Thermochimica Acta, 226 (1993) 333–342
Elsevier Science Publishers B.V., Amsterdam

Selective molecular sorption by high surface area catalyst supports [1]

Gregory S. Hickey * and Pramod K. Sharma

Jet Propulsion Laboratory, California Institute of Technology, 4800 Oak Grove Drive, Pasadena, CA 91109 (USA)

(Received 24 September 1992; accepted 19 April 1993)

Abstract

Three high surface area catalyst supports were studied for the selective molecular sorption of organic compounds. The first was a carbon molecular sieve with a well-defined pore structure. The other two were silica gel and high surface area alumina. Both have a random pore structure. A mixture of phenol and acetic acid was used to qualitatively characterize the intermolecular force potentials and pore selectivity. Thermal gravimetric analysis and mass spectroscopy were used to characterize the desorption kinetics and differential scanning calorimetry was used to study the heats of desorption. The analyses illustrate an approach for characterizing adsorption–desorption processes in catalysts and high surface area materials.

INTRODUCTION

Catalysts with high surface area and porosity usually participate in chemical processes through adsorption and desorption. It is of significant interest to characterize the adsorption and desorption processes in catalyst supports. In addition, high surface area materials such as catalyst supports have a long history for use as adsorbents in the removal of contamination in gas streams. By a combination of pore size distribution and intermolecular attraction, such adsorbents can selectively remove organic vapors by physical and chemical sorption. The nature of the adsorbent–adsorbate intermolecular attraction can be studied by their desorption characteristics [1]. In this study the selective removal of two organic compounds, phenol and acetic acid, were evaluated on three saturated adsorbents. The adsorbents studied were a carbon molecular sieve (CMS), silica gel, and

---

* Corresponding author.

[1] Presented at the 21st Annual NATAS Conference, Atlanta, GA, 13–16 September 1992.

high surface area alumina. The CMS has a well-defined pore structure in a narrow range, as compared to the silica gel and alumina which have random pore structures which include a mixture of small and large pores. The acetic acid and phenol were chosen as test species because they have different characteristic molecular diameters. The characteristic molecular diameter of acetic acid is 4 Å and that of phenol is 6 Å. They were tested in a binary system to study concurrent desorption processes which might represent a mixed gas stream.

EXPERIMENTAL

The carbon molecular sieve was prepared by controlled pyrolysis of polyfurfuryl alcohol. The details of its preparation are described in ref. 2. Detailed characterization [2] of the adsorbent with several probe molecules indicated that it has a uniform pore structure with pore sizes in the range 3.0–4.3 Å. Activated alumina samples were obtained from commercial pellets (0.125-inch pellets, Matheson, Coleman and Bell) and used without further processing. They have a pore size distribution between 40 and 80 Å. The silica gel samples (SC-14618, Sargent-Welch) were preconditioned by drying in an air oven at 250°C for 4 h. The silica gel has a pore size distribution from 10 to 50 Å.

Phenol and acetic acid were used as the specimen species to study sorption characteristics of the adsorbate–adsorbent interactions. Phenol (C_6H_5OH; MW = 94.1, boiling point = 181.7°C) is a solid at room temperature. Acetic acid (CH_3COOH; MW = 60.0, boiling point = 117.9°C) is a liquid at room temperature. Each of the adsorbents were exposed to vapor consisting of a mixture of acetic acid and phenol for one hour to saturate the sample with adsorbent vapor. To accomplish this, a 100–150 mg sample of the catalyst support was placed in a quartz cage with a porous frit and the cage was suspended inside a vacuum flask. Glacial acetic acid and phenol were added to the flask in approximate 100 mg amounts. The flask was sealed and evacuated with the aid of a mechanical pump to remove the air. The flask assembly was then heated to 75°C and held at this temperature for 1 h. The flask assembly was then cooled to room temperature, and the treated samples were retrieved and stored in sealed vials.

Each prepared material and an unexposed baseline sample control were analyzed using a Du Pont 951 thermal gravimetric analyzer (TGA) and a Du Pont 910 differential scanning calorimeter (DSC). The samples were heated at 10°C min^{-1} to 600°C under flowing argon at 100 cm^3 min^{-1}. The outgassing products of the treated samples were characterized independently using a Hiden quadrupole mass spectrometer. The mass spectroscopy was conducted with the samples placed in a heated quartz sample holder with the outgassed products entering the vacuum side of the mass spectrometer through a needle valve. The samples were heated at approximately 5°C min^{-1} to 400°C. The outgassed vapor composition was scanned at m/z ratios of up to 200 atomic mass units, with particular emphasis on the mass spectra at 60 and 94 for acetic acid and phenol, respectively.

