Microwave Radiation's Influence on Sorption and Competitive Sorption in Zeolites

Michael D. Turner, Robert L. Laurence, and W. Curtis Conner
Dept. of Chemical Engineering, University of Massachusetts, Amherst, MA 01003

K. Sigfrid Yngvesson
Dept. of Electrical and Computer Engineering, University of Massachusetts, Amherst, MA 01003

The influence of microwave radiation on adsorption selectivity was studied using the adsorption and desorption of cyclohexane and methanol on high-silica zeolites. The amount of microwave energy absorbed depends on the specific system of adsorbent and adsorbate. The adsorbent, a high-silica zeolite, is effectively "transparent" to microwave radiation, while the two adsorbates reflect high (methanol) and low (cyclohexane) absorption of microwave energy. The measured system temperatures required for desorption by microwave energy were lower than those required for conventional heating. Further, microwave radiation can change the sorption selectivity; the adsorbate with the greater microwave absorptivity is desorbed selectively. It is concluded that the surface and adsorbed species can be heated selectively since the rate of microwave energy absorption can be greater than the rate of heat transfer from the surface.

Introduction

Zeolites and other molecular sieves have the potential to remove volatile organic compounds (VOCs) from process effluents to levels below parts per million. For molecules of the size of the intracrystalline pores, the heats of physical adsorption often exceed 40 kJ/mol. In order for the VOCs to be removed from the adsorbent, however, at least this amount of energy must be supplied. Heating is normally effected by conventional means such as electrical heaters or steam stripping. The entire system (the vessel, the adsorbent, and the adsorbate) then must be raised to the desorption temperature.

Intriguingly, bulk zeolites are essentially transparent to microwave radiation. On the other hand, polar VOCs and the oxide surfaces readily absorb microwave energy. Thus, the desorption might be effected without the necessity of heating the entire system to the desorption temperature (Mezey and Dinovo, 1982; Roussy et al., 1984; Stuerga and Gaillard, 1996).

Many studies have investigated the effects of microwave radiation on catalytic reactions (Burka and Weaver, 1993; Cha, 1993; Kingston and Haswell, 1997); however, relatively few studies in the scientific and patent literature discuss the effect of microwave radiation on the processes of physical sorption from the gas phase onto zeolitic solids (Kobayashi et al., 1994, 1996). These few studies are interesting because they show that microwave radiation has an effect different from conventional heating. However, they provide no explanation of the physical basis of the experimental results.

Since microwave radiation has such complex interactions with materials, three approaches were used. The results are combined to yield a more complete picture of how microwave radiation interacts with our systems. The first study explores the interaction of microwave radiation with the zeolite itself. Although it is often generalized that zeolites are completely transparent to microwave radiation, we have found that the zeolite may, in fact, play an important role in the desorption process. With a base line established for the interaction of the microwave radiation with the support, the second study examines how a single sorbate adsorbed on the zeolite interacts with microwave radiation. How does the dielectric permittivity of the adsorbate affect the adsorbate/adsorbent interaction with the microwave radiation? Finally, the third study assesses the ability of microwave radiation to influence the selectivity of the sorption process. The microwave selectivity results are compared to the conventional heating method by means of the heats of adsorption using the Clausius-Clapeyron equation (V_{ads} vs. temperature).

Correspondence concerning this article should be addressed to W. C. Conner.

Experimental Section

Materials

Our experiments used two zeolites. The first was a hydrophobic silicalite ($Si/Al > 100$) sample from United Catalysts with a "nominal" elliptical pore dimension of 5.3 Å × 5.6 Å for the straight channels, and 5.1 Å × 5.5 Å for the sinusoidal channels (Meier et al., 1996; Cook and Conner, 1999), and a packed-bed density of 0.49 g/cm^3. These were shipped in the form of sixteenth-in. (0.16-cm) extrudates. The second was a hydrophobic dealuminated Y zeolite (DAY) sample from Degussa ($Si/Al > 100$) with a circular pore dimension of 7.4 Å (Meier et al., 1996), a packed-bed density of 0.35 g/cm^3, and a pore volume of 0.3 cm^3/g (Degussa, 1992). These were shipped in the form of quarter-in. (0.64-cm) Raschig rings. These rings were crushed and screened to a Tyler Mesh Size of 10, which is equivalent to the sixteenth-in. extrudates.

The dielectric properties of the zeolites were measured using Hewlett-Packard 8753 and Hewlett-Packard 8510 automated network analyzers in conjunction with a Hewlett-Packard dielectric probe. The real part of the dielectric permittivity was measured to be 1.6 for silicalite and 1.7 for DAY zeolite. Microwave absorption in a material is proportional to the value of the imaginary part of the dielectric permittivity, ϵ'', as discussed in greater detail later. The dielectric probe method was not sufficiently sensitive to measure ϵ'' for pure samples of either zeolite; however, an upper limit of 0.05 was estimated. The other experiments reported in this article clearly establish that the microwave loss of pure zeolites is appreciable, but not so large as to be inconsistent with the upper limit for ϵ'' just given. When a component such as methanol was adsorbed in silicalite, ϵ'' was easily measurable (~ 10 at 2.45 GHz). However, cyclohexane adsorbed on silicalite showed the same dielectric permittivity (ϵ') as for pure silicalite, and ϵ'' was not measurable.

The cyclohexane and methanol adsorbates used were obtained from Fisher Chemical Company with purity greater than 99%. Methanol has a kinetic diameter of 3.85 Å (Harrison et al., 1984) and a dielectric constant of 33.62 as a liquid at 20°C (Lide, 1991), and cyclohexane has a kinetic diameter of ~ 6.3 Å (Harrison et al., 1984) and a dielectric constant of 2.023 as a liquid of 20°C (Lide, 1991). It should be remembered that the dielectric constant is the real part of the permittivity (ϵ') and indicates the ability of the material to be polarized by an electric field, a microwave field, for example. The imaginary part of the dielectric permittivity (ϵ'') is directly related to the real part and has a maximum equal to $\epsilon'/2$ for a particular frequency in the simplest model. Data on ϵ'' are scarce, but the proportionality of ϵ'' (max) to ϵ' makes ϵ' an approximate guide to the strength of interaction of a material with microwaves. Microwave absorption in an adsorbate/adsorbent system is more complex, as there are several forms of energy absorption and energy transfer, as will be discussed below.

Apparatus

The experiments were performed with an apparatus consisting of an inlet manifold connected to a reactor designed for exposure to microwave radiation. Either one or two, adsorbates can be introduced into the system through the inlet manifold (Figure 1) by means of bubble saturators. The concentration of each adsorbate in the gas stream can be adjusted by varying the temperature of the saturator and by adding a diluent stream.

