weak and ν_3 -vibration band of methane splitted into several peaks. This finding suggests that the methane molecules experience non-symmetrical field from the pore wall of the zeolites. However, zeolite beta and cage-type zeolites (NaX, NaY, and Na-SZ18) have larger average pore size (Table 1), thus the adsorbed molecules in the pore have large freedom of rotation and would experience symmetrical field from the pore wall of the zeolites.

A weaker band in the spectra around 2900 cm^{-1} assigned to ν_1 (symmetric) band is actually represents the effect of the electrical field on the adsorption sites rather than a strong dispersion force at the surface of the zeolite. The peak could not be detected during the adsorption of methane on the zeolites. The appearance of ν_4 bands induced by the interaction of adsorbed molecules with the sites creating an electrical field at the surface is shown in cage-type zeolites and beta zeolites. The peaks could not be clearly distinguished from other peaks in other channel-type zeolites. Stronger peak appeared could be due to the unspecific interaction between methane and the pore, which has larger

average pore diameter. However, it has been reported that the interaction between CH₄ and the wall of zeolite structure is not based on the active sites but it is more likely due to the confinement effect [23]. This explains the reason why peaks that assigned to ν_3 and ν_4 are clearly shown in FTIR spectrum of NaX, NaY, and Na-SZ18 zeolites (cage-type structure).

Table 1 The physical properties of channel and cage type zeolites.

Zeolite	Surface area (m ² /g)		Pore volume (cm ³ /g)		Ave. pore diameter (nm)
	BET	Micropore	Micropore	Mesopore /Macropore	
Channel-type					
ZSM-5	428.7	357.7	0.145	0.096	2.25
Zeolite beta	494.0	325.7	0.131	0.730	6.97
Mordenite	520.4	461.1	0.180	0.064	3.04
Ferrierite	290.7	275.4	0.106	0.122	2.31
Cage-type					
NaY	820.0	809.5	0.304	0.024	1.60
NaX	567.4	557.7	0.214	0.017	1.63
NaY _{S18}	813.6	793.8	0.299	0.061	1.78

The magnitude of the ν -peak shift is correlated with the strength of the interaction at the adsorption site [17]. Table 2 shows that at 298 K and 137 kPa, the peaks are shifted to lower wavelength values. These phenomena indicate that there are some interactions between methane and zeolite even though they are only weak interactions. It also suggests that desorption could be easily achieved either by increasing the temperature or reducing the pressure of the adsorption system. It is also known that the band intensity represents the strength and the amount of molecules adsorbed on zeolites. However, peak area does not actually represent total the amount of methane adsorbed, but it relatively indicates the extent of adsorption in each zeolites [22].

Table 2 The peak position of ν_3 and ν_4 bands and peak area of the adsorbed CH₄.

Zeolite	ν_3 band		ν_4 band	
	Peak position (cm ⁻¹)	Area (cm ²)	Peak position (cm ⁻¹)	Area (cm ²)
CH ₄	3020		1306	
Channel:				
Beta	3015 (-5)	14.80	1303 (-3)	9.12
ZSM-5	3013 (-7)	3.23	1307 (+1)	4.56
Mordenite	3011 (-9)	0.95	1303 (-3)	0.13
Ferrierite	3016 (-4)	4.04	1303 (-3)	4.50
Cage:				
NaY	3015 (-5)	18.52	1303 (-3)	11.35
NaX	3012 (-8)	9.67	1303(-3)	10.81
NaY _{S18}	3015 (-5)	15.66	1303 (-3)	11.90

Table 2 also shows that the integrated areas under of the ν_3 and ν_4 bands for cage type structures are higher than channel type zeolites. Even though large surface area

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might be the reason for higher adsorption, the amount adsorbed on mordenite with relatively high the surface area (520 m²/g) and pore volume (0.180 cm³/g) does not follow the general assumption of adsorption. In fact, mordenite with high surface area and micropore volume has lower integrated peak area than zeolite beta. For different structural framework, the integrated peak areas is in the order of NaY > Na-SZ18 > NaX > zeolite beta > ferrierite > ZSM-5 > mordenite. Thus, cage type structure could be better methane adsorbent than channel type zeolites. The presence of supercages and sodalite cages that encapsulated the methane molecules inside the structure could also contribute to higher adsorption of methane.

Channel type structures might have limited adsorption sites, the channel itself act as a channel for diffusion and sites for the methane to adsorb. Adsorption of methane in parallel channel (e.g. mordenite) is considered faster than the zig-zag channel, however once the channel is blocked, the adsorbate could not diffuse further to the adsorption sites. The zig-zag channels (e.g. ZSM-5) might encounter some problems at the intersection as any deposition could either partially or fully obstruct the pathway and thus, affect the adsorption of methane. The existence of zig-zag or sinusoidal channel may also affect the diffusivity of methane (e.g. ZSM-5). Moreover, the accessibility is also denied if the pore blockage or any deposition occurred due to the collapse of the lattice structure. These explain the reasons of low adsorption for several types of zeolites. Thus, zeolites structures such as ZSM-5, mordenite and ferrierite might experience complex adsorption process that results in less methane adsorption.

4.0 CONCLUSIONS

A large numbers of different zeolite structures offer many possibilities for specific application. In order to choose suitable adsorbent, adsorption characteristics of adsorbate-adsorbent need to be well understood. Using FTIR spectroscopy, some information on the extent of adsorption and interaction between methane and zeolites were obtained. Even though the data obtained do not represent the absolute amount of adsorbate molecules adsorbed, instead the relative amount of adsorbates attaches to the active site, the information is important especially in the selection of potential zeolite adsorbent for specific application such as adsorbed gas storage. The results suggest that cage type zeolite could become potential methane adsorbent. This study also shows that surface area is not the only factor to be considered when selecting the adsorbent of gases. Pore network system and structural arrangement might also influence the characteristics of adsorption process.

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