This article was downloaded by:
On: *25 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK

Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Sorption of Sulfur Dioxide on Hydrogen Form and Aluminum-Deficient Mordenites

Suzan Kincal[a]; Ali Çulfaz[a]
[a] DEPARTMENT OF CHEMICAL ENGINEERING, MIDDLE EAST TECHNICAL UNIVERSITY ANKARA, TURKEY

To cite this Article Kincal, Suzan and Çulfaz, Ali(1981) 'Sorption of Sulfur Dioxide on Hydrogen Form and Aluminum-Deficient Mordenites', Separation Science and Technology, 16: 3, 229 — 236

To link to this Article: DOI: 10.1080/01496398108068515

URL: http://dx.doi.org/10.1080/01496398108068515

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

SEPARATION SCIENCE AND TECHNOLOGY, 16(3), pp. 229–236, 1981

Sorption of Sulfur Dioxide on Hydrogen Form and Aluminum-Deficient Mordenites

SUZAN KINCAL and ALI ÇULFAZ
DEPARTMENT OF CHEMICAL ENGINEERING
MIDDLE EAST TECHNICAL UNIVERSITY
ANKARA, TURKEY

Downloaded At: 13:50 25 January 2011

Abstract

The SO_2 sorption characteristics of a commercial H-mordenite and an aluminum-deficient mordenite with a molar SiO_2/Al_2O_3 ratio of 75, prepared from the H-form, were investigated. The sorption isotherms and the reduced sorptive diffusivities were determined in the temperature range 298–358 K and at pressures up to 0.2 atm. It was found that the partially irreversible SO_2 sorption on the H-form became completely reversible by the removal of structural aluminum, while the absolute sorption capacity was decreased by 10–40% and the rate of sorption was improved by 50%.

INTRODUCTION

Adsorptive separation of SO_2 from flue gases is one of the SO_2 pollution abatement methods. The sorbent should be regenerable with high selectivity and sorption capacity for SO_2. Mordenite is one of the most thermally stable and acid-resistant zeolites commercially available (*1*), and has been shown to sorb SO_2 selectively from gas mixtures similar in composition to dry flue gases (*2*, *3*).

The structure of mordenite is orthorhombic with a two-dimensional channel system (*4*). The elliptical main channels, enclosed by 12-membered rings, have free apertures of 0.67 × 0.70 nm and run parallel to one another. The walls of these channels are interconnected through distorted 8-membered rings with a free aperture of 0.29 × 0.57 nm. The aperture size of the side channels being so small, the mordenite structure can be considered as made up of a one-dimensional, parallel channel system except when very small molecules such as H_2O or NH_3 are involved. The

Copyright © 1981 by Marcel Dekker, Inc.

total pore volume in mordenite is 0.2 cm^3/g and the contribution of the main channels is 0.1 cm^3/g (*4*, *5*).

Studies of SO_2 sorption characteristics of mordenites (*3*) have shown that in the temperature range 273–373 K, SO_2 sorption on both the sodium and the hydrogen forms of mordenite was partially irreversible. Some of the sorbed SO_2 could not be desorbed at the isotherm temperature. The separation of the desorption branch from that of sorption was less for the hydrogen form. The possibility of eliminating the residual SO_2 with a further decrease in surface heterogeneity by the dealumination of the structure was investigated in this study.

EXPERIMENTAL

Materials

The H-mordenite, HM(12), was supplied by the Norton Co., U.S.A. (Lot No. HB 33–36), and had a SiO_2 to Al_2O_3 molar ratio of 12. The aluminum-deficient mordenite, HM(75), was prepared from HM(12) by a procedure similar to that of Kranich et al. (*6*). HM(12) was subjected to two 4-h treatments with boiling 6 *N* HCl, each followed by filtration, washing, drying at 383 K, and a 2-h heat treatment at 823 K (*7*). The chemical analyses of the intermediate and final products of dealumination showed that the molar ratio of SiO_2 to Al_2O_3 was raised to 47 after the first acid treatment and to 75 after the second. This corresponds to the removal of 85% of the structural aluminum. The sum of the major peak heights of the X-ray diffraction pattern of HM(75) was 99% of that of HM(12) obtained under the same conditions.

