

Microwaves and Sorption on Oxides: A Surface Temperature Investigation

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Microwave heating is not the same as conventional heating, and it is believed that this difference, the “microwave effect,” may be interpreted to be due to selective, local heating. The temperature at the surface where sorption occurs is “effectively” greater than the measured solid or gas temperature. In these studies, measurements of the amounts of adsorption as functions of the partial pressures of a specific adsorbate in the presence of microwave irradiation were related to the conventional adsorption isotherms. Equating the adsorbate pressure required to achieve a specific coverage (an isostere) in the presence of microwave irradiation to the amount adsorbed for a conventional isotherm allowed for an estimate of the “effective” surface temperature in the presence of microwaves. It was found that the effective surface temperature increased when using adsorbates having a higher permittivity or when increasing the microwave power. The implication of this change in the surface energy for specific species in the presence of microwaves is discussed.

Introduction

It has been found that microwave energy uniquely influences sorption on oxides. Microwave energy induces desorption at temperatures measured in the gas and (bulk) solid phases that are significantly lower than those required for desorption by conventional heating.¹

It is proposed that the “microwave effect” may be interpreted due to selective, local heating. When using oxide sorbents, the temperature at the surface where sorption occurs is “effectively” greater than the measured solid or gas temperature, since oxides have a low permittivity and are relatively transparent to microwaves. Different adsorbates have different capabilities for adsorbing microwave energy (permittivities), resulting in different local temperatures and different sorption selectivities in the presence of microwaves.¹ This confirms that the effect of microwave heating is local. Energy is transferred selectively to the surface via the adsorbate. Microwave heating of this surface region is rapid, and the rate of subsequent heat transfer to the solid and gas phases may be slower. There is a gradient in temperatures, surface > bulk > gas, while the effective surface temperature has not been quantified until this research.

In this research, measurements of the amounts of adsorption as functions of the partial pressures of a specific adsorbate in the presence of microwave energy were related to the conventional adsorption isotherms. By equation of the adsorbate pressure required to achieve a specific coverage (an isostere) in the presence of microwave energy with the amount adsorbed for a conventional isotherm, an estimate of the “effective” surface temperature in the presence of microwave energy was obtained. The resulting relationships between adsorbents, adsorbates, and other variables were examined.

There is no direct method of probing the surface where microwaves are most selectively absorbed on oxides. The surfaces of oxides often are terminated in hydroxyl groups that are more susceptible to absorbing microwave energy than the bulk. Surface temperature measurements in the presence of an

adsorbate are particularly problematic since desorption achieves equilibrium rapidly and is endothermic, and it is documented that systems that comprise adsorbing oxides exposed to microwave radiation are not isothermal. The surface can absorb energy faster than it can be exchanged with the underlying solid or gas phases. It is important to characterize the variations of temperature for all phases of these systems to understand the microwave effect. These measurements must be made in situ, as the variations in temperature due to exposure to microwave radiation will be transitory. Due to the proposed differences in temperature of the phases, the sensitivity to the adsorbate, and the rapid cooling due to desorption, this temperature would be an effective surface temperature. The effective surface temperature represents the conditions of physical sorption in the presence of microwaves.

Background

Microwaves. Microwaves are alternating current signals of electromagnetic energy with electrical wavelengths of 1 mm to 1 m. The absorption of microwave energy by a medium induces some degree of polarization of the medium and conversion of electromagnetic energy into heat and is dependent on a property of the medium called its permittivity, ϵ , which is divided into real and imaginary parts as described by the equation

$$\epsilon = \epsilon' - j\epsilon''$$

This is often expressed relative to the permittivity of free space, ϵ_0 , and the loss tangent, $\tan \delta$, the conductivity, σ , and the angular frequency, ω , by the equations^{2,3}

$$\epsilon' = \epsilon_r \epsilon_0$$

$$\tan \delta = (\omega\epsilon'' + \sigma)/(\omega\epsilon')$$

The ability of a molecule to be polarized by an electric field is expressed by the real part of the permittivity.⁴ The imaginary part of the permittivity accounts for loss in the medium that is converted to heat.⁵ Microwaves will have less of an effect on

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materials with a lower permittivity. The permittivity is a function of frequency.

From Poynting's Theorem, the average dielectric power dissipated in a volume of a medium is

$$P_1 = (\frac{1}{2})\omega\epsilon''|E|^2$$

where ω is the angular frequency, $|E|$ is the magnitude of the electric field, and ϵ'' is the imaginary part of the permittivity of the dielectric material.³

Adsorption. Gaseous molecules collide with any surfaces to which they are exposed, and they either reflect from the surface or interact by absorbing or adsorbing. The most common and weakest type of adsorption is physical adsorption. The amount of physical adsorption is dependent on temperature, pressure, mass of the sample, material being adsorbed (adsorbate), and the adsorbing medium (adsorbent).⁶ Sorption is often expressed as a volume of gas adsorbed (cm^3 at standard temperature and pressure) per weight of sample, i.e., cm^3/g .

The volume of gas adsorbed as a function of pressure or relative pressure at a constant temperature can be represented by a sorption isotherm. Pore characteristics such as surface area and pore size distribution can be determined from physical sorption isotherms. The basic fundamentals of conventional physical adsorption have been well studied and can be found in many books, such as Gregg and Sing.⁶

The adsorption of species on a surface is exothermic, and higher temperatures lead to a smaller amount adsorbed at equilibrium.⁷ The temperature dependence can be related to the heat of adsorption through the Clausius–Clapeyron equation⁸

$$(d \ln P)/(d(1/T)) = \Delta H_{\text{ads}}/R$$

Physical adsorption heats are typically less than twice that of the heat of vaporization, which is 1.34 kcal/mol for nitrogen at 77 K.⁹

Porous materials have the potential to take in larger amounts of condensed gas due to a larger internal surface area and pore volumes. Zeolites are microporous crystalline solid oxides, have a very uniform pore size distribution, and are hence useful for many applications including catalysis and separations. The physical adsorption heats are higher for microporous materials. Many also have a low permittivity.

Adsorbed species have their own permittivities and can also modify the dielectric properties of the surface where they adsorb.^{10–12} In the presence of two or more sorbates with different permittivities, microwave heating can influence the sorption properties in a different way than conventional heating.^{1,11} Since the permittivity is a function of microwave frequency,^{13,14} it is hypothesized that the frequency also will influence sorption.¹⁵ It has been shown that microwave frequency can have an effect on catalytic reactions.¹⁶

Microwaves are also used in the synthesis of many ceramics and zeolites to obtain faster crystallization times,^{17–19} to lower the required heating temperature,¹⁷ and to calcine samples more rapidly.²⁰ Again, the local temperatures of these processes are difficult to measure.

Experimental Methods

Apparatus. An apparatus has been constructed for measurements of adsorption isotherms and isosteres in the presence of microwaves and is shown in Figure 1. It is similar to the high-resolution adsorption system in U. S. patent number 5,637,810,²¹ built to measure equilibrium adsorption isotherms at low

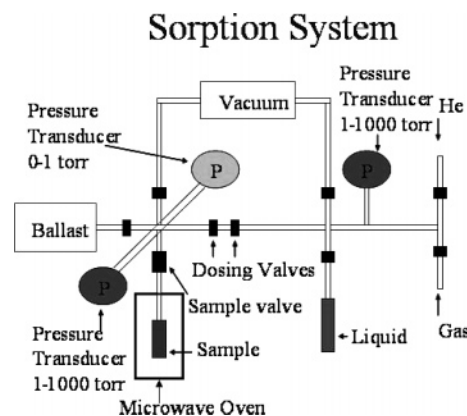


Figure 1. Sorption system.

pressures. This system is ideal for measurement of equilibrium adsorption isotherms since it incorporates larger-diameter tubing and an improved vacuum system to achieve lower pressures. The time allowed for equilibrium can be monitored and varied for a series of measurements.