RESULTS

Figure 1 shows the DSC and TGA scans for the treated CMS sample in the as-received control and binary treated material. There was a high initial weight loss step for the binary material from room temperature to 60°C,

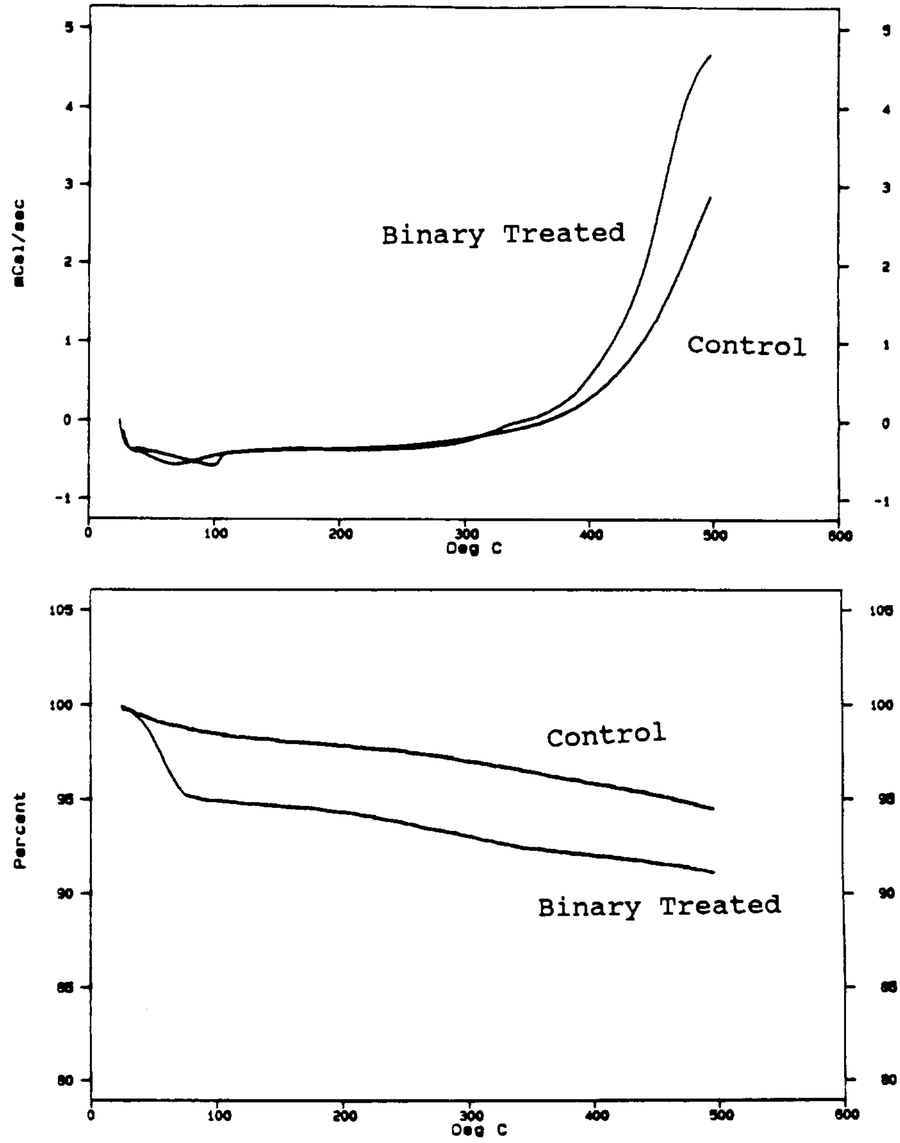

Fig. 1. DSC and TGA curves for the control and binary treated CMS support material.