Downloaded At: 13:50 25 January 2011

Apparatus and Procedures

The sorption rates and capacities were measured in a volumetric gas adsorption apparatus. The mordenites were outgassed at 700 K below 2×10^{-7} atm for 16 h prior to any measurement. At any temperature the reduced sorptive diffusivity was determined from the variation of pressure with time for the first gas charge on the outgassed mordenite, and the subsequent isotherm points were determined by admitting successive amounts of SO_2 and allowing time for the attainment of equilibrium. Desorption points were determined by evacuating a part of the apparatus, expanding the gas phase, and allowing time for desorption equilibrium. Fresh mordenite samples were used for determinations at each temperature. The details of the apparatus and procedures can be found in Kincal (*7*).

RESULTS

Sorption Isotherms

The SO_2 sorption isotherms on the hydrogen form and on the aluminum-deficient mordenites are shown in Figs. 1 and 2, respectively. The isotherms on the H-form, HM(12), were closer to the rectangular shape. The desorption branches were separate from those of sorption, the separation becoming less with increasing temperature.

On the aluminum-deficient form, HM(75), the sorption process was reversible at all temperatures studied. The amounts sorbed were somewhat less than those on the H-form, and the effect of temperature on the sorption capacity was more pronounced.

For most sorbate–zeolite systems, the shape of the isotherm is adequately described by the Langmuir equation (*8*). The following form of the Langmuir equation was used in determining its applicability:

$$\frac{P}{C} = \frac{1}{C_s}P + \frac{1}{bC_s}$$

Plots of P/C versus P of the isotherms were all linear, indicating the adequacy of the Langmuir equation in expressing the sorption equilibrium relationship. The parameters C_s and b were determined from linear least squares fit of P/C to P, and are tabulated in Table 1.

Downloaded At: 13:50 25 January 2011

Reduced Diffusivities

The reduced diffusivities were obtained on the basis of the solution of the diffusion equation for one-dimensional diffusion of a sorbate of limited volume, given by Crank (*9*). This solution is valid when at equilibrium the amount sorbed is proportional to pressure and an exact solution is not available for a nonlinear adsorption isotherm. The SO_2 isotherms on mordenites were approximated as linear adsorption isotherms at low pressures. The graphical solution, in the form of a fractional approach to equilibrium versus the dimensionless group $(Dt/a^2)^{1/2}$, was used for the determination of $(Dt/a^2)^{1/2}$ versus time from the experimental data on a fractional approach to saturation versus time. The behavior of SO_2–mordenite systems permitted first pressure measurements at amounts sorbed of about 40–50% of the final fractional uptake. Plots of $(Dt/a^2)^{1/2}$ versus $(t)^{1/2}$ were linear up to about 85% of the final uptake, which were in the initially linear portion of the isotherms in all cases. The reduced diffusivity was obtained from a least squares fit to the linear portion of the $(Dt/a^2)^{1/2}$ versus $(t)^{1/2}$ data.