The design for this system has been modified to include only metal seals in the valves. This prevents problems of seal degradation for many elastomers employed as valve gaskets that can be caused by some organic species such as alcohols, etc. Also, the sample can be placed in the center of a specially constructed microwave oven that uses microwave chokes (grounded metal tubes of precise length and diameter) to prevent microwave radiation leakage from the oven. This system is employed to measure in situ adsorption in the presence of microwaves. The system includes: (1) large-diameter tubing for faster outgassing, (2) a turbo pump backed by a rough pump to achieve low pressures, (3) multiple pressure transducers on the manifold to accurately measure pressure over a large range, (4) pneumatically controlled valves, (5) manifold ports for the use of vapor or gas adsorbates, and (6) air cooling over the outside of the sample to help maintain a constant bulk gas-phase temperature in the presence of microwaves or for room-temperature experiments. An oil bath around the sample was used in experiments measuring conventional isotherms above room temperature.

Samples. The silica used in the experiments was Aerosil 200 fumed silica from Degussa and was calcined at 385 °C. To prevent elutriation of the sample, the silica was pressed to 5000 psi and broken up into small chunks (about 1–2 mm in size). One of the silica samples was additionally heat-treated by being ramped up to 700 °C at 1 °C/min and held at 700 °C for 4 h to influence the surface hydroxyl concentration. Samples were generally outgassed overnight at a temperature above 120 °C. The silicalite zeolite ($\text{Si}/\text{Al} > 1000$) used was from Union Carbide, lot no. 961884061002-S, and was calcined at 385 °C. Silicalite samples were outgassed overnight at a temperature above 220 °C.

The adsorbates, (1) *n*-pentane, (2) cyclohexane, (3) dichloromethane, (4) 2-propanol, and (5) methanol, were chosen to cover a range of permittivities and had appropriate partial pressures for sorption experiments.

Permittivities were measured with a Hewlett-Packard 8510 Network Analyzer, using a $\frac{3}{4}$ in. diameter probe connected to the instrument by a shielded coaxial cable at room temperature. Liquid permittivities were measured by immersing the probe tip in the liquid far away from the container walls. Powders were measured by hand-packing the powder to about 1 in. thickness and placing the probe on top of the packed powder.

TABLE 1: Measured Permittivities of Materials at 2.45 GHz and 22 °C^{22,23}

material	relative permittivity	
	ϵ'^a	ϵ''^a
Aerosil 200 silica	1.43	-0.08
silicalite	2.41	0.01
<i>n</i> -pentane	1.80	NA
cyclohexane	2.02	0.05
dichloromethane	9.08	0.39
2-propanol	18.30	3.19
methanol	23.04	13.77

^a Values are ± 0.1 .

Permittivities were measured at from 0.5 to 18 GHz and at 22 °C and are shown at 2.45 GHz in Table 1.^{22,23}

Methoxylation was suspected to take place during the adsorption experiments where methanol was adsorbed on the sample in the presence of microwaves. To examine this, samples were prepared for transmission IR spectroscopy. A silica sample was taken and mixed in a 1:10 ratio with KBr powder and pressed at 5000 psi into a thin wafer. The silica samples used were Aerosil 200, temperature-treated Aerosil 200, methoxylated Aerosil 200, and methoxylated temperature-treated Aerosil 200. The wafers were then placed in a sample holder with the IR beam passing through the center of the wafer, and transmittance of the IR beam was analyzed. The sample holder of the wafer was ramped up to 110 °C in nitrogen.

Adsorption. Helium expansion was used for the calculation of the volumes in the system since it is far above its critical point, does not adsorb on the sample, and reached thermal equilibrium quickly. A vessel of a known volume connected to the manifold by a valve was employed to calibrate the manifold volume using the Ideal Gas Law. The sample dead space was calculated in a similar manner.

During sorption isotherms, the amount of gas adsorbed at a particular pressure was calculated by taking the difference between the amount of gas that would have been in the gas phase if no sorption was taking place (calculated using the Ideal Gas Law) and the measured amount of gas in the gas phase at equilibrium after sorption. The sample was initially outgassed, and the sorbate was introduced to the manifold to a known pressure through the dosing valves. Then the sample valve was opened, the system was allowed to come to equilibrium, and the resulting pressure was measured. Additional adsorption data points were obtained by closing the valve to the sample area and incrementally dosing a higher pressure (greater than the equilibrium pressure of the previous step) to the manifold. It is not necessary to evacuate the sample volume before each adsorption step (since the amount in the gas phase and the amount adsorbed are known). Desorption data points were obtained by closing the valve to the sample area and incrementally dosing a lower pressure (lower than the equilibrium pressure of the previous step) from the manifold. A sorption isotherm is obtained by plotting data of the amount adsorbed versus the equilibrium pressure at a constant temperature.

Procedure. A nitrogen isotherm at 77 K was obtained on each sample to characterize the samples, and their surface areas were calculated by constructing a Brunauer–Emmett–Teller (BET) plot and using a multipoint BET method.⁶ The surface area of the Aerosil 200 silica was calculated using a multipoint BET method to be 183 m²/g. There was a small amount of hysteresis observed in the silica isotherms due to the pressing of the silica during sample preparation. This is in agreement with the literature.²⁴ The surface area of the Aerosil 200 silica sample that was temperature-treated at 700 °C was calculated

to be 197 m²/g and still maintained the same outward appearance (no discoloration). The nitrogen isotherms on silicalite showed the typical isotherms for that material and were in agreement with those in the literature. The surface area of the silicalite was calculated using a multipoint BET method to be 369 m²/g, although the BET surface areas for zeolites are not meaningful since the pores are filled at pressures below which the BET theory is valid.

The sample on the adsorption system lies inside of the cavity of a specially modified industrial microwave oven from CEM Corporation, model MDS-81. The microwave oven was a pulsed system with a duty cycle of 1 s and had chokes (grounded metal tubes of precise length and diameter) to prevent the leakage of microwaves into the environment.

An adsorption isotherm was measured up to a particular pressure. The adsorption procedure was then modified by turning on the microwave oven at a low power level, and the system was allowed to come to a steady state where a new pressure, and hence a new amount adsorbed, was measured. In the case of a species with a high permittivity, the minimum pressure in the presence of microwaves was chosen to be above that at which a plasma would form. The microwave power was increased, the system was allowed to come to a new steady state (with a new amount adsorbed), then the microwave power was increased to a higher power level again, and the system was allowed to come to a new steady state and resulting pressure. The microwaves were then turned off, and the system reached equilibrium, matching the original equilibrium data point. Another adsorption point is obtained (without the microwave on). This entire process is repeated for a number of data points and allows for the measurement of isosteres in the presence of microwaves for the different levels of microwave power used.

Measurements of the amounts of adsorption in the presence of microwaves were compared to the conventional adsorption isotherms. By equation of the adsorbate pressure required to achieve a specific coverage (an isostere) in the presence of microwaves with the amount adsorbed for a conventional isotherm, an estimate of the surface temperature in the presence of microwaves was obtained. This is called the “effective surface temperature”.

Results

The initial attempts to obtain isosteres in the presence of microwaves while using 2-propanol and methanol resulted in the formation of a plasma. The adsorbate was dosed to the system to a relatively low pressure. When the sample was exposed to microwaves, after a short time the sample tube began to flash a purple glow when the microwave was on (during the power portion of the duty cycle). The pressure drastically increased, and the sample temperature increased to the point that in one case the glass sample tube began to melt.

To prevent plasma formation in future experiments, the isosteres were obtained only at higher pressures for adsorbates with a high permittivity. Since data could not be obtained at low pressures in these cases, the effective surface temperature was determined by interpolation between conventional isotherms; using the heat of adsorption to estimate the effective surface temperature was not accurate since it is only applicable to the Henry's Law region of the isotherm (at low pressures).

Cyclohexane ($\epsilon'' = 0.05$) on Aerosil 200 Silica. Conventional isotherms for cyclohexane on silica at 22, 32, and 53 °C and isosteres in the presence of microwaves at powers of 60, 120, and 240 W were obtained and are shown in Figure 2.