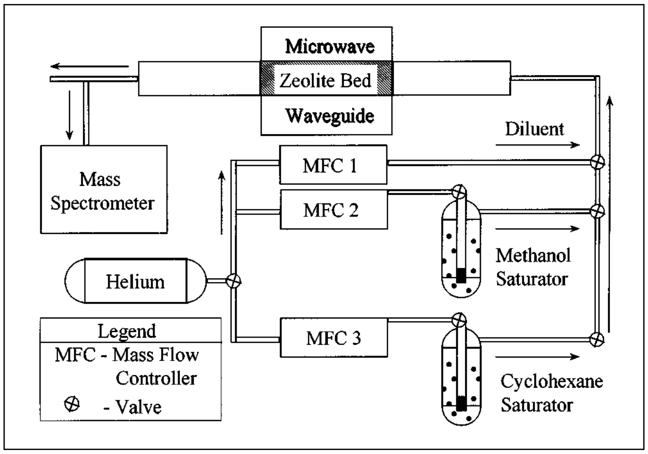

Figure 1. System diagram: inlet manifold for the microwave-mediated sorption experiments.

The on-line mass spectrometer and mass-flow controllers are each computer controlled. The details of the microwave waveguide are discussed in the text and shown in Figure 2.

A Nortech NoEMI-TS Series fiber-optic temperature-measuring system and an on-line Balzers QMG112A Quadrupole Mass Spectrometer were connected to the apparatus. The fiber-optic temperature probes were used to measure the bulk zeolite temperature at the entrance and exit of the zeolite bed. In addition, a probe was placed in the effluent stream to measure the temperature of the gas leaving the zeolite bed. The mass spectrometer was used to measure the concentration of the sorbates in the effluent.

The microwave reactor was designed and built for these experiments. The reactor consists of a Sairem Model GMP 03 K/SM, 300-W maximum, continuous variable power microwave source operating at 2.45 GHz; a Lectronic Corporation coaxial-to-WR284 waveguide adapter; a modified section of a Lectronic Corporation WR284 waveguide; and a Raytheon Corporation 1-kW water dummy load. The reactor system is shown in Figure 2. The microwave source measures both the forward and reflected power through its coaxial output cable. The main body of the reactor is the length of modified rectangular WR284 waveguide. The internal dimensions of the waveguide are 7.214 cm × 3.404 cm (Pozar, 1990). At 2.45 GHz, the electric field inside the waveguide is in the TE_{10} mode. This mode has uniform field strength along the short axis of the waveguide, as seen in Figure 3 (Pozar, 1990). As a result of this field alignment, ports were drilled through the long sidewalls of the waveguide to admit a quartz sample tube, 1.80 cm in diameter, through the microwave waveguide. This modification allows the entire sample to be exposed to a uniform amount of microwave radiation. Microwave chokes (1.91 cm in diameter and 5.08 cm in length) were installed over the ports in order to prevent the operator from being exposed to any spurious microwave radiation emitted from the ports. For a given diameter port, the length of the chokes are calculated from standard equations (Pozar, 1990). The

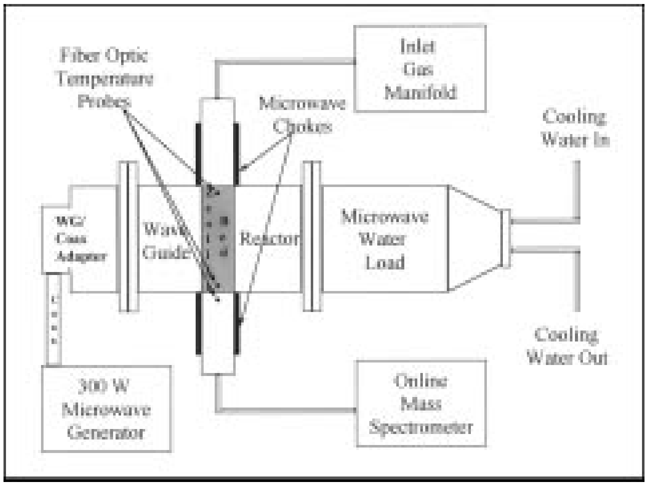

Figure 2. System diagram: microwave waveguide sorption system.

The 2.54-GHz generator was operated from 0 to 300 W of continuous power. The zeolite adsorbent bed passes through the short axis of the 7.2-cm × 3.4-cm rectangular waveguide.

water load is used to remove any radiation transmitted through the waveguide. In addition, the water load can be used to perform an energy balance on the system. The water load is a sink that minimizes reflection of the microwave radiation inside the reactor. The power supply never showed more than 3 W of power reflected back to the microwave source.

Procedure

Sample Preparation. The zeolites used were calcined at 500°C for 24 h under a flow of air. This removes any preadsorbed moisture, hydrocarbons, and templates. In order to avoid thermal shock to the zeolites, heating rates were never above 10°C/min. The zeolites were subsequently heated to 150°C in a microwave field under a dry helium stream for 2 h to remove residual moisture prior to each experiment.

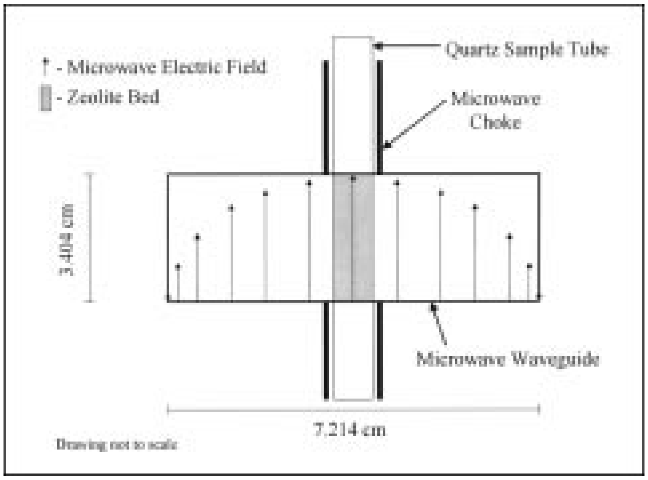

Figure 3. Microwave field orientation and relative strength in the TE mode of a cross section of a WR284 waveguide.

The position of the zeolite adsorbate bed takes advantage of the maximum in microwave power parallel to the short side.

The length of the bed was constrained to 3.404 cm, the length of the short axis side of the waveguide; thus, the bed volume was 8.65 cm^3. The bed contained either 4.26 g of silicalite or 3.01 g of DAY. The total flow rate through the bed for all experiments was 30 cm^3/min of ultrahigh-purity helium.

Microwave Heating of Dry Zeolites. At the start of the experiment, a 30-cm^3/min flow of ultrahigh-purity helium was introduced into the system. The temperature of the zeolite at the current room temperature was used as the base line for any temperature increases. With the flow rate unchanged, the microwave power was then increased from 0 W to 40 W and the temperature history recorded. Similarly, the power was increased from 40 W to 80 W and then from 80 W to 120 W with the temperature history recorded at each new power level. The procedure was then reversed and the temperatures were recorded at each power level as the power was dropped from 120 W to 80 W, then from 80 W to 40 W, and finally from 40 W back to 0 W. The microwave power levels described here are the forward power levels as indicated by the microwave source. Reflected power never exceeded 1% of the forward power.

Single Component. For the single-component adsorption, the adsorbate entered the system through a saturator in the inlet manifold. The concentration of the adsorbate in the gas phase was determined by adjusting the temperature of the saturator and by adding a diluent stream. The concentration of the effluent from the reactor was measured by an on-line mass spectrometer. Fiber-optic temperature probes were placed inside the bed at locations near the entrance and exit. Also, a probe was placed immediately after the end of the bed, and suspended away from the tube wall, in order to measure the temperature of the gas leaving the bed.