Downloaded At: 13:50 25 January 2011

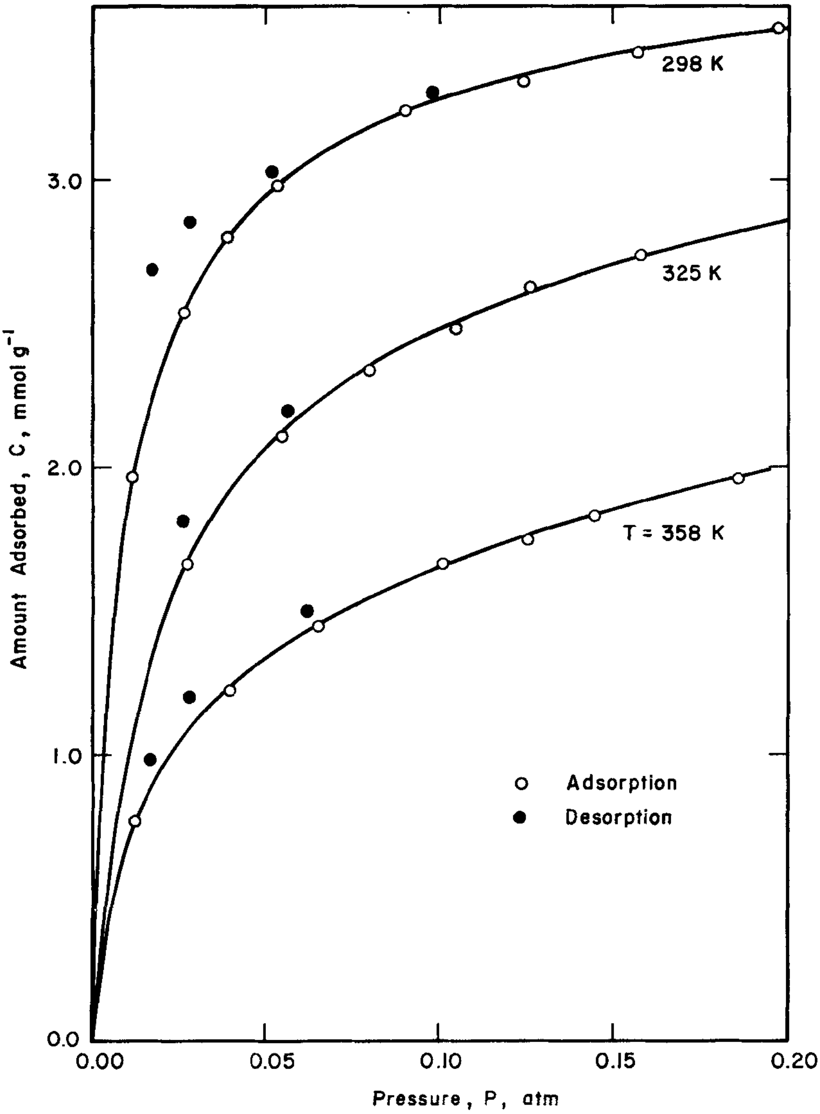

FIG. 1. SO_2 sorption isotherms on H-mordenite, HM(12).