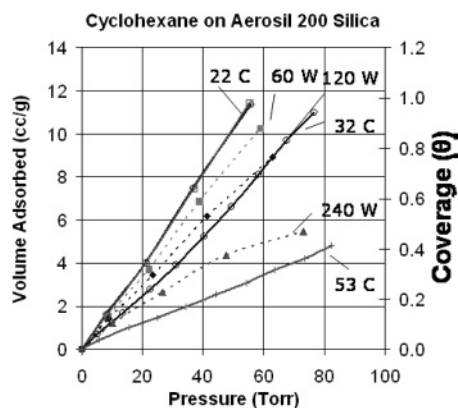


Figure 2. Adsorption isotherms for cyclohexane on Aerosil 200 silica as a function of microwave power employed.

Since the slope of the isotherm was not steep in the low-pressure region, the pressure at which a specific amount adsorbed could be determined accurately. The heat of adsorption could be estimated reasonably well. This was done by using the Clausius–Clapeyron equation⁸

$$(d \ln P)/(d(1/T)) = \Delta H_{\text{ads}}/R$$

For an ideal gas

$$\ln P|_{\theta} = -\Delta H_{\text{ads}}/RT + \text{constant}$$

From isotherms at several temperatures (plots of the amount adsorbed versus pressure at a constant temperature), a series of plots of isosteres were generated ($\ln P$ versus $1/T$ at a constant volume adsorbed). From the above equation, the heat of adsorption was found since the slope of the isostere is equal to $-\Delta H_{\text{ads}}/R$.

Once the isosteres were generated, the effective temperature in the presence of microwaves (at a particular volume adsorbed) can then be estimated using the slope and intercept of the isosteres and the above equation and solving for the temperature

$$T_{\text{eff}} = -\Delta H_{\text{ads}}/R(\ln P - \text{constant})$$

or from the plots of the isosteres

$$T_{\text{eff}} = \text{slope}/(\ln P - \text{intercept})$$

The effective surface temperature in the presence of microwaves (as a function of pressure) was also estimated by interpolating the volume adsorbed with the conventional isotherms. Both methods of calculating the effective surface temperature gave similar results and are shown in Figure 3.

Cyclohexane had a relatively small slope in the plot of the effective surface temperature versus pressure, due to the very low permittivity of cyclohexane. In this case the presence of cyclohexane in the gas phase or adsorbed phase has a small significance on the increase of the effective surface temperature.

The effective surface temperature of the adsorbent when no adsorbate is present can be estimated by extrapolating to zero adsorbate pressure (or zero coverage). The change in effective surface temperature is not zero, so the adsorbent surface is not completely transparent to microwave energy.

Dichloromethane ($\epsilon' = 0.39$) on Aerosil 200 Silica. Conventional isotherms for dichloromethane on silica at 22, 42,

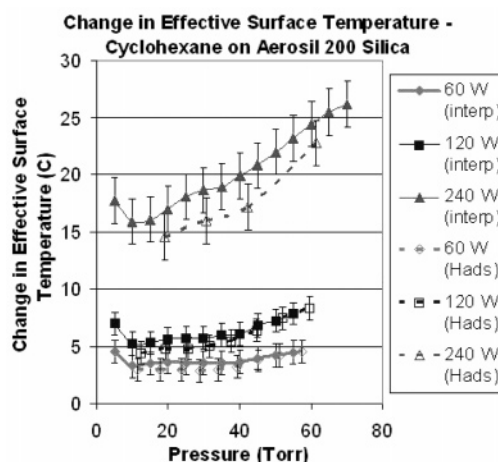


Figure 3. Change in effective surface temperature of cyclohexane on Aerosil silica as a function of microwave power employed, using interpolation (solid lines) and the heat of adsorption (dashed lines) to calculate the effective surface temperature.

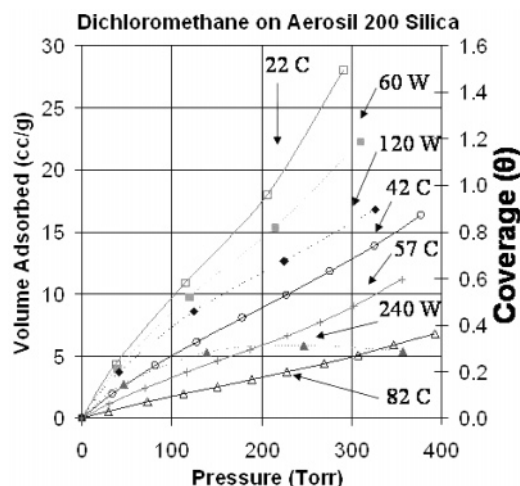


Figure 4. Adsorption isotherms for dichloromethane on Aerosil 200 silica as a function of microwave power employed.

57, and 82 °C and isosteres in the presence of microwaves at powers of 60, 120, and 240 W were obtained and are shown in Figure 4.

The heat of adsorption could be estimated reasonably well and was used to find the effective surface temperature, as above. The effective surface temperature in the presence of microwaves (as a function of pressure) was also estimated by interpolating the volume adsorbed with the conventional isotherms. Both methods of calculating the effective surface temperature gave similar results and are shown in Figure 5.

The effective surface temperature increase during dichloromethane adsorption was greater than that for cyclohexane (for the same microwave power used) due to the higher permittivity of dichloromethane.

It was noticed that the calculated volume adsorbed begins to decrease at high pressures for the isostere for dichloromethane on silica at 240 W. For conventional isotherm measurements, a decrease in the amount adsorbed with increasing pressure is contradictory. We conclude that this is a result of a nonisothermal condition in the gas phase. The air cooling over the sample at higher pressures is no longer sufficient to keep the temperature of the gas phase at 22 °C. The calculations for the amount adsorbed are based on an isothermal gas phase.

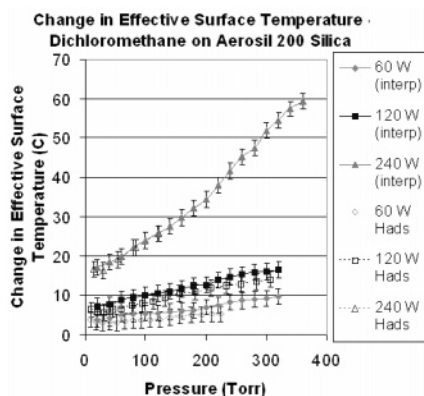


Figure 5. Change in effective surface temperature of dichloromethane on Aerosil 200 silica as a function of microwave power employed, using interpolation (solid lines) and the heat of adsorption (dashed points) to calculate the effective surface temperature.

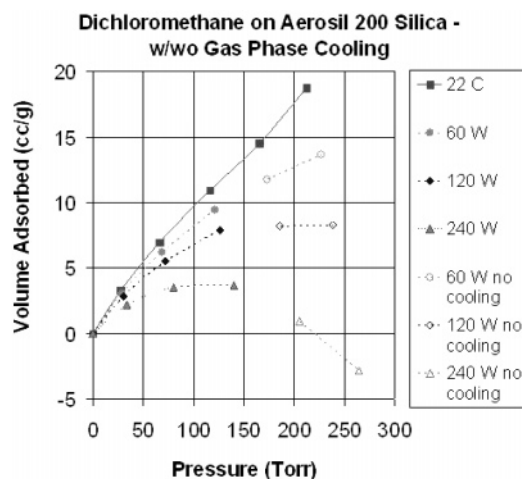


Figure 6. Isotherms for dichloromethane on Aerosil 200 silica as a function of microwave power employed, with and without gas-phase temperature control.

To confirm this, an experiment was carried out adsorbing dichloromethane at 240 W without air cooling. The calculated amount adsorbed begins to decrease at higher pressures and even drops to a negative value. A diagram of the results of this experiment is shown in Figure 6. After observation of this behavior, experiments were carried out at a microwave power where we estimate that the air cooling would be sufficient to achieve a steady state in the presence of microwaves. This effect also depends on the permittivity of the adsorbate. A higher permittivity adsorbate necessitates use of a lower maximum microwave power to maintain an isothermal gas phase.

2-Propanol ($\epsilon'' = 3.19$) on Aerosil 200 Silica. As stated earlier, a plasma was formed during the initial experiments with 2-propanol as the adsorbate. This contaminated the samples. New samples were prepared, and plasma formation was prevented by exposing the sample to microwaves at an adsorbate pressure greater than 10 Torr. Conventional isotherms for 2-propanol on silica at 22, 42, and 67 °C and isosteres in the presence of microwaves at powers of 30, 60, and 120 W were obtained and are shown in Figure 7.