At time zero, a stream of 15 cm^3/min of helium saturated at 20°C with one adsorbate was mixed with a diluent stream of 15 cm^3/min of helium. This gas stream was introduced into the system through the inlet manifold. Initially, the bed contained no adsorbates. Adsorption commenced with the introduction of the saturated helium stream. The system was determined to be at steady state when the concentration of the effluent equaled the inlet concentration. Desorption was induced by means of microwave radiation. With no changes made to the inlet manifold flow rates, the microwave power source was raised to 40 W of continuous microwave power. The mass spectrometer measured the changes in the effluent concentration, and the fiber-optic probes measured the system temperatures. A new steady state having been established, the power level was increased by 40 W to 80 W, and the responses were measured. Again, the power level was increased by 40 W to 120 W, and the responses were measured. Once steady state was established at the highest power setting, the power was decreased in the reverse sequence in which it was raised, waiting for steady state at each power level.

Multicomponent. The competitive adsorption of two sorbing species was studied on each zeolite. Since single-file diffusion is known to occur in zeolites, the order in which the sorption process occurs may influence desorption. There are three possible permutations for the binary adsorption process. Two of the three permutations are sequential adsorption of the adsorbates on the zeolite. The third is the simultaneous adsorption of both components.

Case 1. Cyclohexane adsorption steady state is achieved. Methanol is then introduced and the system is allowed to reach a new steady state with both adsorbates present.

Case 2. Methanol adsorption steady state is achieved. Cyclohexane is then introduced and the system is allowed to reach a new steady state with both adsorbates present.

Case 3. Both methanol and cyclohexane are introduced simultaneously over the zeolite and the system is allowed to reach a new steady state with both adsorbates present.

For Case 1 and Case 2. At time zero, a stream of 15 cm^3/min of helium saturated at 20°C with one adsorbate was mixed with diluent stream of 15 cm^3/min of helium. This gas stream was introduced into the system through the inlet manifold. Initially, the bed contained no adsorbates. Adsorption commenced with the introduction of the saturated helium stream. Steady state was established when the concentration of the effluent equaled the inlet concentration. Once steady state was achieved, the diluent stream was diverted through a second saturator containing the second adsorbate. With the first adsorbate stream unchanged, the second sorbate was adsorbed on the zeolite until a new steady state was established, which might result in some desorption in the first adsorbate.

For Case 3. At time zero, a stream of 15 cm^3/min of helium saturated at 20°C with cyclohexane was mixed with a stream of 15 cm^3/min of helium saturated at 20°C with methanol. This gas stream was introduced into the system through the inlet manifold. Initially, the bed contained no adsorbates. Adsorption commenced with the introduction of the saturated helium stream. Steady state was established when the concentrations of the effluent equaled the inlet concentrations.

With steady stated established in all cases, the competitive adsorption proceeded using microwave radiation. With no changes made to the inlet manifold flow rates, the microwave power source was raised to 40 W of microwave power. The mass spectrometer measured the changes in the effluent concentrations, and the fiber-optic probes measured the system temperatures. The power level was increased by 40 W to 80 W, and the responses were measured. Again, the power level was increased by 40 W to 120 W, and the responses were measured. Once steady state was established at the highest power setting, the power was decreased in the reverse sequence by which it was raised, back to zero, waiting for steady state at each power level.

Results and Discussion

Microwave heating of the zeolites themselves

Silica comprises the zeolites used in these experiments. Pure silica has a dielectric loss approaching zero ($\epsilon'' \sim 1E-4$ to $1E-3$) and does not heat appreciably when exposed to microwave radiation. However, zeolites are high surface-area materials, and because silica bonds ends in silanols at a surface or defect, the concentrations of silanols in the zeolite may be large. Values in the literature range from about 5 OH/nm^2 to 16 OH/nm^2 (Guermeur and Jacolin, 1994). The larger value is calculated as the total amount of OH, including the internal OH, divided by the BET surface area measured by nitrogen adsorption.

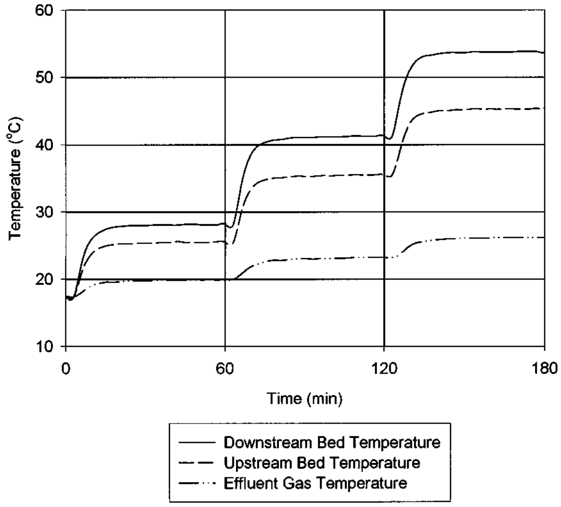

Figure 4. Heating curves at two positions in the zeolite bed and in the gas effluent for silicalite exposed to microwave radiation–temperature vs. time.

Silanols differ from bulk silica in that they do have a significant dielectric loss. Thus, when the silanols are exposed to microwave radiation, the OH groups can become rotationally excited producing heat, thus leading to an overall temperature increase (Guermeur and Jacolin, 1994). There are two principal mechanisms by which the heat can be transferred from the silanol-surface to the solid, and from the surface to gas phase. The rates of heat transfer by each of these mechanisms are not the same. The Biot number was calculated as 0.01, confirming that the transfer to the solid is much more rapid than the transfer to the gas. The amount of heat transferred depends on the masses and heat capacities of the different phases. In this system, the mass of silanol-surface is much lower than either the gas or bulk phases present.

Figures 4 and 5 show the heating of silicalite and DAY, respectively, in the presence of microwave radiation. The heating takes place in 40 W power increments from 0 W to 120 W under a 30 cm^3/min flow of dry helium. The zeolites were pretreated to remove any adsorbed species. Consequently, the increase in temperature of the zeolite can be attributed to the interactions of the microwaves with the silanol groups and the surface. This provides a basis for comparison with those cases when microwave radiation interacts with adsorbed species.

The average temperature increases above ambient for the silicalite sample were 9°C, 21°C, and 32°C at 40 W, 80 W, and 120 W, respectively, whereas the temperature increases for the DAY sample were only 5°C, 12°C, and 17°C at the same power levels. These differences can be attributed to two factors. First, the densities of the zeolites differ, 0.49 g/cm^3 for silicalite and 0.35 g/cm^3 for DAY; thus, there is more silicalite per unit volume with which the microwaves interact.