Downloaded At: 13:50 25 January 2011

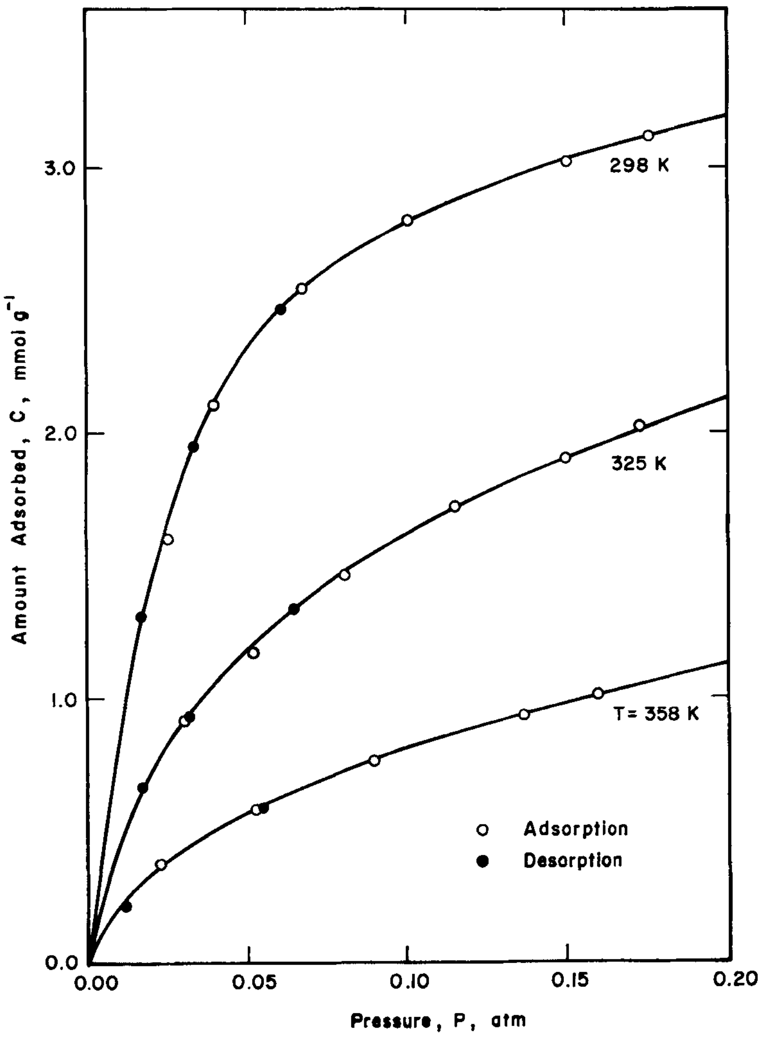

FIG. 2. SO_2 sorption isotherms on aluminum-deficient mordenite, HM(75).

TABLE 1

The Langmuir Parameters for SO_2 Sorption on HM(12) and HM(75)

	C_s (mmol/g) on		b (atm^{-1}) on	
T (K)	HM(12)	HM(75)	HM(12)	HM(75)
298	3.825	3.624	65.1	34.3
325	3.182	2.518	36.8	18.5
358	2.336	1.388	31.9	15.8

TABLE 2

Reduced Diffusivities and Diffusional Activation Energies of SO_2 on HM(12) and HM(75)

	$(D/a^2) \times 10^4$ (s^{-1}) at			
Sample	298 K	325 K	358 K	E_D (kJ/mol)
HM(12)	8.2	14.6	23.1	15.1
HM(75)	11.6	21.6	31.9	14.7

Downloaded At: 13:50 25 January 2011

The reduced diffusivities and the diffusional activation energies determined on the basis of the Arrhenius type of dependency of diffusivity on temperature are given in Table 2. The variation of the diffusivities with temperature is illustrated in Fig. 3.

The removal of most of the aluminum from the structure has resulted in about a 50% increase in the reduced SO_2 diffusivity at the temperatures studied. The temperature dependence of the reduced diffusivity, however, remained the same as shown by the similar activation energies.

DISCUSSIONS

The saturation capacity of H-mordenite at 298 K is in agreement with earlier reports in the literature (*2*, *3*). The separation of the desorption branch indicating partially irreversible sorption as reported by Roux et al. (*3*) was also observed in this work (Fig. 1).

Upon removal of 85% of the aluminum from the structure, SO_2 sorption became completely reversible (Fig. 2). The residual SO_2 was eliminated and the desorption branches coincided with those of sorption. This is in support of the view that the residual SO_2 is due to the presence of cations (*3*).

The amounts sorbed were less on the aluminum-deficient form, and the difference in the sorption capacity between these two forms increased with increasing temperature. The pore volume per unit mass of mordenite have