The isotherms for 2-propanol on silica were not linear in nature. Unlike the isotherms for cyclohexane or dichloromethane, there was more adsorbed at lower pressures, so interaction of the first layer of the adsorbate with the adsorbent was stronger than the interactions of the subsequent layers of

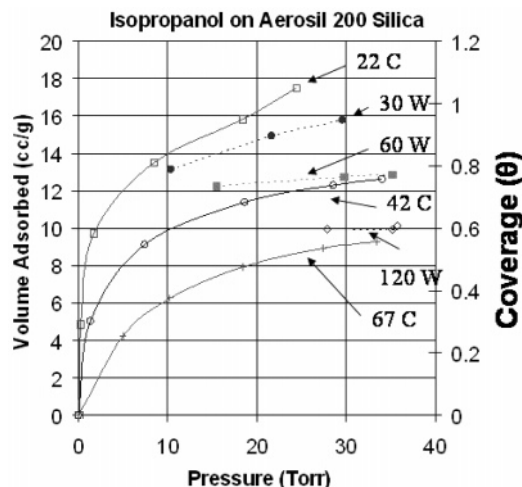


Figure 7. Adsorption isotherms for 2-propanol on Aerosil 200 silica as a function of microwave power employed.

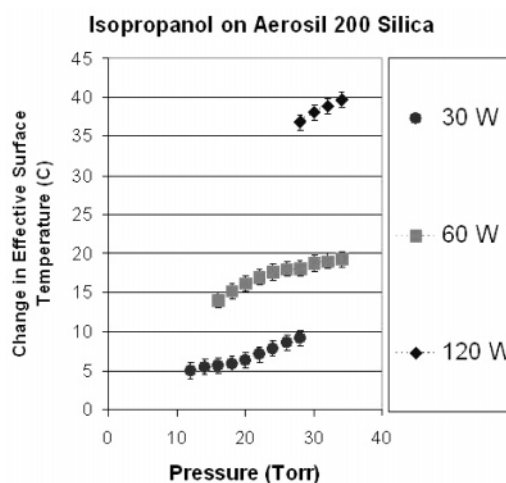


Figure 8. Change in effective surface temperature of 2-propanol on Aerosil 200 silica.

adsorbate with itself. This is probably due to the hydrogen bonding of the 2-propanol.

The heat of adsorption could not be estimated well using the Clausius–Clapeyron equation because data were not obtained at low pressures in the Henry's Law region (to prevent plasma formation).

The effective surface temperatures in the presence of microwaves (as a function of pressure) were estimated by interpolating the volume adsorbed with the conventional isotherms. Data were available over a limited range of pressures because the experiments had to be started at higher pressures to prevent plasma formation. The effective surface temperature increase during 2-propanol adsorption was greater than that for dichloromethane (for the same microwave power used) due to the higher permittivity of 2-propanol. A diagram of the effective surface temperature for 2-propanol on Aerosil 200 Silica is shown in Figure 8. 2-Propanol had a steeper slope than dichloromethane and cyclohexane in the plot of the effective surface temperature versus pressure, due to the high permittivity of 2-propanol.

Methanol ($\epsilon'' = 13.77$) on Aerosil 200 Silica. It was noticed from previous results that the amount of methanol adsorbed was not completely reversible before and after exposure to microwaves, so it was suspected that the methanol had reacted with the surface. Previous work by Meier²⁵ denotes that in the

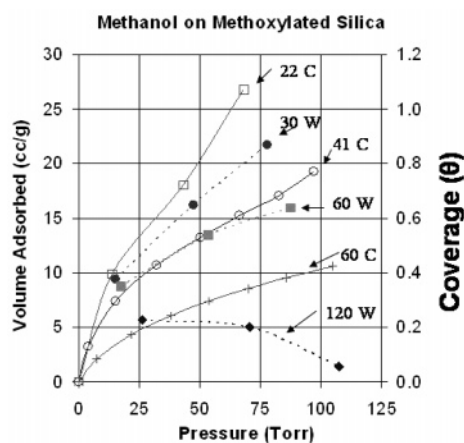


Figure 9. Adsorption isotherms for methanol on methoxylated Aerosil 200 silica as a function of microwave power employed.

presence of microwaves methanol can replace the surface O—H bonds of the sample with methoxylate and change its adsorption properties.

Since the adsorption properties of the surface were changing in the presence of microwaves and it was suspected that some degree of chemisorption was taking place, the amount adsorbed and the effective surface temperature cannot be directly compared to other adsorbates on silica, because the surface properties of the silica are changed by the adsorption of methanol. Once the methanol has fully reacted with the surface, the isotherms and isosteres in the presence of microwaves can be obtained, and an effective temperature in the presence of microwaves can be obtained for methanol on the methoxylated surface.

Conventional isotherms for methanol on methoxylated silica at 22, 41, and 60 °C and isosteres in the presence of microwaves at powers of 30, 60, and 120 W were obtained and are shown in Figure 9.

The isotherms for methanol on silica were similar in nature to the isotherms for 2-propanol, and the heat of adsorption could not be estimated well using the Clausius–Clapeyron equation because data were not obtained at low pressures in the Henry's Law region (to prevent plasma formation).

The effective surface temperature in the presence of microwaves (as a function of pressure) was estimated for the methoxylated surface by interpolating the volume adsorbed with the conventional isotherms. It was noticed that the volume adsorbed begins to decrease at high pressures for the isostere for methanol at 120 W, similar to that of dichloromethane on silica at 240 W as above. By similar reasoning, it is suspected that when the volume adsorbed decreases with an increase in pressure the assumption that the gas phase is at a constant temperature is no longer valid. The air cooling over the sample during experiments using high microwave power and higher pressures of a high permittivity adsorbate is no longer sufficient to keep the temperature of the gas phase at 22 °C. This behavior could also be due to the reaction of methanol to form dimethyl ether. Meier²⁵ found that methanol reacts on silicalite under microwave irradiation to form dimethyl ether. The effective surface temperature increase in the presence of microwaves during methanol adsorption was only slightly greater than that for 2-propanol (for the same microwave power used), because even though methanol has a much higher permittivity, the methanol reacted with the silica to alter the surface properties. A figure of the effective surface temperature for methanol on methoxylated Aerosil 200 Silica is shown in Figure 10.

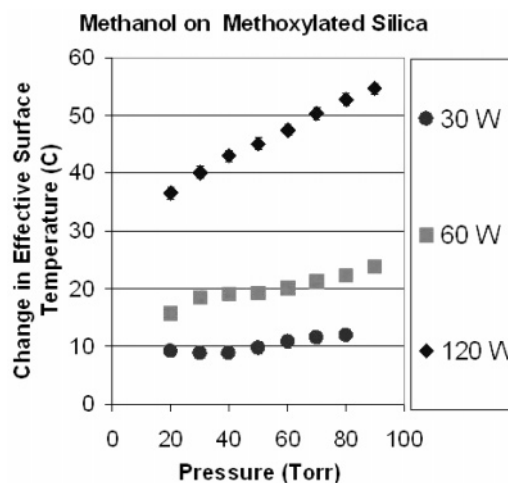


Figure 10. Change in effective surface temperature of methanol on methoxylated Aerosil 200 silica.

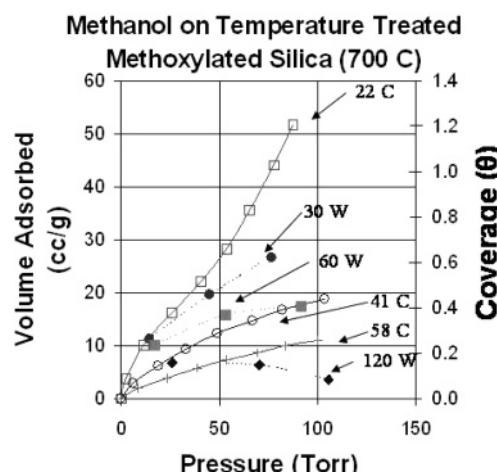


Figure 11. Adsorption isotherms for methanol on temperature-treated (700 °C) methoxylated Aerosil 200 silica as a function of microwave power employed.

