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Adsorption of Methane, Ethane, Ethylene, and Carbon Dioxide on High Silica Pentasil Zeolites and Zeolite-like Materials Using Gas Chromatography Pulse Technique

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ABSTRACT

Adsorption of methane, ethane, ethylene, and carbon dioxide in H-ZSM-5, Na-ZSM-5, H-ZSM-8, Na-ZSM-8, Silicalite, and ALPO-5 at 303–473 K has been investigated using a gas chromatography pulse technique. The zeolites have been compared for the heat of adsorption of the adsorbates at near zero adsorbate loading and also for the specific retention volume (or thermodynamic adsorption equilibrium constant) of ethane, ethylene, and carbon dioxide relative to that of methane. Among the zeolites, ALPO-5 has a high potential for the separation of methane, ethane, ethylene, and carbon dioxide from their mixture.

INTRODUCTION

Depleting oil reserves and the comparative abundance of natural gas have focused the attention of the world toward the better and more efficient utilization of natural gas. Methane is the major component of natural gas. Hence extensive efforts are being made worldwide for the development of energy efficient and commercially feasible processes for the direct conversion of methane to value-added products such as ethylene, methanol, and liquid hydrocarbon fuels (1–4). Methane, ethane, and carbon dioxide are components of natural gas. These, along with ethylene, are also part of the product stream in the oxidative coupling of methane (1, 5, 6). As the concentration of C_2 hydrocarbons in these gas mixtures (natural gas/products in oxidative coupling of methane) is very low (<10%), the conventional methods of separation are not suitable for the separation of C_2 hydrocarbons. The adsorptive separation of the hydrocarbons is a possible alternative, due to its highly selective nature and low energy requirement. Zeolites are popular commercial adsorbents used in many adsorptive separation processes (7–9). In a previous paper (10) we reported the adsorption of methane, ethane, ethylene, and carbon dioxide in X, Y, L, and M zeolites using gc pulse technique. The zeolites were compared for the heat of adsorption and specific retention volume of methane, ethane, ethylene, and carbon dioxide. It has been suggested that the gc pulse method provides a simple means of measuring adsorption properties useful for the fast screening of a large number of adsorbents for achieving a particular separation. It is also very interesting to compare pentasil zeolites (viz., ZSM-5, ZSM-8, and Silicalite) and ALPO-5 for the adsorption of methane, ethane, ethylene, and carbon dioxide. The present investigation was therefore undertaken as an extension of our adsorbent screening program for the quick and systematic comparison of the adsorption properties of ZSM-5, ZSM-8, Silicalite, and ALPO-5 under similar experimental conditions for the adsorption of methane, ethane, ethylene, and carbon dioxide by the gc pulse technique.

EXPERIMENTAL

Zeolites

H-ZSM-5 was prepared by deammoniating NH_4-ZSM-5 (Si/Al = 31.1, Na/Al = 0.01, crystal size = 2.1 μm) at 773 K in a flow of nitrogen (10 $cm^3 \cdot min^{-1}$, 4 hours). Na-ZSM-5 (degree of H^+ exchange = 0.45) was prepared by repeatedly exchanging the H-ZSM-5 with 1 M $NaNO_3$ solution at 353 K, washing the zeolite with deionized water, drying (at 393 K for 4 hours), and calcining in air at 773 K for 12 hours. H-ZSM-8 (degree of H^+ exchange = 0.96) was prepared by repeatedly exchanging Na-ZSM-8 zeolite (Si/Al = 29.6, degree of H^+ exchange = 0.08, crystal size = 3.5 μm) with 0.1 M HCl at 353 K, followed by washing, drying (at 393 K for 12 hours), and calcination in static air at 813 K for 12 hours. ALPO-5 was obtained by removing the organic template from Pr_3N–$AlPO_4$-5 (Al/P = 1.0) by heating it in air at 813 K for 12 hours. The Silicalite (Si/Al > 1000, crystal size = 0.3 μm) used was ZSM-5 type. The zeolites were pressed binder-free and crushed to particles of 0.2–0.3 mm size. Before use, the zeolites (packed in a gc column) were pretreated/calcined in situ at 623 K for 12 hours in a flow (10 $cm^3 \cdot min^{-1}$) of helium, which was the carrier gas for the gc pulse experiments. The detailed preparation/synthesis and characterization of ZSM-5 (11, 12), ZSM-8 (13), and Silicalite (ZSM-5 type) (14) zeolites and ALPO-5 (15) were given earlier.