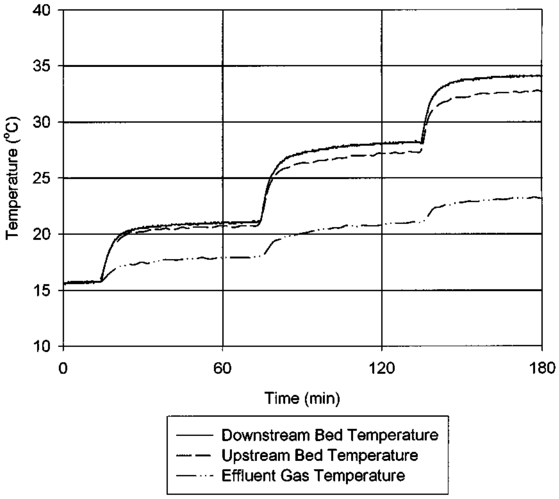

Figure 5. Heating curves at two positions in the zeolite bed and in the gas effluent for DAY exposed to microwave radiation–temperature vs. time.

Second, there may be differing hydroxyl content in each of the samples. However, we did not measure this quantity by other means.

Measured in these experiments are the temperature of the bulk zeolites at the beginning and end of the bed, and of the gas phase passing over the sample. The instantaneous temperature of the silanol-surface is not measured. The obvious temperature difference across the bed is due to convection. There is also a temperature difference between the bed and the gas passing over the bed. At 40 W, 80 W, and 120 W of applied microwave power, the temperature increases between the end of the bed and the gas were 6.9°C, 15.3°C, 23.4°C for silicalite (Figure 4) and 2.9°C, 6.8°C, 10.1°C for DAY (Figure 5). This suggests that heat transfer is not sufficiently rapid to achieve thermal equilibrium in these experiments. The rate by which microwave energy is selectively absorbed by the silanols is greater than the rate by which heat is transferred to the bulk phase. The zeolite bed has a measured overall heat transfer coefficient of 1.5 $W/°C * m^2$. We conclude that $T_{silanols}$ (not measured) $> T_{bulk} > T_{gas}$ phases. The energy absorbed is localized on the surface and transfer is too slow to reach thermal equilibrium.

If adsorbed species are present, they can modify the amount of energy absorbed because the adsorbates are concentrated on the surface. In addition, the adsorbed species can have dielectric properties, which differ substantially from the other phases present. Further, adsorbed species can modify the dielectric properties at the surface where they adsorb (Guermeur and Jacolin, 1994). These interactions were studied individually and then in concert in the experiments described below.

Single component

Four single-component desorption experiments in the presence of microwave radiation were executed to investigate:

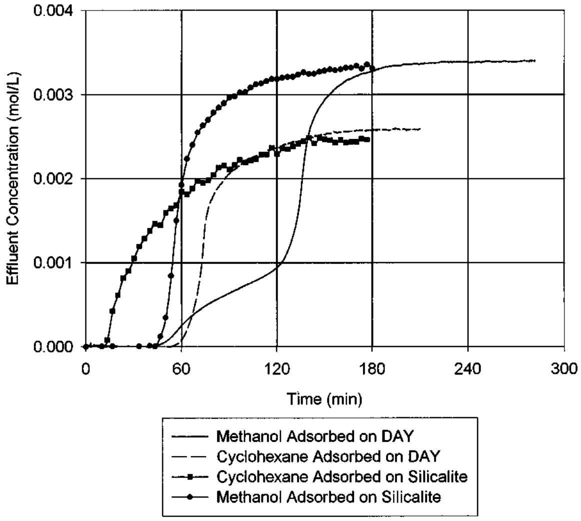

Figure 6. Single-component adsorption breakthrough curves: effluent concentration vs. time after introduction of the adsorbate (methanol or cyclohexane) into the 30-cm^3/min He diluent stream.

1. How microwave radiation interacts with the adsorbate.
2. How microwave radiation can affect the desorption of the adsorbate.

The experiments were performed with DAY and silicalite zeolites using a component with a low dielectric loss, cyclohexane, and a component with a high dielectric loss, methanol. A detailed explanation and comparison of each of the four possible combinations is presented below.

Adsorption. Each of the four experimental breakthrough curves is shown in Figure 6. The loadings of each of the four systems, shown in Table 1, were obtained by integration of the breakthrough curves. The loadings are based on moles of adsorbate per gram of adsorbent. These data show that the loading of the DAY zeolite is two to three times that of the silicalite for either adsorbate.

In addition to loading, a qualitative assessment of the diffusion of each adsorbate in the different adsorbents can be made based on the characteristics of the breakthrough curve. The rate of diffusion is based on the elapsed time from the initial breakthrough to the time at which adsorption equilibrium is achieved. The smaller that time, the more rapid the diffusion of the adsorbate in the adsorbent. Figure 6 compares the breakthrough curves of the cyclohexane/silicalite system with the cyclohexane/DAY system and the

Table 1. Loading Summary for Single-Component Adsorption

System	Loading (mol Adsorbate /kg Adsorbent)
Cyclohexane/DAY	2.10
Cyclohexane/silicalite	0.95
Methanol/DAY	4.50
Methanol/silicalite	1.70

methanol/silicalite system with the methanol/DAY system. It is apparent that both cyclohexane and methanol diffuse more rapidly in DAY than in silicalite. This is expected since the pore diameter of DAY, 7.4 Å, is larger than that of the silicalite, 5.3 Å×5.6 Å straight channels and 5.1 Å×5.5 Å sinusoidal channels (Meier et al., 1996). In addition, methanol diffuses much more rapidly than cyclohexane in both zeolites due to the smaller kinetic diameter of methanol, 3.85 Å, as compared to the kinetic diameter of cyclohexane, 6.3 Å (Harrison et al., 1984).

Desorption. Once an adsorption steady state had been established, the single-component desorption experiments using microwave radiation were performed. Figure 7 represents the raw data collected for the desorption of the methanol-silicalite system. With no changes made to the inlet manifold flow rates, the microwave power source was increased to 40 W of microwave power at 180 min. The mass spectrometer measured the changes in the effluent concentration, and the fiber-optic probes measured the system temperatures. Desorption occurred rapidly after the introduction of microwave radiation. This is observed in Figure 7 as the effluent concentration of methanol and the bulk zeolite temperature increased simultaneously. The amount of methanol desorbed from the zeolite was calculated by integrating the area enclosed by the effluent concentration and the base-line value of methanol at the start of the experiment. Once steady state had been established at 230 min, the power level was increased by 40 W to 80 W and the responses were measured. Again, the power level was increased by 40 W to 120 W and the responses measured. Once steady state was established at the highest power setting, the power was decreased in the reverse sequence, from 120 W to zero in 40 W increments, waiting for steady state at each power level.

The strong interaction of methanol with the microwave radiation can be seen in the temperature history of the zeolite. At 230 min, the microwave power is increased from 40 W to 80 W. As the temperature of the zeolite bulk increases, it appears to "overshoot" its equilibrium value at that power level. However, this overshoot is related to the concentration history of the adsorbed methanol, in that, as more methanol is desorbed from the zeolite, the temperature decreases. Thus, as the amount of methanol decreases, the microwave radiation interactions decrease and less heat is absorbed, leading to a decrease in the bulk zeolite temperature. However, this is not seen in the cyclohexane systems. Thus, we conclude that cyclohexane adsorbed on the zeolite has weak interactions with the microwave radiation. Also, the net desorption ceases as a steady state is reached. Thus, the temperature is established as a result of a balance between the microwave power absorbed and the total heat loss.