Methanol on Temperature-Treated (700 °C) Aerosil 200 Silica. To investigate the possible methoxylation of the surface, A sample of Aerosil 200 silica was temperature-treated by heating it to 700 °C at 1 °C/min and holding it at 700 °C for 4 h to remove a fraction of the surface hydroxyl groups, reducing the amount of methoxylation of the surface that could occur. Studies by Gallas et al.²⁶ and Morrow and Gay²⁷ have measured the number of surface OH groups as a function of thermal treatment temperature between 200 and 800 °C, and their results show that the number of OH groups significantly decreases when heated. A multipoint BET calculation was performed on isotherms using nitrogen to check for any surface area loss caused by the temperature treatment. It was found that the surface area was approximately the same, and the sample had the same appearance (no discoloration). Conventional isotherms for methanol on the temperature-treated methoxylated silica at 22, 41, and 58 °C and isosteres in the presence of microwaves at powers of 30, 60, and 120 W were obtained and are shown in Figure 11.

The shape of the adsorption isotherm for methanol on the temperature-treated sample was similar to that of a sample with standard preparation; however, the surface properties of the silica were changed, and the effective surface temperature was lower for the temperature-treated sample.

Also similar to the previous sample, it was noticed that there is a similar behavior for the isostere for methanol at 120 W;

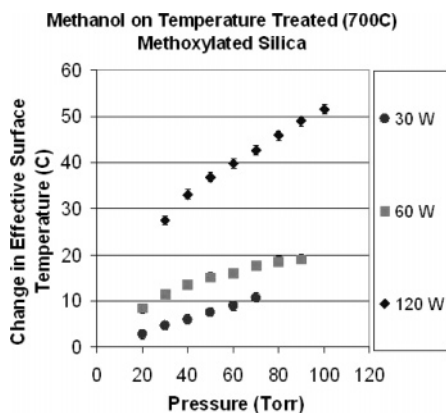


Figure 12. Change in effective surface temperature of methanol on temperature-treated (700 °C) methoxylated Aerosil 200 silica.

TABLE 2: Infrared Peaks for Chemical Groups^{31–34}

wavenumbers	attributed species
3748	isolated and geminal Si–OH stretch
3400–3550	associated hydroxyls stretch
2997, 2960, 2857	CH stretches from Si–O–CH ₃
1865	Si–O
1630	OH bend
1470	CH ₃ bend

the volume adsorbed begins to decrease at high pressures and is explained above.

A figure of the effective surface temperature for methanol on temperature-treated methoxylated Aerosil 200 silica is shown in Figure 12.

Infrared Spectroscopy of Aerosil 200 Silica and Methoxylated Samples. To confirm that a chemical reaction was taking place with methanol in the presence of microwaves and to investigate the changes of the silica surface with temperature treatment, IR spectroscopy was performed to investigate changes on the surface of the Aerosil 200 silica with five different sample treatments: (1) uncalcined Aerosil 200, (2) Aerosil 200 with standard pretreatment (calcined to 385 °C), (3) methoxylation of the surface of Aerosil 200 when methanol was adsorbed in the presence of microwaves, (4) temperature-treated Aerosil 200 (700 °C for 4 h), to investigate changes in the hydroxyl content due to temperature treatment, and (5) temperature treatment followed by methoxylation of the surface. Significant peaks in the spectrums will be discussed, and Table 2 above is given for reference.

This transmission IR spectroscopy was used because the samples, after adsorption in the presence of microwaves, could afterward easily be studied with minimal sample preparation to determine the presence of methoxyl groups. Because we were studying surface characteristics using a bulk technique, the signal resolution was not high; however, the methoxyl peaks were still evident. Methanol reacted with the silica in the presence of microwaves to methoxylate the silica surface and reacted to a lesser extent with on the sample treated to 700 °C. It is hypothesized that the temperature treatment reduces the surface hydroxyl concentration so that there are fewer reactive sites with which methanol can react to form a methoxyl group. A figure of the methoxyl peaks is shown in Figure 13.

***n*-Pentane on Silicalite.** Conventional isotherms for *n*-pentane on silica at 22, 35, and 48 °C and isosteres in the presence of microwaves at powers of 60, 120, and 240 W were obtained and are shown in Figure 14.

The shapes of the adsorption isotherms for all of the adsorbates used on silicalite were steep in the low-pressure

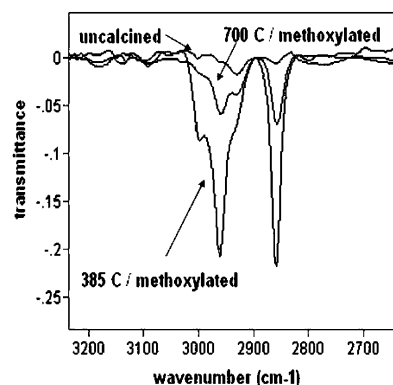


Figure 13. Transmission IR spectroscopy of methoxylated Aerosil 200 silica.

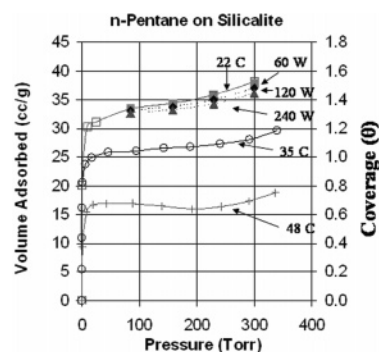


Figure 14. Adsorption isotherms for *n*-pentane on silicalite as a function of microwave power employed.

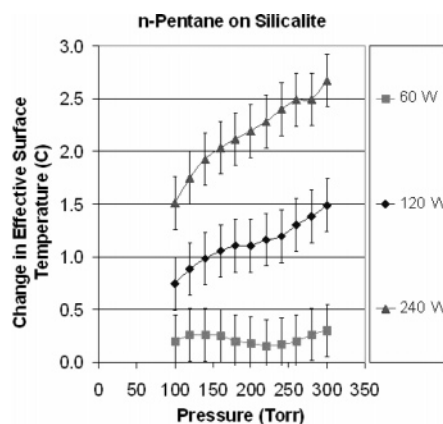


Figure 15. Change in effective surface temperature of *n*-pentane on silicalite.

region, since the adsorbent is microporous. The effective surface temperature in the presence of microwaves (as a function of pressure) was estimated by interpolating the volume adsorbed with the conventional isotherms.

Similar to cyclohexane on silica, *n*-pentane on silicalite showed a very small increase in the effective surface temperature with microwave exposure due to its low permittivity. A plot of the effective surface temperature versus pressure is shown in Figure 15.

Dichloromethane ($\epsilon'' = 0.39$) on Silicalite. Conventional isotherms for dichloromethane on silicalite at 22, 38, and 52 °C and isosteres in the presence of microwaves at powers of 30, 60, and 120 W were obtained and are shown in Figure 16.

Dichloromethane had an intermediate slope in the plot of the effective surface temperature versus pressure. A plot of the effective surface temperature versus pressure is shown in Figure 17.

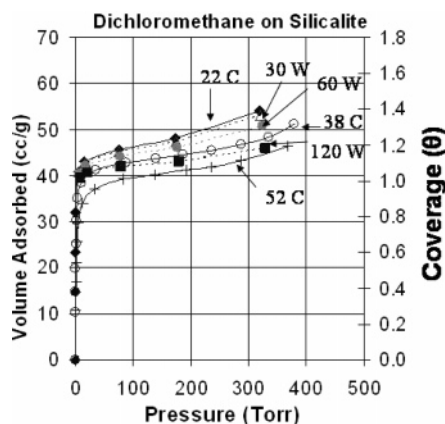


Figure 16. Adsorption isotherms for dichloromethane on silicalite as a function of microwave power employed.