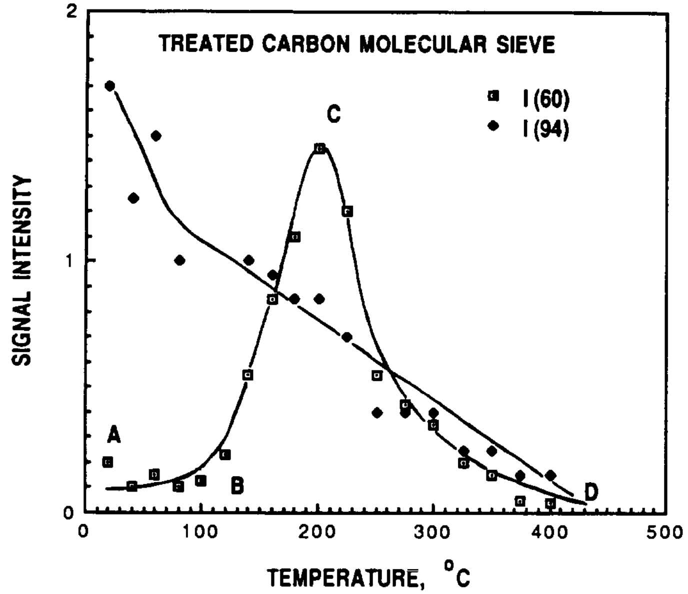

Fig. 2. Mass spectrometric data from the treated carbon molecular sieve.

followed by a second weight loss step at 200°C. The remaining part of the curve followed the same slope as the control sample. The CMS treated with phenol and acetic acid showed a small endotherm with a peak at 102°C that the control did not exhibit. The enthalpy was 8.22 mcal mg^{-1} for the vaporization. Above 350°C, the baseline increased as part of an exotherm. This exotherm was also seen in the control, and may be related to a physical change in the CMS or to the decomposition of phenol for the treated material. Figure 2 shows the signal intensity curves for the primary peaks for phenol (I_{94}) and acetic acid (I_{60}) from the mass spectrometer for the treated CMS material. The mass spectrometer also showed the desorption of H_2O, N_2, O_2, Ar, and CO_2, as trace gases adsorbed on the sorbent. These gases were seen on all three adsorbents and were expected. As seen in Fig. 2, there was an initial high rate of desorption of phenol which declined with increasing temperature. The desorption of acetic acid was initially low, and peaked at 200°C. This two-step desorption for the binary mixture agrees qualitatively with the TGA results. Above 350°C, there was an increase in the $m/z = 12$ peak corresponding to carbon.

Figure 3 shows the DSC and TGA scans for the control and binary treated silica gel adsorbent. For the treated silica gel there was only a single weight loss step starting at 40°C and continuing to 200°C. This corresponded directly with the endotherm of the DSC scan. The enthalpy for this endotherm was 30.85 mcal mg^{-1}, after subtracting out the endotherm from the control in this region. As with the CMS sample, there was an exotherm beginning above 350°C. Figure 4 shows the phenol and acetic acid intensity