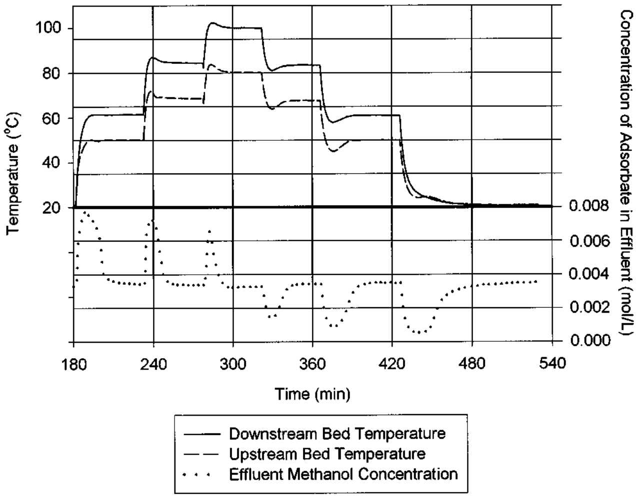

Figure 7. Desorption of methanol from silicalite by microwave radiation: temperature (above) and effluent concentration (below) vs. time with changes in microwave energy from 0 → 40 → 80 → 120 → 80 → 40 → 0 W.

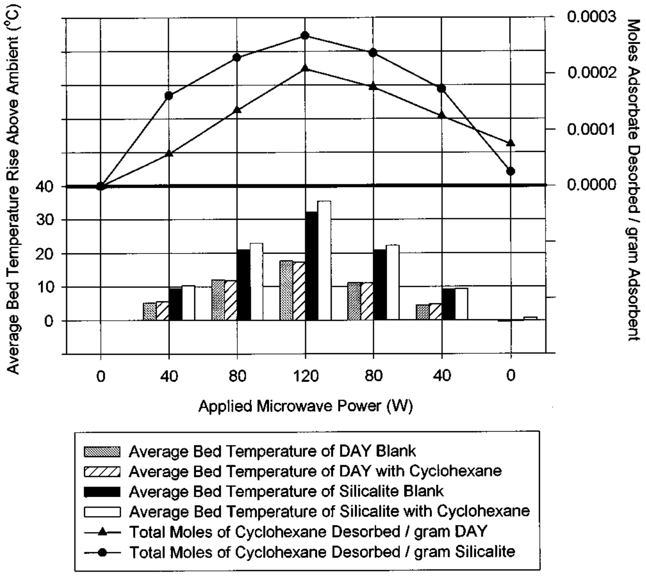

Figure 8. Single-component desorption experiments performed with cyclohexane: temperature and amount of cyclohexane desorbed from silicalite or DAY zeolites vs. microwave power.

Figures 8 and 9 are a graphical summary of all the raw data gathered in the four single-component adsorption experiments. Figure 8 summarizes the desorption of cyclohexane from silicalite and DAY zeolites, and Figure 9 summarizes the desorption of methanol from silicalite and DAY. These figures show the temperature of the zeolite (shown in bar-graph format) and the amount of adsorbate desorbed from the zeolite (shown in linear format) as a function of the applied microwave power. Figures 8 and 9 show both the temperature of the zeolite loaded with adsorbate and zeolite without adsorbate. This information was used to ascertain what portion of the microwave heating can be attributed to microwave interactions with the adsorbate and what portion attributed to the adsorbent. The microwave interactions with the adsorbed species are described below.

Microwave Interactions with Molecules. If a polar molecule is exposed to an alternating electric field, a torque is applied to the molecule. This torque causes the molecule to rotate in an attempt to align its dipole moment in the direction of the electric field. However, molecules cannot always orient them-

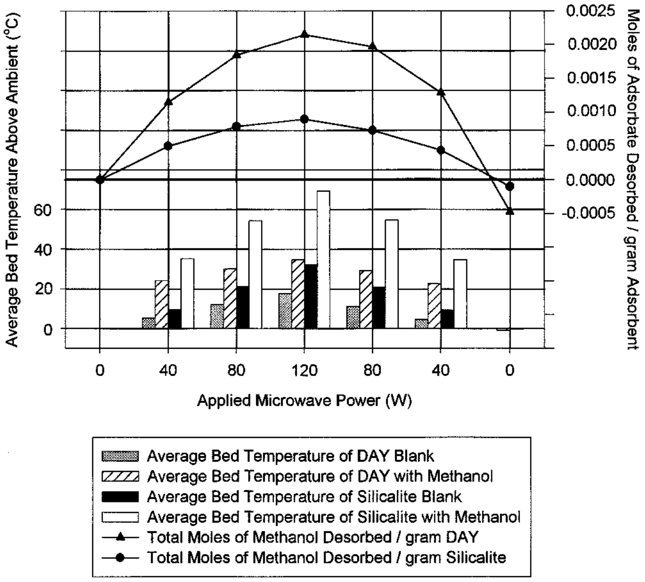

Figure 9. Single-component desorption experiments performed with methanol: temperature and amount of methanol desorbed from silicalite or DAY zeolites vs. microwave power.

selves completely at microwave frequencies since the electric field changes orientation approximately two billion times per second. It is this phase lag between the dipole moment of the molecule and the electric field that produces a molecule's dielectric loss. The dielectric loss is a measure of a molecule's ability to convert microwave radiation into heat. Since each molecule present interacts with the microwave radiation, it converts a portion of the radiation to heat. Thus, the interaction of microwave radiation with the adsorbed species is dependent on the magnitude of the dielectric loss and the amount of the species adsorbed (Buffler, 1993; Zlotorzynski, 1995).

A quantitative formulation of the preceding concepts introduces real and imaginary parts of the complex (relative) dielectric permittivity:

$$\epsilon = \epsilon' - i\epsilon''. \tag{1}$$

The out-of-phase component, ϵ'', gives rise to the absorption of microwave power, and the absorbed power per unit volume material is

$$P_{\text{abs}} = \epsilon''\epsilon_0 \omega E^2, \tag{2}$$

where ω is the angular microwave frequency; ϵ_0 the dielectric permittivity of vacuum (8.85×10^{-12} F/m); and E the microwave electric field (interior to the sample). Our measurements were performed at a constant frequency of 2.45 GHz. The absorbed power is thus proportional to three quantities: ϵ'', the volume of the adsorbing species, dV, and E^2. The latter is, in turn, proportional to the microwave power density in the sample, which was controlled by varying the output power of the microwave source.

Of the various media investigated, the zeolite had the largest volume, and a relatively low value of ϵ'', as shown by our dielectric probe measurements. The adsorbed cyclohexane had a small volume, and also a very small ϵ''. The adsorbed methanol had a small volume, but a large value for ϵ''. The conclusions drawn from our single-component desorption experiments are consistent with the relative magnitudes of these quantities. This should be kept in mind as we discuss the results of the measurements related to competitive sorption.