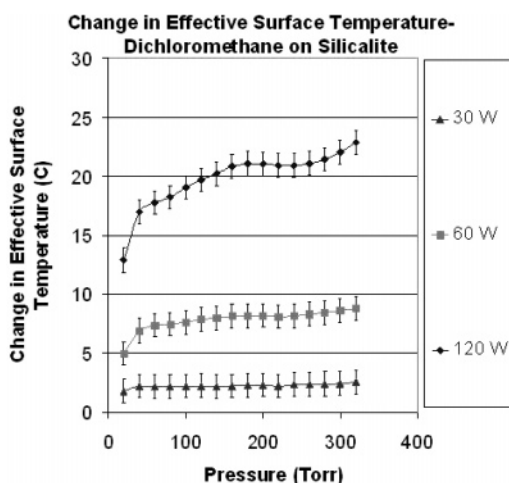


Figure 17. Change in effective surface temperature of dichloromethane on silicalite.

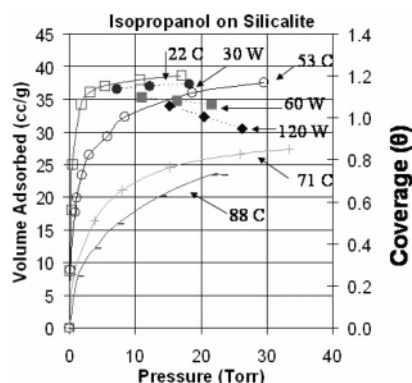


Figure 18. Adsorption isotherms for 2-propanol on silicalite as a function of microwave power employed.

2-Propanol ($\epsilon'' = 3.19$) on Silicalite. Conventional isotherms for 2-propanol on silicalite at 22, 53, 71, and 83 °C and isosteres in the presence of microwaves at powers of 30, 60, and 120 W were obtained and are shown in Figure 18.

The effective surface temperature in the presence of microwaves (as a function of pressure) was estimated by interpolating the volume adsorbed with the conventional isotherms. It was noticed that the volume adsorbed begins to decrease for the isosteres of 2-propanol on silicalite at 60 and 120 W, similar to the experiment for dichloromethane on Aerosil 200 silica at 240 W. It is suspected that when the volume adsorbed decreases with an increase in pressure that the assumption that the gas

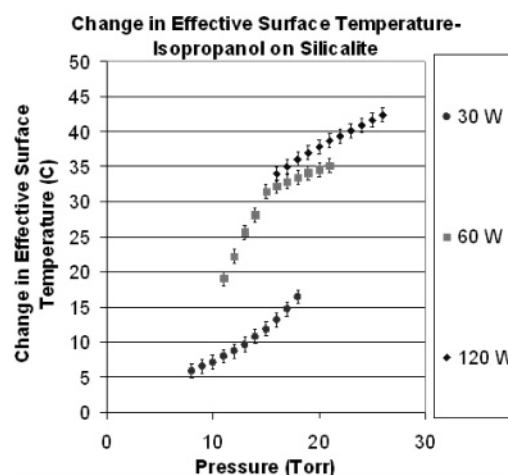


Figure 19. Change in effective surface temperature of 2-propanol on silicalite.

TABLE 3: Summary of Experiments Performed

adsorbate/adsorbent	isotherms (°C)	isosteres (W)
cyclohexane/silica	22, 32, 53	60, 120, 240
dichloromethane/silica	22, 42, 57, 82	60, 120, 240
2-propanol/silica	22, 42, 67	30, 60, 120
methanol/methoxylated silica	22, 41, 60	30, 60, 120
methanol/temperature-treated methoxylated silica	22, 41, 58	30, 60, 120
<i>n</i> -pentane/silicalite	22, 35, 48	60, 120, 240
dichloromethane/silicalite	22, 38, 52	30, 60, 120
2-propanol/silicalite	22, 53, 71, 88	30, 60, 120

phase is at a constant temperature is no longer valid. The air cooling over the sample at higher pressures is no longer sufficient to keep the temperature of the gas phase at 22 °C. The trend of the decrease in the volume adsorbed versus pressure begins at a lower power for 2-propanol than the other adsorbates because it has a higher permittivity, and it also begins at a lower power on silicalite than on silica because the adsorbates adsorb at a lower pressure on silicalite due to the microporous network structure. A plot of the effective surface temperature is shown in Figure 19.

A summary of the experiments performed is given in Table 3. The effective surface temperature increased with the bulk liquid permittivities of the adsorbates, for a particular adsorbent, surface coverage (θ), and microwave power used. This is discussed further in the next section.

Discussion

The effect of microwaves on the adsorption equilibrium relationship (and hence the amount adsorbed) can be visualized in two equivalent ways: (1) The microwaves can increase the energy level of the adsorbed state to a higher level within its potential energy well, or (2) the microwaves can raise the potential energy of the well itself, shifting the entire well upward in energy. This is depicted in Figure 20. In the first case, this is equivalent to a new effective temperature wherein the distribution-occupied energy states due to exposure to micro-

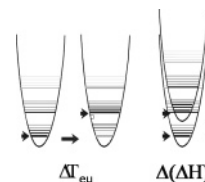


Figure 20. Energy potentials of systems upon exposure to microwaves.

wave energy could be viewed as the same as if the initial system had been raised to a higher level. In the case of sorption on oxides, the effect of microwaves on the effective temperature depends specifically on interactions with the adsorbed state.

Similarly, it is shown mathematically that the change in the equilibrium constant due to the presence of microwaves can be viewed as a change in the enthalpy of the adsorbed phase (or the heat of adsorption) due to microwaves or to a change in the effective temperature due to microwaves.

The equilibrium constant for adsorption can be expressed as

$$K_a = e^{Q/RT} = e^{-(H_a - H_g)/RT}$$

where K_a is the equilibrium relationship for adsorption, Q is the heat of adsorption, H_a is the enthalpy of the adsorbed phase, and H_g is the enthalpy of the gas phase, both related to the same standard states. The equilibrium constant for adsorption in the presence of microwaves can be expressed as

$$K_{a\mu} = e^{Q_\mu/RT} = e^{-(H_{a\mu} - H_g)/RT} = e^{Q/RT_{e\mu}}$$

where $K_{a\mu}$ is the equilibrium constant for adsorption in the presence of microwaves, Q_μ is the heat of adsorption in the presence of microwaves, $H_{a\mu}$ is the enthalpy of the adsorbed phase in the presence of microwaves, and $T_{e\mu}$ is the effective temperature in the presence of microwaves. If the equilibrium constant in the presence of microwaves is divided by the equilibrium constant, then

$$\frac{K_{a\mu}}{K_a} = e^{-(H_{a\mu} - H_a)/RT} = e^{Q/R((1/T_{e\mu}) - (1/T))}$$

so

$$\frac{-(H_{a\mu} - H_a)}{T} = Q \left(\frac{1}{T_{e\mu}} - \frac{1}{T} \right)$$

or

$$\frac{\Delta H_\mu}{Q} = \frac{\Delta T_\mu}{T_{e\mu}}$$

where ΔH_μ is the change in the heat of adsorption due to the presence of microwaves $-(H_{a\mu} - H_a)$ and ΔT_μ is the change in the effective temperature due to the presence of microwaves $(T_{e\mu} - T)$. The change in effective temperature due to microwaves can be expressed as

$$\Delta T_\mu = \frac{\Delta H_\mu T_{e\mu}}{Q}$$

and the effective temperature can be expressed as

$$T_{e\mu} = \frac{T}{1 - \frac{\Delta H_\mu}{Q}}$$

The change in the amount adsorbed due to microwaves (and change in enthalpy of the adsorbed phase due to microwaves ΔH_μ) is expected to be a function of (1) the adsorbate used, (2) the adsorbent used, (3) the amount adsorbed (θ), (4) the permittivity of the adsorbed phase (which is a function of the amount adsorbed for $\theta < 3^{28}$), and (5) the strength of the electric field. The amount adsorbed (θ) is itself a function of temperature, the adsorbate used, the adsorbent used, and the pressure

of the adsorbate in the gas phase. It is expected that ΔH_μ is proportional to ϵ'' and proportional to $|E|^2$, due to Poynting's Theorem, the average dielectric power dissipated in a volume of a medium³

$$P_1 = (\frac{1}{2})\omega\epsilon''|E|^2$$

As a first assumption, if microwave power is only dissipated in the adsorbed phase, then the amount of heat generated at steady state will be

$$Q_g = \frac{1}{2}\omega\epsilon''|E|^2 V_m \theta$$

where Q_g is the heat generated by microwaves, V_m is the monolayer volume, and θ is the fractional surface coverage.