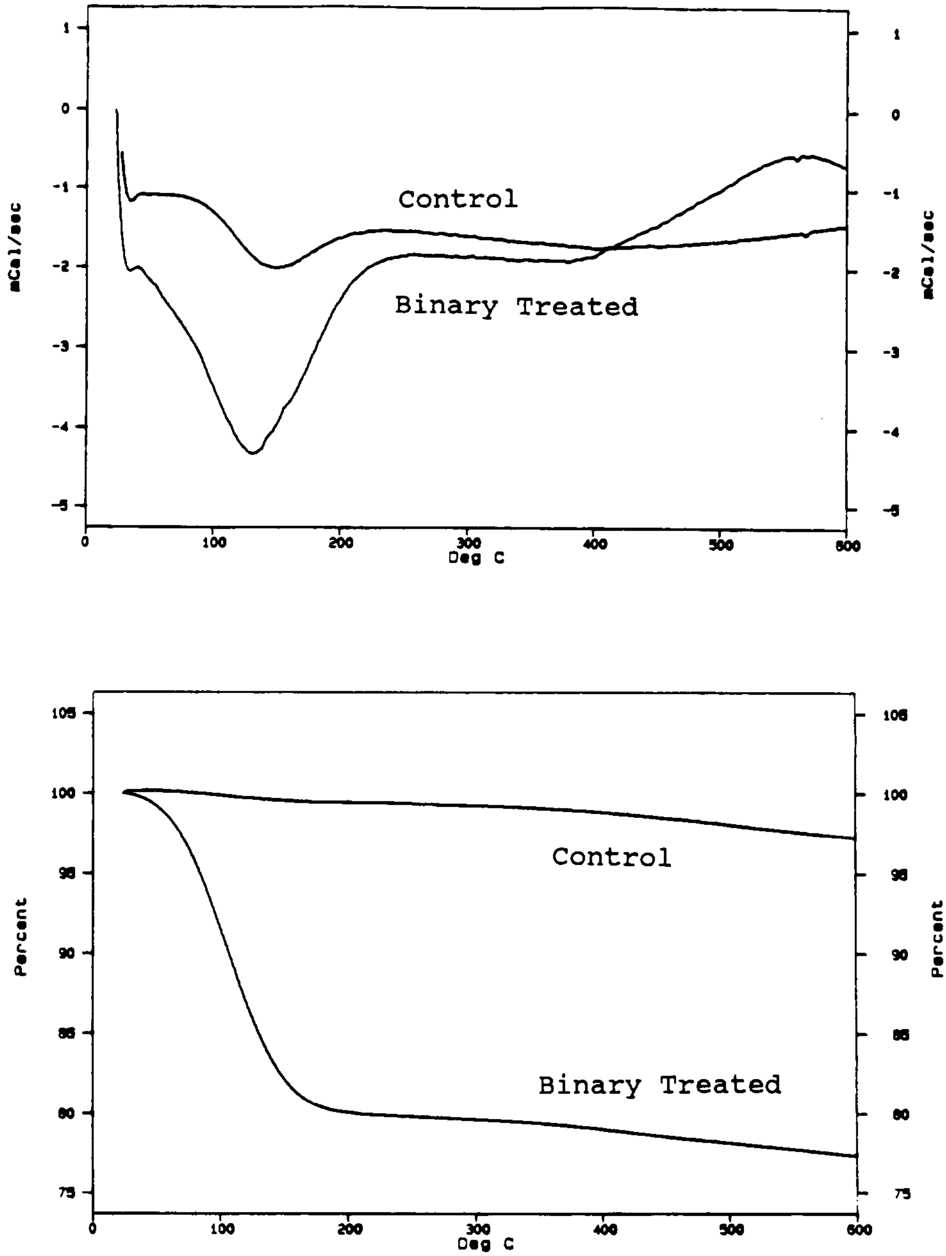

Fig. 3. DSC and TGA curves for the control and binary treated silica gel support.

curves from the mass spectrometer. The acetic acid initially appeared at a high rate and slowly declined. At room temperature, the rate for phenol desorption was low and increased as the sample was heated until a maximum rate at 225°C, at which point it remained nearly constant.

Figure 5 shows the DSC and TGA scans for the control and binary

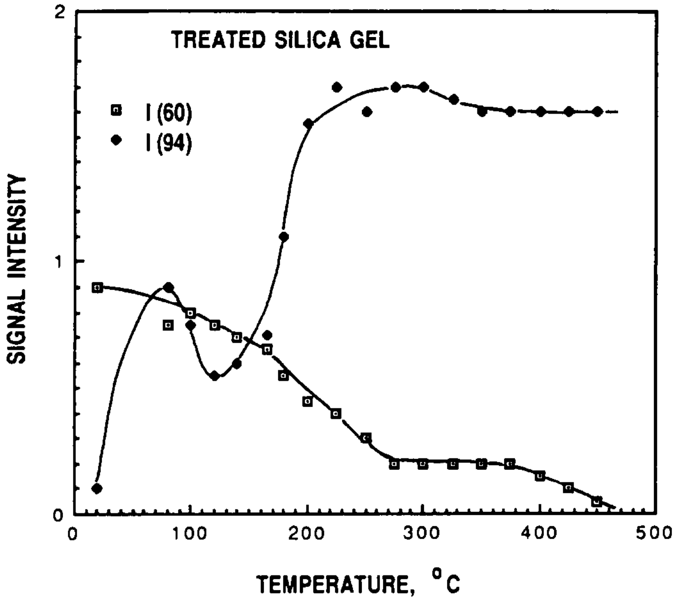

Fig. 4. Mass spectrometric data from the treated silica gel support.