Figure 8 shows that virtually all of the heating came from the microwave's interactions with the adsorbent when cyclohexane, a material with a low dielectric loss, was adsorbed onto either the silicalite or the DAY zeolite. The adsorbent temperature was the same, within experimental error, whether the cyclohexane was or was not adsorbed. Therefore, the dielectric loss of cyclohexane is sufficiently small such that little microwave radiation is converted to heat. Thus, it fails to raise the temperature of the adsorbent. This is consistent with the very low value for ϵ'' obtained in our dielectric probe measurements.

However, Figure 9 indicates that when methanol was the adsorbate on either zeolite, a large portion of the microwave heating was due to the microwave interactions with the adsorbed methanol. This heating effect was manifested as temperature rises as much as 19°C above the blank DAY sample and 37°C above the blank silicalite sample. These interactions were dependent on the amount of methanol adsorbed on the zeolite. In the case of methanol adsorbed on DAY, the difference in temperature between the methanol/DAY system and the DAY blank was relatively constant. A value of 17°C−19°C occurred over a range of microwave power. The total amount of methanol desorbed from the DAY increases as the incident microwave power increases. Thus, as the power is increased, the interaction of the microwaves is stronger, but there is less methanol adsorbed on the DAY for the microwaves to interact. These two processes offset each other, and the temperature difference remains constant.

These series of experiments show that a steady state between the amount of methanol or cyclohexane that remains adsorbed is achieved within several minutes as the amount of microwave energy is changed from 0 W to 120 W. However, the temperatures measured in the gas phase or within the bed differ at each level of microwave energy above zero. It should be possible to estimate the heats of adsorption from a Clausius-Clapeyron (V_{ads} vs. temperature) plot of these data. Different heats of adsorption, however, would be calculated from the use of either the gaseous or the bed temperatures. We believe that microwave radiation does not modify the heat of adsorption. Rather, we believe that we have not actually measured the "effective" temperature in the presence of microwave radiation. Further, these systems are saturated systems where the amount of sorbate adsorbed is essentially independent of pressure. Thus, isosteric heats of adsorption cannot be estimated from these data.

Low-Temperature Desorption. In the systems where cyclohexane was the adsorbate, we observed desorption of cyclohexane at temperatures lower than expected. At the 40 W power level in the DAY/cyclohexane system, the temperature of the DAY increased approximately 5°C above ambient due to the DAY self-heating. At this temperature, it was not expected that desorption would occur; however, a significant amount of cyclohexane was desorbed at a system temperature of only 25°C. We have measured temperatures in the zeolite bed and in the gas phase after the bed. These are not the local temperatures at the surface where microwave energy is primarily absorbed. If the desorption rate is greater than the rate at which heat is transferred to achieve thermal equilibrium, the measured temperatures do not reflect the effective surface temperatures. Thus, the desorption is found to occur without the necessity of heating the system to the same temperatures required if thermal equilibrium is achieved.

The process of desorption is somewhat different from the simple heating of the system by microwave radiation; the process of desorption is significantly endothermic. Thus, the system is locally cooled as the desorption takes place. These findings suggest that the microwave-induced desorption processes are quite complex. Most importantly, desorption is found to occur without heating the whole system to the same temperature as for a conventional process. What are the effective temperatures in this system: the gas-phase temperature, the bulk temperature, the instantaneous surface temperature (with species adsorbed), or the "effective" surface temperature after desorption? We conclude that these differences in temperature are inherent to the evident "microwave effect" found for desorption induced by microwave radiation.

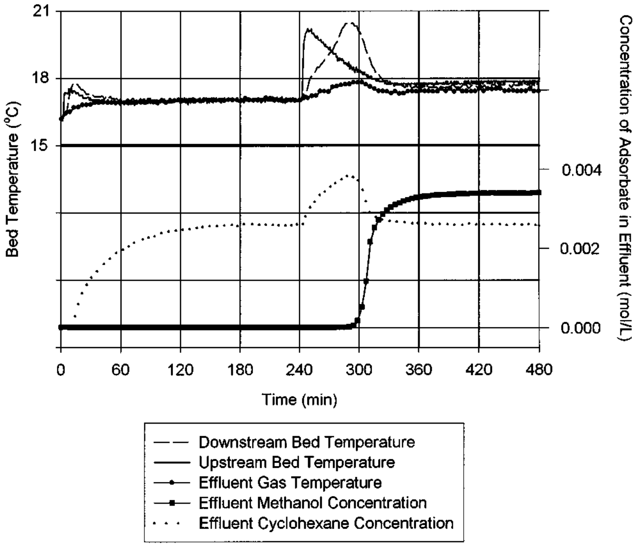

Figure 10. Initial adsorption, for Case 1 (cyclohexane adsorbed before methanol is introduced at 240 min), of the cyclohexane–methanol–silicalite system.

Temperatures in the bed (upstream and downstream) and in the gas effluent are shown above, while the effluent concentrations of methanol and cyclohexane (dotted) are shown below.

Competitive adsorption

We have shown that there are inherent differences in the desorption of cyclohexane and methanol. These differences show that the adsorbate has a direct influence on the absorption of microwave energy. We also have argued that absorption of microwave energy by a high-surface area, partially transparent adsorbent is a local surface phenomenon. Six multicomponent competitive adsorption experiments in the presence of microwave radiation investigated:

1. What happens when two adsorbing species are present?
2. Is the selectivity of adsorption influenced by microwave radiation?

The experiments were performed with DAY and silicalite zeolites using a binary adsorption system consisting of one component with a low dielectric loss, cyclohexane, and a second component with a high dielectric loss, methanol. A detailed explanation and comparison of each of the six possible permutations is presented below. These experiments show that microwave radiation can have a unique influence in competitive adsorption, which is independent of the order in which the components are adsorbed.

Initial Loading for Competitive Adsorption Experiments. There are three protocols for loading the zeolites with two components of the competitive adsorption experiments: sequential or simultaneous adsorption. Figure 10 represents the raw data collected for the initial loading, based on Case 1, of the cyclohexane–methanol–silicalite competitive adsorption experiment. At time zero, a stream of 15 cm^3/min of helium saturated at 20°C with cyclohexane was mixed with a diluent stream of 15 cm^3/min of helium. This gas stream was introduced into the system through the inlet manifold. Initially, the bed contained no adsorbates. Adsorption commenced with the introduction of the saturated helium stream. A typical breakthrough curve was observed between time zero and 240 min, with breakthrough occurring at approximately 60 min. The exotherm associated with the adsorption of the cyclohexane was observed as an increase in the bulk temperature of the zeolite between zero and 60 min. With steady state established at 240 min and the cyclohexane stream unchanged, the diluent stream was diverted through a second saturator containing the methanol at 20°C. As the methanol began to adsorb, it displaced some of the cyclohexane already adsorbed. This is evident as the cyclohexane concentration increases above its steady-state value, between 240 min and 360 min. Also, between 240 min and 360 min the exotherm associated with the adsorption of methanol is observed and due to the fact that the sorption capacity for methanol is larger than for cyclohexane. At 360 min, breakthrough of the methanol occurs, as marked by the rapid increase in the concentration of methanol in the effluent. By 480 min, both cyclohexane and methanol concentrations had reached the new steady states. Similar results were obtained in the other five experiments.