Gases

The hydrocarbon gases methane (obtained from Matheson, USA), ethane (obtained from Airco Industrial Gases, USA), and ethylene (obtained from L'Air Liquide, France) were of purity >99.9%. High purity carbon dioxide and helium were obtained from Indian Oxygen Ltd., Bombay. Nitrogen (Iolar, Grade II, obtained from Indian Oxygen Ltd., Bombay) was used as a nonadsorbate for the dead volume corrections.

Apparatus

The gc pulse measurements were carried out using a Chemito (Toshiniwal-Dani) gas chromatograph with thermal conductivity detector (TCD) and using helium as the carrier gas. The zeolite was packed in a stainless steel column (15 cm long, 2 mm i.d.), one end of which was connected directly to the TCD, and the second end to the injection port through a 1.6 cm o.d. stainless steel tube. The samples gases were diluted with the carrier gas (He) to a concentration of 2–3 mol% and injected into the zeolite column using a gas sampling valve having a sample loop of 0.3 cm^3. A carrier gas flow rate of 10 $cm^3 \cdot min^{-1}$ (measured at STP) was used for the experiments. The pressure drop across the zeolite column was negligibly small. The chromatograms were recorded using a Spectra-Physics integrator.

RESULTS AND DISCUSSION

The heat of adsorption of the different adsorbates on the zeolites were calculated from the slopes of the linear plots of log V_R versus $1/T_c$ according to the relation (16)

$$\log V_R = a - \Delta H/(2.303RT_c)$$

where a is a constant, ΔH is the heat of adsorption, R is the gas constant, and T_c is the column temperature. The corrected retention volume V_R was calculated by using the equation

$$V_R = (t_r - t_d)F(T_c/T_F)$$

where t_r and t_d are the retention times for the adsorbate and the nonadsorbate (N_2), respectively, F is the carrier gas flow rate, and T_F is the temperature at which F is measured.

The specific retention volume β was calculated from the chromatographic retention time data by using the equation (16)

$$\beta = t_m U_e/L = V_R/V_P$$

where t_m is the corrected retention time, U_e is the superficial gas velocity, L is the column length, and V_P is the volume of the zeolite adsorbent.

For the determination of heat of adsorption and/or specific retention volume by the gc pulse method, it is essential that the data should correspond to the linear region of the adsorption isotherm (17). This was achieved by the use of a sample pulse of very low concentration (2–3%) and small volume (0.3 cm^3). Further, there was no significant change in the retention volumes of any of the adsorbates on changing the carrier gas flow rate from 10 to 30 cm^3·min^{-1} at the lowest temperature of study.