treated alumina. The treated material has weight losses occurring in three steps; from room temperature to 150°C, from 150 to 250°C, and then up to 600°C. There was an endotherm corresponding to the first step with an energy of 17.21 mcal mg^{-1}, after subtracting out the endotherm from the control. The DSC scan provided no information for the second step, but showed a transition at 290°C. As with the CMS and the silica, there was an exotherm at higher temperatures. This may be related to the decomposition of the phenol, but no conclusive information was obtained from the mass spectrometer data. Figure 6 shows the phenol and acetic acid intensity curves from the mass spectrometer for the treated alumina. The acetic acid initially appeared at a high rate, which decreased with temperature until approximately 50°C above its boiling point when its desorption rate remained constant. Above 300°C the rate decreased, probably as the mass adsorbed was exhausted. The desorption characteristics of the phenol adsorbed on the alumina were similar to those on silica gel.

DISCUSSION

Adsorption characteristics of molecules adsorbed on surfaces can often be studied by their temperature-programmed desorption characteristics. Molecules that are adsorbed on a surface by physical adsorption have low binding energies and can be removed by adding energy to the system by raising the temperature. Molecules that are chemisorbed onto surfaces require orders of magnitude more energy to overcome the chemical attraction. In the case of porous materials, the pore size distribution

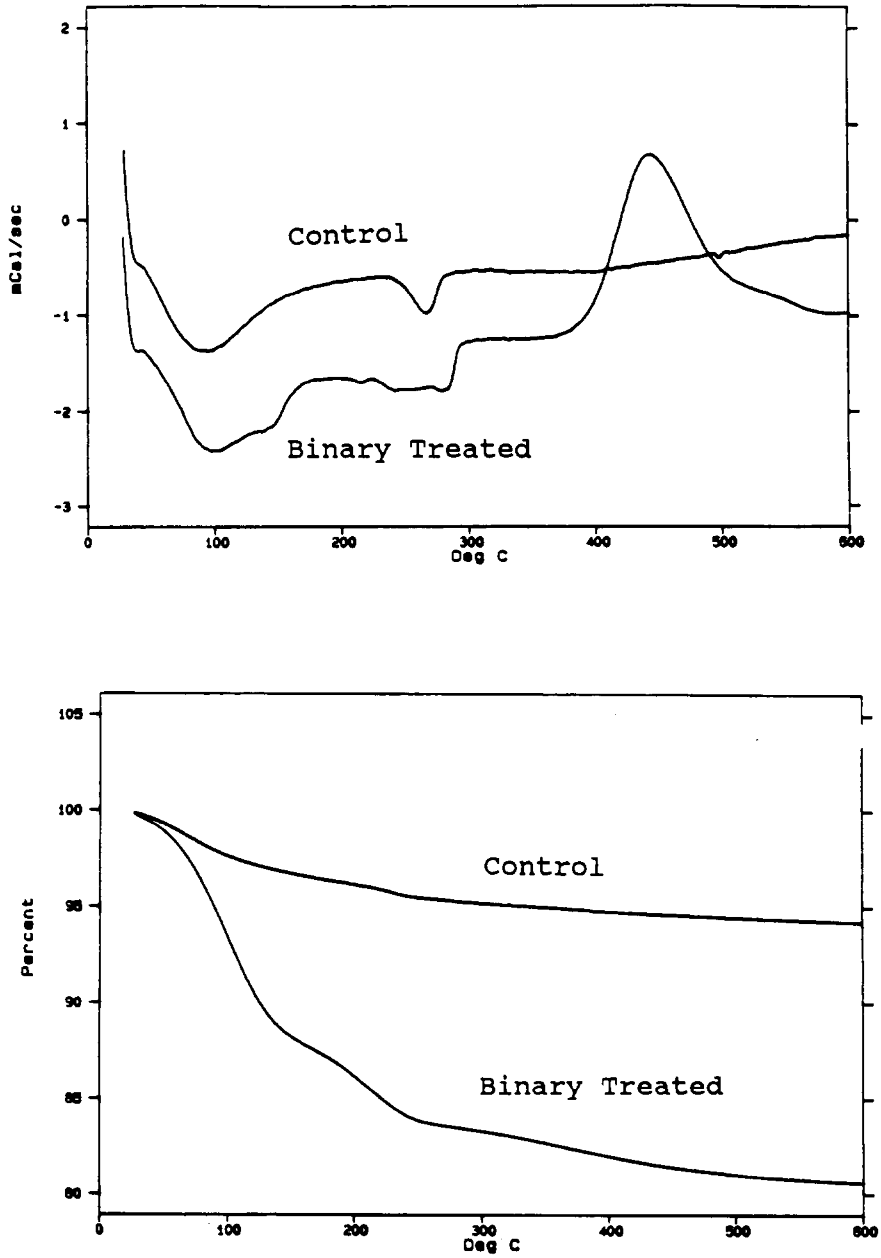

Fig. 5. DSc and TGA curves for the control and binary treated activated alumina support.