Downloaded At: 13:50 25 January 2011

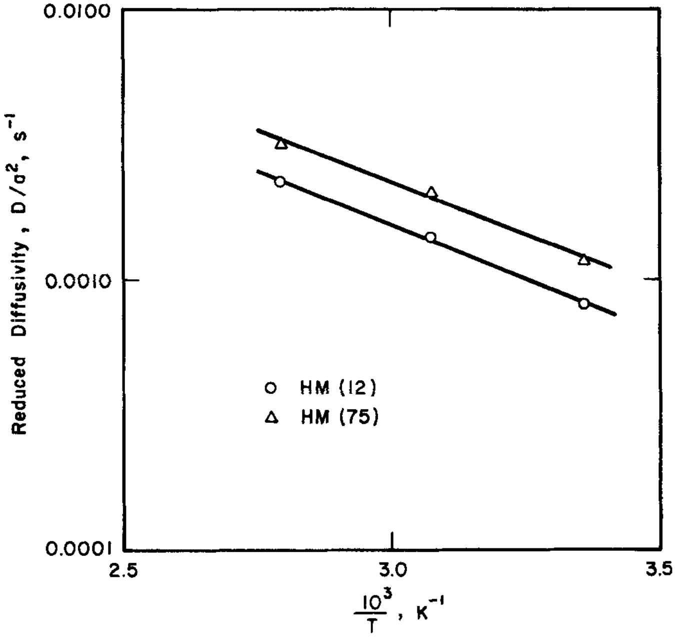

FIG. 3. Variation of the reduced diffusivity of SO_2 on HM(12) and HM(75) with temperature.

been reported to remain unchanged when H-mordenite was dealuminated down to a SiO_2 to Al_2O_3 molar ratio of 65 (*10*). The forces of attraction between the pore walls and the sorbed molecules must then be different. This is also indicated by the elimination of the irreversibility of sorption via dealumination. The pronounced dependency on temperature is another indication that SO_2 sorption on the dealuminated form is more physical in nature. The SO_2 sorption on the H-form probably occurs according to a chemisorptionlike, temperature insensitive and irreversible mechanism on the aluminum atoms and/or the cations in addition to physical adsorption. On the dealuminated form, with most of the aluminum atoms and the accompanying cations removed, the former does not occur to a detectable extent, and physical adsorption with an effectively increased temperature dependency is observed.

The reduced SO_2 diffusivity was found to be improved by about 50% by dealumination while the diffusional activation energy remained the same. Similar activation energies indicate similar energy barriers to be overcome although stronger forces of attraction between SO_2 and the H-form than those between SO_2 and the dealuminated form are suggested by the isotherms.

The explanation for the increase of the diffusivity with dealumination may also lie in the altered physical properties. The impurities which are probably present in the commercial H-mordenite were removed during dealumination, the pore openings might have been slightly enlarged by the removal of aluminum, or the average particle size might have been slightly reduced by the severe acid treatment.

SYMBOLS

a	half pore length (m)
b	Langmuir adsorption equilibrium constant (atm^{-1})
C	adsorbed phase concentration (mmol/g)
C_s	adsorbed phase concentration at saturation (mmol/g)
D	adsorbate diffusivity (m^2/s)
E_D	diffusional activation energy (kJ/mol)
P	pressure (atm)
t	time (s)

REFERENCES

1. D. W. Breck, *Zeolite Molecular Sieves*, Wiley, New York, 1974.

2. J. I. Joubert and I. Zwiebel, "Molecular Sieve Zeolites—II," *Adv. Chem. Ser.*, *102*, 209 (1971).

3. A. Roux, A. A. Huang, Y. H. Ma, and I. Zwiebel, *AIChE Symp. Ser.*, *134*(69), 46 (1973).

4. W. M. Meier, *Z. Krist.*, *115*, 439 (1961).

5. R. M. Barrer and D. L. Peterson, *Proc. R. Soc. London*, *280A*, 466 (1964).

6. W. L. Kranich, Y. H. Ma, L. B. Sand, A. H. Weiss, and I. Zwiebel, "Molecular Sieve Zeolites—I," *Adv. Chem. Ser.*, *101*, 502 (1971).

7. N. S. Kincal, "Mordenites for Sulfur Dioxide Adsorption and Oxidation," PhD Thesis, Middle East Technical University, Ankara, 1980.

8. P. E. Eberly, in *Zeolite Chemistry and Catalysis*, (J. A. Rabo, ed.), American Chemical Society, Washington, D.C., 1976.

9. J. Crank, *The Mathematics of Diffusion*, Oxford University Press, London, 1956.

10. D. K. Thakur and S. W. Weller, "Molecular Sieves," *Adv. Chem. Ser.*, *121*, 596 (1973).

Received by editor June 9, 1980

Downloaded At: 13:50 25 January 2011