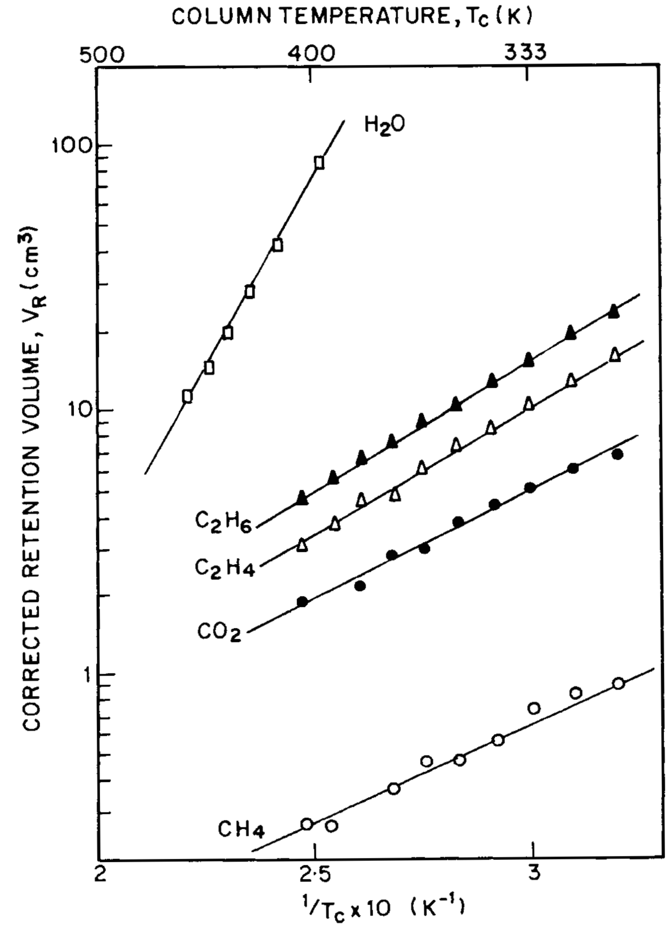

FIG. 1 Representative plots of log V_R vs $1/T_c$ for the sorption of methane, ethane, ethylene, carbon dioxide, and water on ALPO-5.

TABLE 1
Heat of Adsorption of Methane, Ethane, Ethylene, and Carbon Dioxide in the Zeolites

	Heat of adsorption ($kJ \cdot mol^{-1}$)			
Zeolite	Methane	Ethane	Ethylene	CO_2
H-ZSM-5	19.0	28.0	33.7	26.1
Na-ZSM-5	21.2	30.0	34.0	42.0 (350–450 K)
H-ZSM-8	14.5	26.5	34.6	27.0
Na-ZSM-8	19.4	26.6	35.8 (400–473 K)	35.9
Silicalite	18.4	28.3	26.5	21.7
ALPO-5	14.3	18.7	22.6	16.0

Representative plots of log V_R vs $1/T_c$ for the adsorption of methane, ethane, ethylene, and carbon dioxide on ALPO-5 are given in Fig. 1. The heats of adsorption (at near zero coverage) of methane, ethane, ethylene, and carbon dioxide on the different adsorbents are given in Table 1. The variation of specific retention volume (which is equivalent to the thermodynamic equilibrium constant) with the temperature for the adsorption of the adsorbates in the zeolites is shown in Figs. 2–4.

The values of the heat of adsorption obtained by the gc pulse method for the different adsorbates on Silicalite and ALPO-5 are compared with those reported earlier in Table 2. Water is strongly sorbed on all the zeolites and is not desorbed at lower temperatures. The values of the heat of adsorption of methane and ethane on Silicalite are quite comparable

TABLE 2
Comparison of the Present and Reported Heat of Adsorption Values for Various Adsorbates on Different Zeolites

		Heat of adsorption ($kJ \cdot mol^{-1}$)		
Zeolite	Adsorbate	Present (by gc pulse)	Reported data	Ref.
Silicalite	CH_4	18.4	18.0,[a] 19.9	18, 19
	C_2H_6	28.3	29.8[b]	20
	CO_2	21.7	27.9[b]	20
ALPO-5	CH_4	14.3	18.4	21
	C_2H_6	18.7	23.9	21

[a] Theoretical value estimated by Monte-Carlo simulation.
[b] Theoretical value estimated by molecular statistical calculations.