becomes significant and pore diffusion has to be considered [3]. When the molecule is smaller than the pore, it can diffuse into the interior surfaces. For molecules larger than the pore diameter, they only can be physically adsorbed on exterior surfaces. When the adsorbed molecules are of the same order of magnitude in size as the pore, intermolecular attraction becomes the dominant force and influences the heat of desorption.

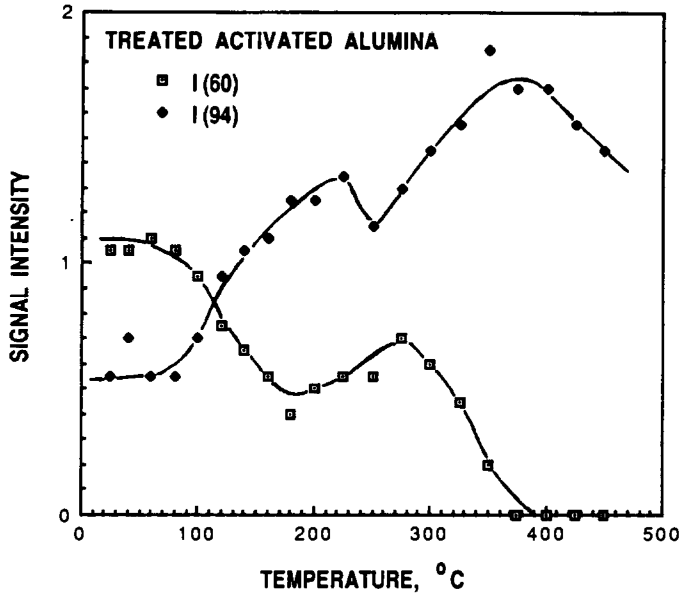

Fig. 6. Mass spectrometric data from the treated activated alumina support.

The CMS used in this study has a maximum pore diameter of 4.3 Å. Both the silica gel and the alumina have large pores in a broad pore-size distribution. Phenol and acetic acid have characteristic molecular diameters of about 6 Å and 4 Å respectively. Because the adsorbent CMS has no pores greater than 4.3 Å, phenol cannot penetrate into its pores and must reside primarily on external surfaces. However, acetic acid can penetrate the pores and should primarily reside inside the pores. As a consequence, the desorption characteristics of phenol and acetic acid from the CMS would be expected to be different from each other. This is indeed quite apparent from Fig. 2. The signal intensity for phenol ($m/z = 94$) gradually decreases with increasing temperature. The intensity for acetic acid ($m/z = 60$) initially increases, passes through a maximum and then gradually decreases. The alumina and the silica gel adsorbents have a random pore structure covering a broader pore size distribution. Because of their large pore size, it is expected that the phenol and acetic acid would both reside within the pores. These adsorbents do not show well-defined trends in the desorption curves for acetic acid and phenol. Both show a constantly declining rate for the acetic acid, and an initial low rate for phenol which increases above its melting point.

Differential scanning calorimetry provides some information about the heat of desorption for physically adsorbed species, and thermogravimetric analysis provides information about capacity. But kinetic results are difficult to obtain for these experimental systems due to the concurrent desorption of acetic acid and phenol, which tends to obscure the results for both the TGA and DSC. Analysis of the mass spectroscopy data allows the separation of the temperature-dependent desorption of the phenol and acetic acid. In the case of the acetic acid on the CMS support, the physical process is dominated by the desorption from internal pores. In this specific case the heat of desorption can be determined from the mass spectrometer data.