The adsorption loadings of each of the three cases for each zeolite (shown in Table 2) were obtained by integration of the breakthrough curves, similar to the curve in Figure 10. The loadings are based on moles of adsorbate per gram of adsorbent.

Influence of Microwave Radiation. Once the initial loading of the zeolites was complete, the competitive adsorption experiments using microwave radiation were performed. Figure 11 represents the raw data collected for the cyclohexane–methanol–silicalite competitive adsorption experiments that was initially loaded using Case 1. At 480 min, the adsorbate/adsorbent were exposed to microwave radiation by

Table 2. Zeolite Loadings after Initial Binary Adsorption for All Cases

Zeolite	Adsorption Method	mol C_6H_{12}/ kg Adsorbent	mol CH_3OH/ kg Adsorbent
Silicalite	Case 1	0.35	1.74
Silicalite	Case 2	0.15	1.74
Silicalite	Case 3	0.21	2.14
DAY	Case 1	0.80	1.40
DAY	Case 2	1.53	1.20
DAY	Case 3	1.06	1.50

a step change in the incident power from zero to 40 W. Since the zeolite is saturated with equilibrium amounts of both cyclohexane and methanol, any increase in the zeolite temperature will cause desorption to occur. Thus, both the concentrations of the cyclohexane and of the methanol begin to rise immediately after the microwave radiation is applied and the bulk temperature of the zeolite rises. However, microwave radiation has a greater interaction with methanol than with cyclohexane, as observed earlier. Therefore, as the methanol is desorbed, the cyclohexane, having weak interactions with microwaves, can readsorb preferentially into the zeolite in lieu of the methanol, thus changing the adsorption selectivity. This is evident in Figure 11 as the concentration of cyclohexane in the effluent drops below its initial steady-state value and as the concentration of methanol in the effluent rises above its initial steady-state value.

Because the microwave interactions with the adsorbed species cause the zeolite temperature to increase, one could argue that pure heating effects are the cause of the differences in the species sorbed at steady state and not the microwave radiation. However, the heat of sorption for methanol in silicalite, 43 kJ/mol (Thamm, 1989), or methanol in DAY, 45 kJ/mol (Izmailova et al., 1994), is lower than the heat of sorption for cyclohexane in silicalite, 63 kJ/mol (Cavalcante and Ruthven, 1995), or cyclohexane in DAY, 50 kJ/mol (Barthomeuf and Ha, 1973). Thus, the species with the larger heat of adsorption (cyclohexane) should be the component that desorbs more with increasing temperature. Yet, experiments show that the amount of cyclohexane adsorbed actually increases. This is due to the ability of methanol to absorb microwave energy more efficiently than cyclohexane.

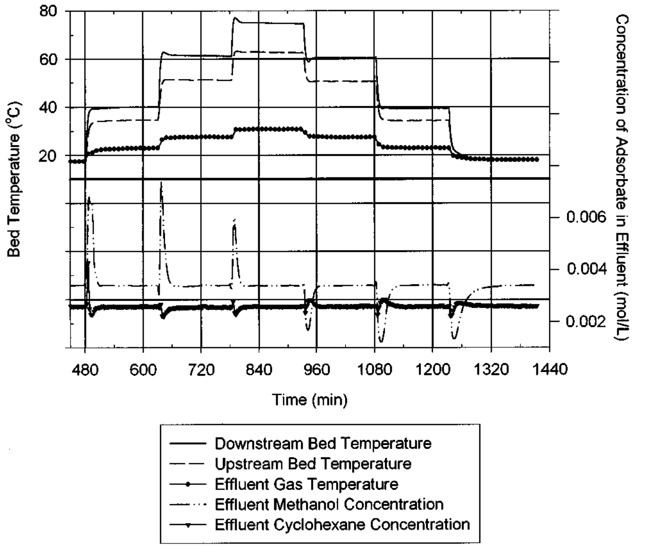

Figure 11. Competitive sorption of the cyclohexane–methanol–silicalite system initially loaded using Case 1 (Figure 10).

Temperatures in the bed (upstream and downstream) and in the gas effluent are shown above, while the effluent concentrations of methanol and cyclohexane (dotted) are shown below.

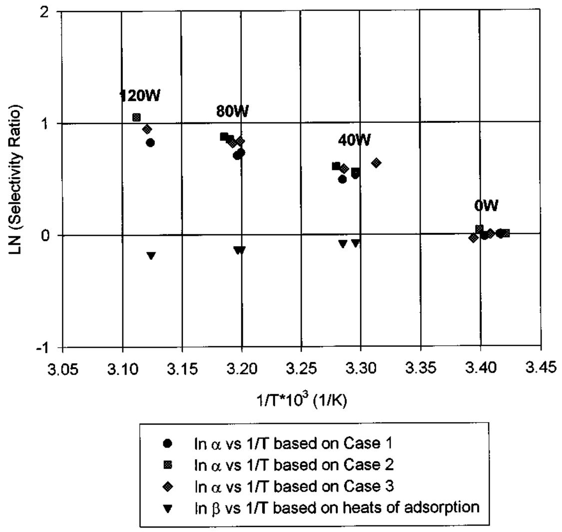

Figure 12. Competitive adsorption experiments performed on the zeolite DAY: ln (selectivity ratio: α or β) vs. $1/T$ (see text for definition).

After steady state is established at the 40 W power level, at approximately 635 min, the power level is changed to 80 W in a stepwise manner. Results similar to those at the 40 W power level are obtained. The same is true for the 120 W power level. Once steady state was established at the highest power setting, the power was decreased in the reverse sequence, from 120 W to zero in 40 W increments, waiting for steady state at each power level.

Figures 12 and 13 are a graphical summary of raw data collected during these six competitive adsorption experiments. Figure 12 is the summary of the three competitive adsorption experiments performed on the DAY sample, and Figure 13 is the summary of the three competitive adsorption experiments performed on the silicalite sample. The plots are of the form ln α or ln β vs. $1/T$ where α and β are defined as follows:

$$\alpha = \frac{q_{\text{Cyclohexane}}^{\text{Microwave Power}} / q_{\text{Methanol}}^{\text{Microwave Power}}}{q_{\text{Cyclohexane}}^{\text{Microwave Power = 0}} / q_{\text{Methanol}}^{\text{Microwave Power = 0}}}$$

$$\beta = e\left(\frac{\Delta H_{nr} \Delta H_c}{R}\right) \cdot \left(\frac{1}{T} - \frac{1}{T_o}\right)$$

where q is the adsorbate loading and ΔH_c and ΔH_m are the heats of adsorption for cyclohexane and methanol, respectively.