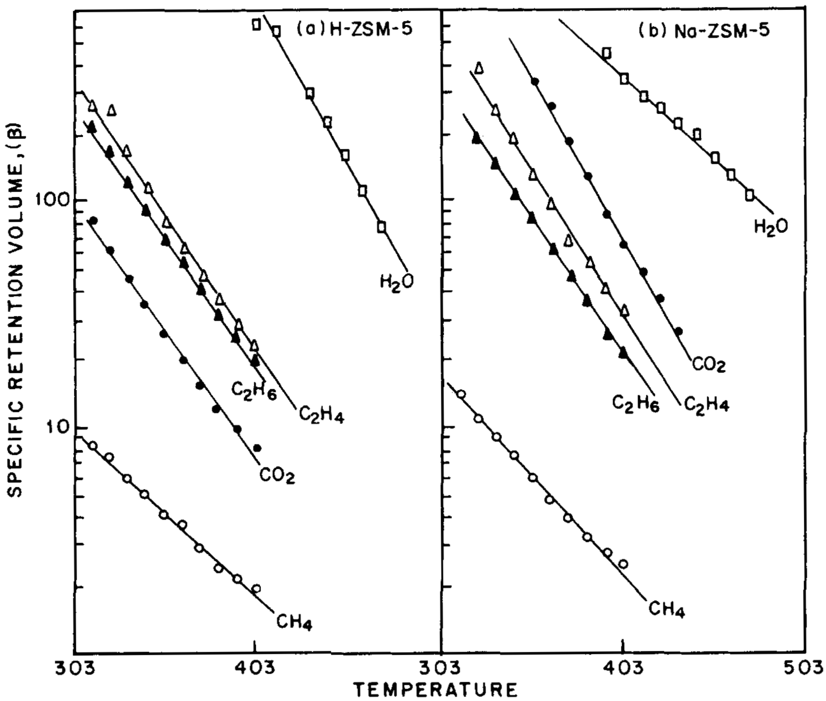

FIG. 2 Temperature dependence of specific retention volume of methane, ethane, ethylene, carbon dioxide, and water on ZSM-5 zeolites.

with those reported in the literature whereas the heat of adsorption of carbon dioxide on Silicalite is lower than that predicted by molecular statistical calculations (20). In the case of methane and ethane on ALPO-5, the values obtained by the gc pulse method are somewhat lower than those reported earlier (21).

The heat of adsorption of an adsorbate on an adsorbent is a measure of adsorbate–adsorbent interaction. A high value of the heat of adsorption is attributed to strong adsorbate–adsorbent interactions, and hence desorption of the adsorbate from the adsorbent is difficult. The specific retention volume of an adsorbate for a particular zeolite is a measure of adsorption of the adsorbate in the zeolite. Thus, it is possible to compare the zeolites for the adsorption of methane, ethane, ethylene, and carbon dioxide at different temperatures.

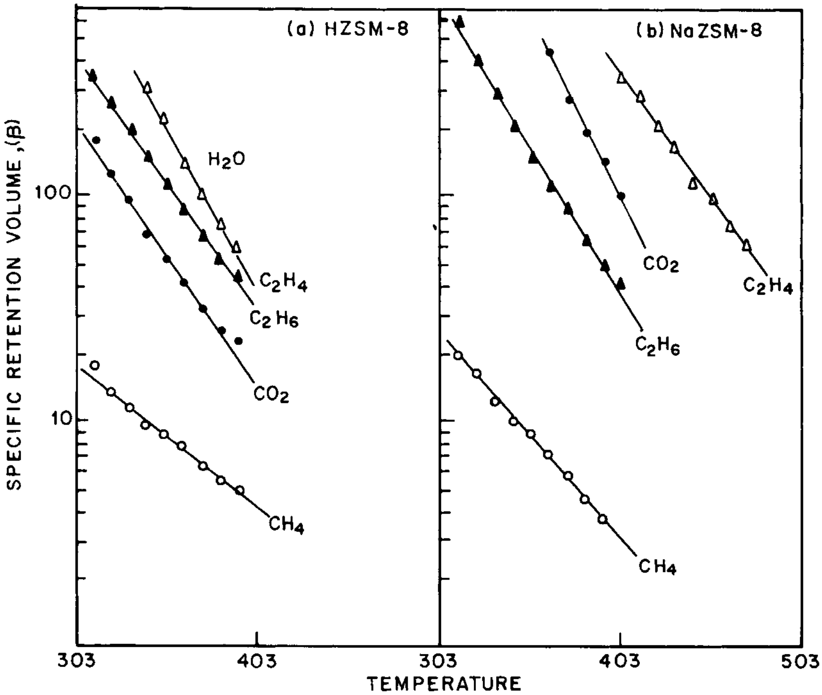

FIG. 3 Temperature dependence of specific retention volume of methane, ethane, ethylene, carbon dioxide, and water on ZSM-8 zeolites.

Comparison of Zeolites for Their Sorption Properties

Heat of Sorption

Among the adsorbates, the heat of adsorption of methane is lowest in all the zeolites. The order of the adsorbates for their heat of adsorption in different zeolites varies from zeolite to zeolite as follows:

For H-ZSM-5 and ALPO-5: $CH_4 < CO_2 < C_2H_6 < C_2H_4$.
For H-ZSM-8: $CH_4 < C_2H_6 \leq CO_2 < C_2H_4$.
For Na-ZSM-5 and Na-ZSM-8: $CH_4 < C_2H_6 < C_2H_4 < CO_2$.
For Silicalite: $CH_4 < CO_2 < C_2H_4 < C_2H_6$.

It is also interesting to compare zeolites for the heat of adsorption of the different adsorbates. The zeolites show the following orders for the heat of adsorption of the different adsorbates.