As a first approximation, the permittivity of the adsorbed phase is assumed to be the same as that of the liquid phase of the adsorbate and is generally valid for $\theta > 3$.²⁸ However, very few measurements of the permittivity of adsorbed phases and of two-dimensional surfaces are available in the literature. As the amount adsorbed decreases, the permittivity of the adsorbed phase is expected to be lower than that of the bulk liquid phase to the value of the permittivity of the surface as θ approaches zero. Thorp²⁹ studied water on alumina and benzene on alumina and suggested that unless the adsorbent surface polarized the monolayer to any great extent, the value of the permittivity would be expected to be equal to that of the solid. Thiebaut et al.³⁰ suggested that for small values of θ , ϵ' increases linearly with θ and ϵ'' increases by a polynomial relationship to the second power for water on X13 zeolite. It still would be expected that when comparing the permittivities of adsorbed phases when adsorbing single components to the same value of θ , their permittivities would be proportional to their bulk liquid permittivities. Permittivity is also a function of temperature but as a first approximation can be treated as being proportional to the bulk liquid permittivity at room temperature. Although the permittivity of bulk liquids changes with temperature, Thiebaut et al.³⁰ found that the permittivity of moistened zeolite showed little variation with temperature compared to the expected corresponding variation for bulk liquid water.

Figure 21 shows the change in effective temperature versus the bulk liquid permittivity of the adsorbate used. It shows a linear trend for each adsorbent because the change in effective surface temperature is proportional to the bulk liquid permittivities, but the slopes and intercepts depend on the microwave power used and the surface coverage of the adsorbate. Also, the y-intercepts are much closer to zero for silicalite than silica; this indicates that with no adsorbate present the silica absorbs more microwave energy than silicalite. This is reasonable since the permittivity of the silica is expected to be higher than that of silicalite due to the higher concentration of hydroxyl groups on the surface of silica. The experiments with methanol on methoxylated Aerosil 200 silica were not included because chemisorption takes place with that particular adsorbate/adsorbent pair and alters the surface of the adsorbent, also changing the interactions for physical adsorption and preventing a direct comparison.

The power delivered to the system by the microwave oven is approximately proportional to the average electric field, so the amount of heat generated should be approximately proportional to the square of the power delivered. This will not be exact because the electric field within the adsorbate will not necessarily be proportional to the average electric field delivered in the oven, because the sample will distort the electric field in the oven to varying amounts depending on the permittivity of

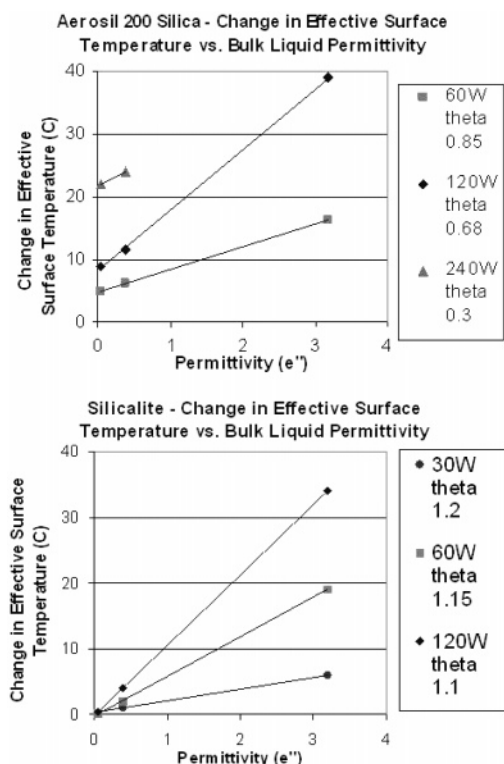


Figure 21. Change in effective surface temperature versus bulk liquid permittivity for Aerosil 200 silica (top) and silicalite (bottom).

the adsorbate, the amount adsorbed, and the geometry of the sample. The increase in effective temperature with microwave power shown in Figures 23 and 25 shows this general trend.

At steady state, the amount of heat generated by the adsorbed layer in the presence of microwaves must be transferred through the glass sample tube. The cooling air over the outside of the glass sample tube was adequate to transfer the heat in most cases, except when a high microwave power and high permittivity adsorbate were used. As a first approximation, the heat transfer can be described as being transferred by convection

from the adsorbed phase to the gas phase using a heat transfer coefficient

$$Q_g = hA(T_{eq} - T)$$

where h is the heat transfer coefficient and A is the surface area through which heat is transferred. T is the temperature of the gas phase and is assumed to be the same temperature as the cooling air on the outside of the glass sample tube. It is also assumed that the effective T_{eq} for adsorption will also be the same temperature for heat transfer purposes. The area of heat transfer from the adsorbate to the gas phase is the sample surface area times θ for $\theta < 1$ and the surface area for $\theta > 1$; however, some of the heat conducted into the solid phase may be convected to the gas phase when $\theta < 1$. For heat transfer by convection from an adsorbed layer to the gas phase, it would be expected that h decreases as θ increases.

For adsorption in zeolites, it would also be expected that the network effects of a zeolite such as silicalite would have an effect on the permittivity of the adsorbed phase, changes with the area for heat transfer between the adsorbed phase and the gas phase, and possibly the heat transfer coefficient.

Plots of the change in effective surface temperature versus the fractional surface coverage were made. The surface area of the adsorbent was found from a multipoint BET calculation using nitrogen. The monolayer volume for the adsorbate of interest (volume of adsorbate to achieve coverage of one monolayer) was then found by accounting for the difference in the surface area factor between the adsorbate of interest and nitrogen. The volume adsorbed at a particular pressure and calculated effective surface temperature in the presence of microwaves was then divided by the monolayer volume to obtain the fractional surface coverage. Plots for Aerosil 200 silica are shown in Figure 22 (grouped by microwave power) and Figure 23 (grouped by adsorbate). Plots for silicalite are shown in Figure 24 (grouped by microwave power) and Figure 25 (grouped by adsorbate).

Extrapolating the data to where no adsorbate is present ($\theta = 0$) yields an effective surface temperature that is greater than room temperature and increases with increasing microwave

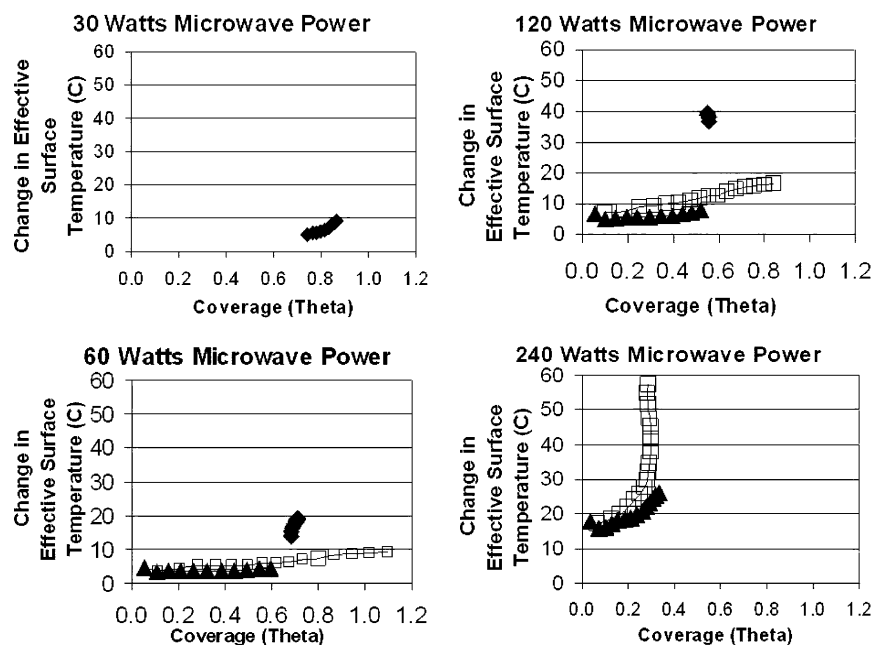


Figure 22. Change in effective surface temperature versus coverage (θ) on Aerosil 200 silica (grouped by microwave power): 2-propanol (filled diamonds), dichloromethane (open squares), cyclohexane (filled triangles).