Because acetic acid has a molecular size which is similar to the pore dimensions of the CMS, its molecules are likely to experience a strong interaction potential with the surface. Its desorption and subsequent pore diffusion is then likely to be controlled by the intermolecular interaction force field. Only at high temperatures are the desorbing molecules imparted sufficient energy to overcome the effect of pore diffusion restrictions. For acetic acid in Fig. 2, the portion ABC may be explained qualitatively. In portion AB, most of the acetic acid molecules do not have sufficient energy to cross the interaction potential barrier resulting from the combination of attractive and repulsive intermolecular forces. With a further increase in temperature (portion BC), the molecules gradually desorb depending on their pore size and the corresponding potential field. At point C, a majority of the adsorbed acetic acid molecules have sufficient energy to cross the potential barrier and the intensity subsequently decreases as the concentration level decreases. The portion BC of the desorption curve is then likely to be controlled by the intermolecular interaction potential.

The heat of desorption can be computed from the desorption data. From the van't Hoff equation [4], the heat of desorption is given as

$$Q = RT^2(\mathrm{d}\ln c/\mathrm{d}T) + RT/2$$

where c is the species concentration, R is the universal gas constant, and T is temperature. The concentration c is proportional to the partial pressure and hence to the signal intensity. Replotting the desorption data in Fig. 2 on a semi-logarithmic basis yields Fig. 7. An average value of the desorption energy of approximately 8.6 kcal g^{-1} is obtained from the slope of the portion BC of the curve in Fig. 7. This desorption energy is likely to be directly related to the intermolecular interaction potential between the carbon and the acetic acid molecules and is of the order of magnitude expected. This analysis is only valid for molecules within pores. For molecules adsorbed on external surfaces, the intermolecular interaction potential cannot be determined from the desorption data with this technique.

CONCLUSIONS

The adsorption characteristics of organics on typical catalyst supports may be investigated by a combination of TGA, DSC, and mass spectroscopy. Intermolecular forces dominate the desorption of molecules with characteristic sizes similar to the pore dimensions. It has been shown that for the binary mixture of phenol and acetic acid, there are different

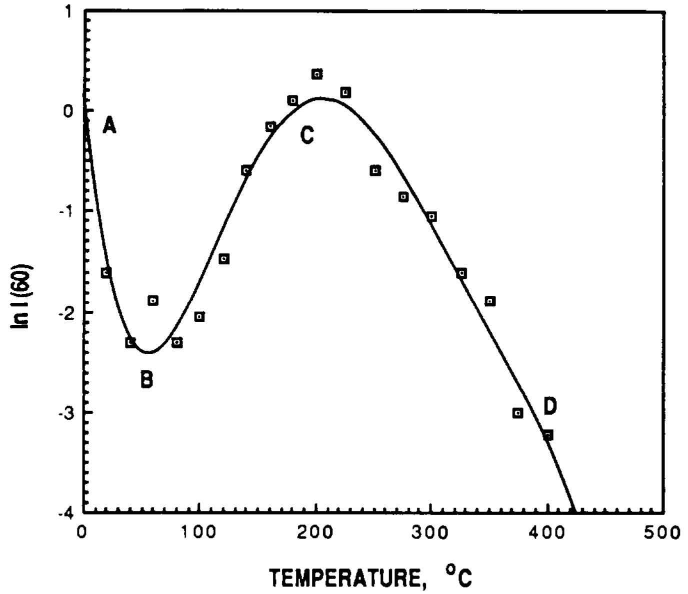

Fig. 7. Plot of acetic acid signal intensity versus temperature for the CMS support.

mechanisms for adsorption for the narrow pore distribution CMS as compared to the broad pore distribution catalyst supports alumina and silica gel. For acetic acid, which has a characteristic diameter smaller than the CMS pore, intermolecular forces dominate its adsorption–desorption characteristics.

ACKNOWLEDGMENT

The research described in this paper was carried out at the Jet Propulsion Laboratory, California Institute of Technology, under contract with the National Aeronautics and Space Administration (NASA). This work is part of a comprehensive strategy for contamination control/management for NASA's Modular Containerless Processing Facility for Microgravity research.

REFERENCES

1 S.D. Bischke, et al., The Extraction of Site-Energy Distributions From Temperature Programmed Desorption Spectra, in A.B. Mersmann and S.E. Scholl (Eds.), Fundamentals of Adsorption, Engineering Foundation Press, New York, 1990, p. 145.
2 P.K. Sharma and P.K. Seshan, Gas Separation and Purification, 4 (1990) 203.
3 H. Jutgen, Carbon, 15 (1977) 273–283.
4 M. Suzuki, Adsorption Engineering, Elsevier, Tokyo, 1990, p. 52.