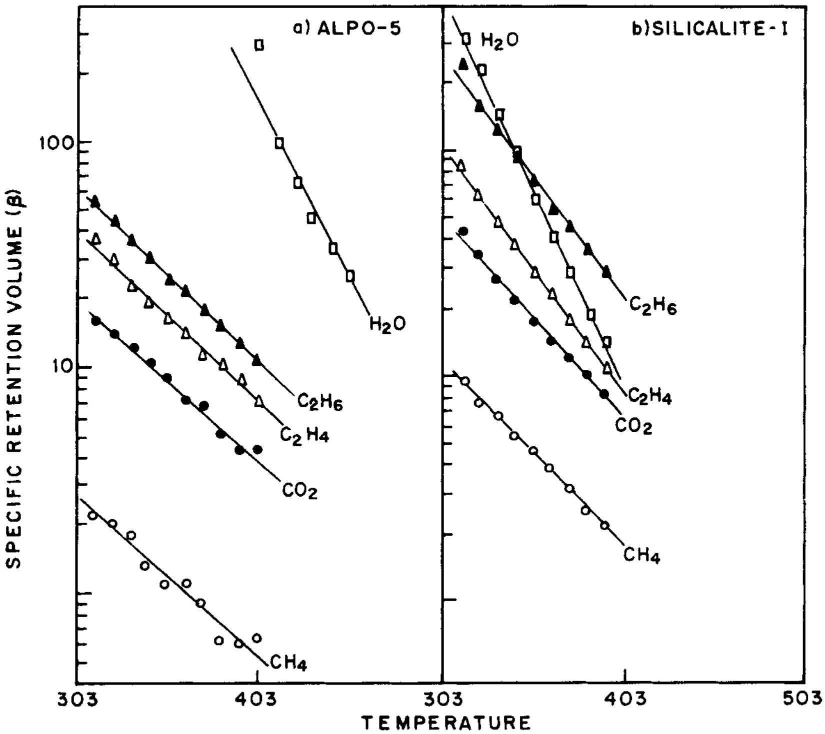

FIG. 4 Temperature dependence of specific retention volume of methane, ethane, ethylene, carbon dioxide, and water on ALPO-5 and Silicalite.

For the heat of adsorption of methane: Na-ZSM-5 > Na-ZSM-8 > H-ZSM-5 > Silicalite > H-ZSM-8 > ALPO-5.

For the heat of adsorption of ethane: Na-ZSM-5 > Silicalite > H-ZSM-5 > Na-ZSM-8 > H-ZSM-8 > ALPO-5.

For the heat of adsorption of ethylene: Na-ZSM-8 > H-ZSM-8 > Na-ZSM-5 > H-ZSM-5 > Silicalite > ALPO-5.

For the heat of adsorption of carbon dioxide: Na-ZSM-5 > Na-ZSM-8 > H-ZSM-8 > H-ZSM-5 > Silicalite > ALPO-5.

The above comparisons reveal that the adsorbate–adsorbent interactions for a particular adsorbate vary from adsorbent to adsorbent, and also that the order for the heat of adsorption of the adsorbates depends on the adsorbent. In general, all the adsorbates exhibit the lowest heat of adsorption on ALPO-5.

Specific Retention Volume

The results in Figs. 2 and 3 show that the specific retention volume for the adsorbates at different temperatures varies from zeolite to zeolite. Also, for each of the zeolites, there is a large difference in the specific retention volume of the different adsorbates. For the purpose of comparison, three base temperatures (323, 373, and 423 K) were chosen and the specific retention volumes of the adsorbates relative to that of methane at the different temperatures are given in Table 3. The second column in Table 3 gives the actual value of the specific retention volume for methane, and the other columns give the specific retention volume of the adsorbate relative to that of methane (i.e., relative retention volume). For all the adsorbents studied, the relative retention volume at 323 K is $\gg 1$, indicating that good separation of methane from the other adsorbates is possible.