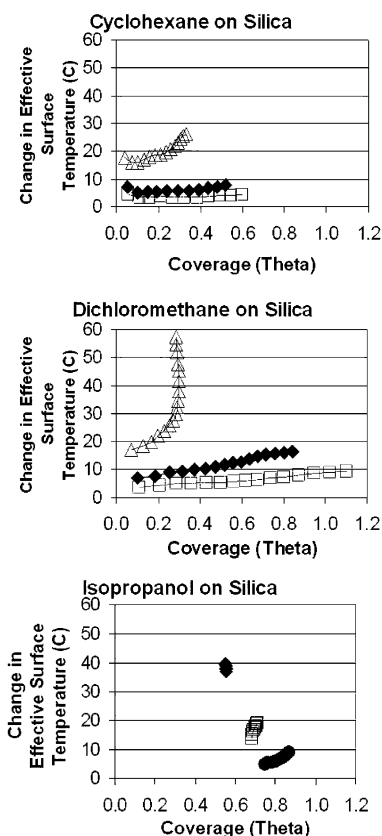


Figure 23. Change in effective surface temperature versus coverage (θ) on Aerosil 200 silica (grouped by adsorbate): 30 W (filled circles), 60 W (open squares), 120 W (filled diamonds), 240 W (open triangles).

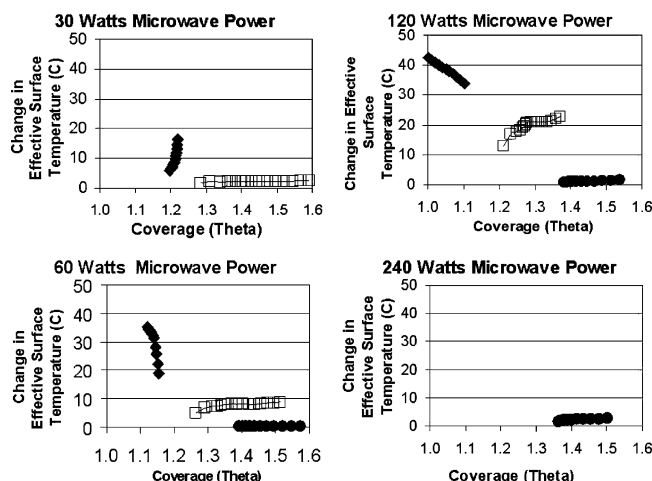


Figure 24. Change in effective surface temperature versus coverage (θ) on silicalite (grouped by microwave power): 2-propanol (filled diamonds), dichloromethane (open squares), *n*-pentane (filled circles).

power. The assumption that the adsorbent is transparent to microwave energy is good for low microwave power, because the permittivity of the adsorbent is very low. Since it is not zero, there is a small increase in the effective surface temperature when no adsorbate is present.

The effective surface temperature versus θ increases at a higher rate for adsorbates with a higher permittivity, because as θ increases the permittivity of the adsorbed phase becomes closer to the bulk liquid permittivity and increases the ability of the adsorbate to absorb microwave energy.

A steep slope (almost 90° angle) of effective surface temperature versus θ corresponds to an isostere (volume

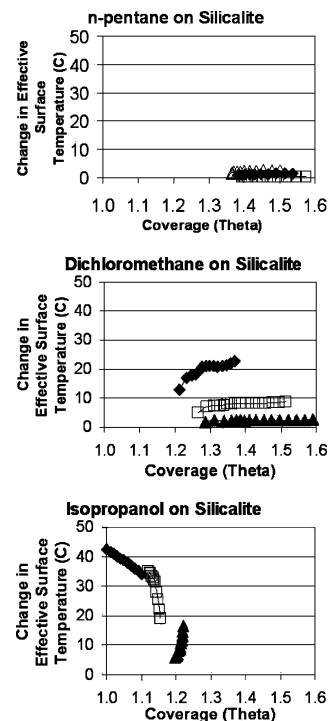


Figure 25. Change in effective surface temperature versus coverage (θ) on silicalite (grouped by adsorbate): 30 W (filled circles), 60 W (open squares), 120 W (filled diamonds), 240 W (open triangles).

adsorbed versus pressure) that would be near horizontal. A slope of effective surface temperature versus θ greater than a 90° indicates that the amount adsorbed is decreasing with increasing θ (which corresponds to increasing pressure) and that the assumptions used to measure the amount adsorbed are breaking down as described in the results section with dichloromethane on Aerosil 200 Silica at 240 W; it is suspected that when the volume adsorbed decreases with an increase in pressure that the assumption that the gas phase is at a uniform temperature is no longer valid. The air cooling over the sample at higher pressures is no longer sufficient to keep the temperature of the gas phase at 22 °C. The amount adsorbed is measured by the difference of the total amount of adsorbate in the system and the amount in the gas phase. Since the Ideal Gas Law is used to calculate the amount of adsorbate in the system and the gas phase, a change the temperature of a given volume of adsorbate will change the measured pressure, which leads to error in the calculated volume adsorbed.

Conclusions

It has been shown that microwave heating is not the same as conventional heating, and it is believed that this difference, the microwave effect, may be interpreted to be due to selective, local heating. The temperature at the surface where sorption occurs is effectively greater than the solid or gas temperature. In these studies, measurements of the amounts of adsorption as functions of the partial pressures of a specific adsorbate in the presence of microwave irradiation were related to the conventional adsorption isotherms. Equating the adsorbate pressure required to achieve a specific coverage (an isostere) in the presence of microwave irradiation to the amount adsorbed for a conventional isotherm allowed for an estimate of the effective surface temperature in the presence of microwaves. It was found that:

1. The effective surface temperature of the adsorbed phase during adsorption in the presence of microwaves can be found

by relating the conventional adsorption isotherms to isosteres obtained in the presence of microwaves.

2. The assumptions used for the calculation of the amount adsorbed began to deteriorate when using high microwave power and high permittivity adsorbates, as the cooling of the sample was no longer sufficient to maintain the constant temperature of the gas phase in the presence of microwaves.

3. The effective surface temperature increased and was proportional to the bulk liquid permittivities for adsorbates having a higher permittivity, for a particular adsorbent, surface coverage (θ), and microwave power used.

4. The effective surface temperature increased with increasing the microwave power, approximately proportional to the square of the microwave power, for a particular adsorbent, adsorbate, and relative pressure used.

5. The adsorbates 2-propanol and methanol formed plasma when a microwave field was applied (30 W or greater) when they were at low pressures (below 10 Torr).

6. Methanol chemically reacted with the Aerosil 200 silica surface in the presence of microwaves, altering the surface characteristics for adsorption. It was found that methanol reacted to form a methoxyl group which replaced a hydroxide group on the surface.

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List of Symbols

ΔH_μ = change in heat of adsorption due to microwaves
 ΔH_{ads} = heat of adsorption
 ΔT_μ = change in temperature due to microwaves
 ϵ = permittivity
 ϵ_0 = permittivity of free space
 ϵ' = real permittivity
 ϵ'' = imaginary permittivity
 ϵ_r = relative permittivity
 θ = fractional surface coverage
 λ_D = Debye length
 σ = conductivity
 ω = angular frequency
 A = area for heat transfer
 E = electric field
 H_a = enthalpy of the adsorbed phase
 $H_{a\mu}$ = enthalpy of the adsorbed phase in the presence of microwaves
 H_g = enthalpy of the gas phase
 h = heat transfer coefficient
 K_a = equilibrium constant for adsorption
 $K_{a\mu}$ = equilibrium constant for adsorption in the presence of microwaves
 P = pressure
 P_1 = power dissipated
 Q = heat of adsorption

Q_μ = heat of adsorption in the presence of microwaves

Q_g = heat generated by microwaves

R = gas constant

T = temperature

T_{eu} = effective temperature in the presence of microwaves

$\tan \delta$ = loss tangent

V_m = monolayer volume

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