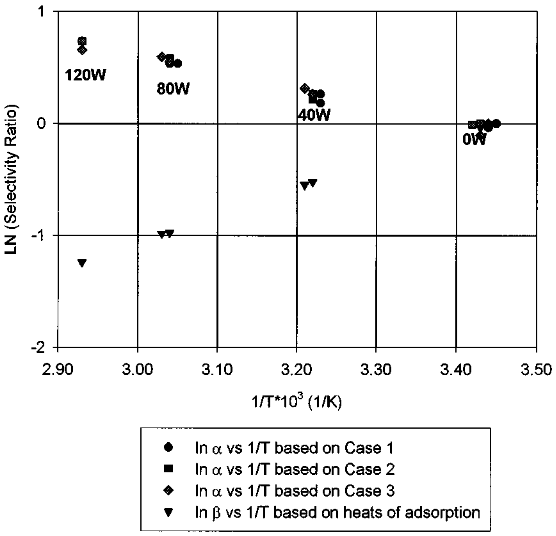

Figure 13. Competitive adsorption experiments performed on the zeolite silicalite: ln (selectivity ratio: α or β) vs. $1/T$ (see text for definition).

The ratios α and β can be viewed as adsorption selectivities based on the relative amounts of methanol and cyclohexane adsorbed in the zeolite at conditions produced by microwave radiation and conventional heating, respectively. Each of the ratios is normalized to ambient conditions, room temperature with no applied source of radiation. Figures 12 and 13 show how microwave radiation changes the adsorption selectivity of cyclohexane over methanol vs. conventional heating in both DAY and silicalite. As microwave radiation is applied to the system, the selectivity for adsorption of cyclohexane over methanol increases. This increase in the adsorption selectivity is seen in both Figures 12 and 13 as an increase in ($\ln \alpha$) with increasing microwave power and ultimately increasing bulk zeolite temperature. However, if this experiment were conducted using conventional heating, the resulting adsorption selectivity (β) would be based on the heats of adsorption of methanol and cyclohexane on the zeolite. Figures 12 and 13 show that the resulting adsorption selectivity of cyclohexane over methanol actually decreases with $1/T$. These results clearly show that microwave radiation changes the adsorption selectivity of both the cyclohexane–methanol–silicalite and cyclohexane–methanol–DAY systems. However, the magnitude of the changes differs with the zeolite. There is no significant influence of the order of adsorbate introduction.

Conclusions

The interaction of microwave radiation with materials is complex. To deconvolute these interactions, three types of experiments were performed. The results from these studies were combined to yield a more complete picture of the interactions of microwave radiation with our sorbing systems. The first study examined the interaction of microwave radiation with the zeolite itself. Our results show that zeolites are only partially transparent to microwave radiation. We conclude that interaction between the microwaves and zeolites is due to the surface and silanol groups on the surface of the zeolite. Silanols have a significant dielectric; therefore, they can selectively absorb microwave energy. The fiber-optic temperature probes are not able to measure the temperature of these surface silanols. However, we are able to measure the temperature of the zeolite and of the gas passing over the zeolite. These temperatures suggest that the heat transfer is not rapid enough to achieve thermal equilibrium. Thus, the rate by which the microwave energy is absorbed by the surface silanols is greater than the rate by which the heat is transferred to zeolite and finally to the gas phase. We conclude that the temperature profile in the system is T_{silanol} (not measured) $> T_{\text{bulk}} > T_{\text{gas}}$.

With a base line established for the interaction of the microwave radiation with the support, the second study was to understand how a single adsorbate on the zeolite interacts with microwave radiation. Based on the temperatures measured during the desorption experiments, cyclohexane has weak interactions with the microwave radiation. This is manifested by temperature rises above ambient that were the same, within experimental error, as the zeolite without sorption. Conversely, during the methanol desorption the temperature increase was significant, as much as 20°C above the blank zeolite temperature. This leads us to conclude that methanol has a rather strong interaction with the microwave radiation. These results are not surprising in that the dielectric constants for these adsorbates suggest that cyclohexane (dielectric constant of 2.023) should have weak interactions with microwave radiation, whereas methanol (dielectric constant of 33.62) should have strong interactions. This was also confirmed with the microwave probe measurements.

In addition to measuring the strength of the interactions of the microwave radiation with the zeolite, we observed the desorption of cyclohexane at temperatures, between ~25°C and ~60°C, that were lower than would be expected in conventional heating (~80°C). The temperatures that we have measured in the zeolite bed and in the gas phase after the bed are average bulk temperatures and not the local temperatures at the surface where microwave energy is primarily absorbed. Thus, the desorption is found to occur without the necessity of heating the system to the same temperature required if thermal equilibrium were achieved. The desorption process induced by microwaves is complex. The effective temperatures in this system are the gas-phase temperature, the solid temperature, the instantaneous surface temperature (with species adsorbed), or the "effective" surface temperature after desorption. We conclude that differences between these temperatures are inherent to the evident "microwave effect" found for desorption induced by microwave radiation.

Finally, the third study examined the ability of microwave radiation to influence the selectivity of the sorption process. The results of these experiments show that with an increase in the microwave power, and thus the temperature of the system, that methanol is desorbed and cyclohexane adsorbed in its place. This result is the obverse to what would occur in conventional heating. Since the heat of adsorption of methanol is lower than the heat of adsorption of cyclohexane, cyclohexane should have been desorbed and methanol should have been adsorbed in its place or desorbed to a lesser extent. Thus, these results show that independent of how the zeolite was initially loaded, the microwave radiation changes the adsorption selectivity of both the cyclohexane−methanol−silicalite and cyclohexane−methanol−DAY systems. We hypothesize that this change in selectivity will occur for other competitive sorption processes in the presence of microwave radiation. The changes in selectivity will depend on the dielectric properties of the adsorbate/adsorbent system.

Microwave radiation would be expected to have a similar influence on sorption for other systems where the bulk is essentially transparent to microwaves. This would include oxides and mixed metal oxides that have low permittivity (such as silicas, aluminas, silica-aluminas, and zeolites, but not activated carbons). However, the ability of the surfaces of these adsorbents to absorb microwave radiation would depend on the surface chemistry (such as hydroxylation) and the permittivity of the adsorbed species. We suggest that all surfaces possess higher permittivities than the bulk due to the potential polarizability of the terminal bonds.

There are three advantages of the use of microwave radiation to influence sorption. First, the overall energy demands for desorption (regeneration) induced by microwave energy are less than those induced by conventional resistive heating or steam stripping. The conventional approaches of regenerating an adsorbent require that the whole system (adsorbent and gas phases as well as the container, etc.) must be raised to the desorption temperature. Microwave-induced desorption need only directly heat the surface/adsorbed phases. Our measurements show that less than half the energy is required for regeneration by microwave energy than that required with conventional approaches. This will be described in a subsequent publication. Second, the time required for regeneration by microwave heating can be significantly less than the time required by conventional approaches. Microwave energy is transferred more rapidly and can be more selectively absorbed by the adsorbed phase. Finally, the selectivity of desorption can be controlled. This control is possible if the permittivities of the adsorbates differ.

Acknowledgments

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Notation

Biot number = hR/k
h = measure overall heat-transfer coefficient, W/°C·m^2
ΔH_{ads} = isosteric heat of adsorption, kJ/mol
k = thermal conductivity of zeolite, W/°C·m
R = radius of zeolite bed, m
V_{ads} = volume of adsorbate adsorbed on the zeolite, cm^3

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