For all adsorbents, the relative retention volumes for ethane, ethylene, and carbon dioxide are decreased with increasing temperature; the decrease, however, is relatively small in the case of ALPO-5. In general, the

TABLE 3
Comparison of Relative Specific Retention Volumes for Different Adsorbates on the Zeolites at Different Temperatures

Zeolite	Temperature (K)	$V_R(CH_4)$	$\frac{V_R(C_2H_6)}{V_R(CH_4)}$	$\frac{V_R(C_2H_4)}{V_R(CH_4)}$	$\frac{V_R(CO_2)}{V_R(CH_4)}$
H-ZSM-5	323	7.0	21.4	28.6	8.6
	373	2.9	13.9	15.5	5.4
	423	1.3[a]	10.8[a]	9.6[a]	3.4[a]
Na-ZSM-5	323	11.0	17.3	29.1	86.4[a]
	373	4.1	11.3	16.7	44.2
	423	1.5[a]	6.3[a]	11.3[a]	24.4
H-ZSM-8	323	13.0	18.8	43.8	9.2
	373	6.1	10.7	16.3	5.0
	423	3.1[a]	6.1[a]	6.5[a]	2.7
Na-ZSM-8	323	16.0	24.4	268[a]	219[a]
	373	5.8	14.9	124[a]	46.9
	423	2.0[a]	10.0[a]	103	23.0[a]
Silicalite	323	7.9	19.6	7.7	4.3
	373	3.1	14.5	5.6	3.8
	423	1.2[a]	11.2[a]	4.3[a]	3.8[a]
ALPO-5	323	1.95	22.6	14.6	7.2
	373	0.9	20.1	12.6	8.0
	423	0.4[a]	19.2[a]	13.1[a]	7.4[a]

[a] Values extrapolated from graph.

retention volume of all the adsorbates is smaller in Silicalite and ALPO-5 as compared to the ZSM-5 and ZSM-8 zeolites. The adsorbents could be arranged in the decreasing order of the retention volume for the various adsorbates (viz., CH_4, C_2H_6, C_2H_4 and CO_2) at two different temperatures (323 and 423 K) as follows:

For CH_4 (at 323 K): Na-ZSM-8 > H-ZSM-8 > Na-ZSM-5 > Silicalite > H-ZSM-5 > ALPO-5.
For CH_4 (at 423 K): H-ZSM-8 > Na-ZSM-8 > Na-ZSM-5 > H-ZSM-5 > Silicalite > ALPO-5.
For C_2H_4 (at 323 K): Na-ZSM-8 > H-ZSM-8 > Na-ZSM-5 > H-ZSM-5 > Silicalite > ALPO-5.
For C_2H_4 (at 423 K): Na-ZSM-8 $\gg$ H-ZSM-8 > Na-ZSM-5 > H-ZSM-5 > ALPO-5 $\geq$ Silicalite.
For C_2H_6 (at 323 K): Na-ZSM-8 > H-ZSM-8 > Na-ZSM-5 > Silicalite > H-ZSM-5 > ALPO-5.
For C_2H_6 (at 423 K): Na-ZSM-8 > H-ZSM-8 > H-ZSM-5 > Silicalite > Na-ZSM-5 > ALPO-5.
For CO_2 (at 323 K): Na-ZSM-8 > Na-ZSM-5 $\gg$ H-ZSM-8 > H-ZSM-5 > Silicalite > ALPO-5.
For CO_2 (at 423 K): Na-ZSM-8 > Na-ZSM-5 > H-ZSM-8 > Silicalite > H-ZSM-5 > ALPO-5.

The above comparison shows that the order of the adsorbents for the retention volume of the different adsorbates is influenced by temperature.

The data on the relative retention volume for C_2H_6, C_2H_4, and CO_2 on the different adsorbates at the two temperatures are summarized in Table 4. The comparison in Table 4 shows that for all the adsorbents except H-ZSM-5, the order of relative retention volume of the adsorbates does not vary with temperature. Silicalite and ALPO-5 show a similar order for the relative retention volume of the adsorbates at both the temperatures under consideration.

TABLE 4

Zeolites	Temperature (K)	Order of the relative retention volume for adsorbates
H-ZSM-5	323	$C_2H_4 > C_2H_6 > CO_2$
H-ZSM-5	423	$C_2H_6 > C_2H_4 > CO_2$
Silicalite, ALPO-5	323 and 423	$C_2H_6 > C_2H_4 > CO_2$
H-ZSM-8	323 and 423	$C_2H_4 > C_2H_6 > CO_2$
Na-ZSM-5	323 and 423	$CO_2 > C_2H_4 > C_2H_6$
Na-ZSM-8	323 and 423	$C_2H_4 > CO_2 > C_2H_6$

Selection of Adsorbent for Separation

The important characteristics deciding the suitability of an adsorbent for a particular separation are the efficiency of separation (separation factor), adsorption capacity, ease of regeneration, its reactivity toward the adsorbates, structural stability, and cost. It is rarely possible to have an adsorbent with all favorable characteristics. It is often necessary to compromise between the favorable and unfavorable characteristics of an adsorbent, based on its capability to achieve an efficient separation.

The heat of adsorption at zero coverage is a measure of the adsorbate–adsorbent interaction and can be taken as indicative of the energy input required for adsorbent regeneration. Very high values of heat of adsorption indicate stronger interactions and hence difficulty in regeneration. Among the adsorbents studied, on ALPO-5 all the adsorbates show the lowest heat of adsorption. Methane, ethane, and carbon dioxide show the highest heat of adsorption on Na-ZSM-5 and ethylene on Na-ZSM-8. These results show that it is comparatively easy to desorb the adsorbates from ALPO-5 and Silicalite. As the adsorbates are strongly adsorbed on Na^+ exchanged forms of ZSM-5 and ZSM-8, the regeneration of these zeolites, if used as adsorbents, will be difficult.

The relative retention volumes (relative to methane) obtained from the gc pulse data may be taken as a rough measure of the separation factor. A high value of relative retention volume is indicative of a high separation factor. At 323 K, all the adsorbents have a relative retention volume much greater than unity for the adsorbates studied. Methane has the highest specific retention volume, and the other adsorbates have the highest relative retention volume on Na-ZSM-8. However, ZSM-5 and ZSM-8 type zeolites are reactive toward ethane and ethylene, and hence they are not suitable for the separation of mixtures containing these hydrocarbons. For the remaining two adsorbents (i.e., ALPO-5 and Silicalite), all the adsorbates have higher relative retention volumes on ALPO-5. Also, the relative retention volumes for ethane, ethylene, and carbon dioxide on ALPO-5 differ from each other by a larger extent. Further, since the heat of adsorption of the adsorbates on ALPO-5 is lower compared to that on Silicalite, the regeneration of ALPO-5 in the separation process will be easier. All these facts show that ALPO-5 is superior to Silicalite for the separation of the adsorbates.

CONCLUSION

From studies on the adsorption of various adsorbates (viz., methane, ethane, ethylene, and carbon dioxide) on the pentasil zeolites and ALPO-5 by the gc pulse technique, the following conclusions have been drawn.

1. Among the adsorbates, the heat of adsorption of methane is the lowest and that of ethylene is the highest for almost all the zeolites. However, when the zeolites are arranged in the order of their heat of adsorption for the different adsorbates, the order varies from adsorbate to adsorbate. This reveals that the adsorbate–adsorbent interactions for a particular adsorbate vary from zeolite to zeolite.

2. The relative retention volume of ethane, ethylene, and carbon dioxide decreases with increasing temperature for all the zeolites. But for ALPO-5, the influence of temperature is relatively small. The order of the relative retention volumes for the adsorbates is not influenced by temperature for most of the zeolites. Further, for all the zeolites tested, the relative retention volume at 323 K is $\gg 1$, indicating that a good separation of methane from the other adsorbates is possible.

3. Among the adsorbents, ALPO-5 exhibits the lowest heat of adsorption for all the adsorbates. The relative retention volumes of the different adsorbates for ALPO-5 (at 323–423 K) are much greater than unity and also differ from one another. Hence, ALPO-5 can be considered as an adsorbent with high potential for the separation of methane, ethane, ethylene, and carbon dioxide from their gas mixture.

NOMENCLATURE

a	constant
F	flow rate ($cm^3 \cdot min^{-1}$)
ΔH	heat of adsorption ($kJ \cdot mol^{-1}$)
L	length of the zeolite column (cm)
R	gas constant
T_c	temperature of zeolite column (K)
T_F	temperature at which F is measured (K)
t_r	retention time of adsorbate (min)
t_d	retention time of N_2 (min)
t_m	$t_r - t_d$
U_e	superficial gas velocity ($cm \cdot min^{-1}$)
V_R	retention volume (cm^3)
V_P	volume of zeolite in the column (cm^3)

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