Adsorption of Hexane Isomers on Ion-Exchanged Mordenite

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To remove lead from petrol and thereby promote a cleaner environment, other means must be found to keep the "octane number" or "anti-knock" qualities of the petrol high. It is found that this can be accomplished by increasing the proportion of highly branched chain hydrocarbon isomers in the fuel. This in turn promotes processes for the separation of the hydrocarbon isomers and in the case of hexane, it is an easy matter to separate out *n*-hexane from the more substituted isomers but it is difficult to separate out the mono- from the di-branched isomers (Gray, 1984). This work addresses itself to such challenging separations using modified zeolites as the separating agent, and by studying the heats of sorption of these isomers on zeolites using gas chromatographic techniques to find a trend in the potential abilities of these modified zeolites to effect a good separation. Heats of sorption unlike retention times are independent of the temperature, amount of zeolite or length of column and carrier gas flow rates, and therefore give an indication of the absolute ability of the modified zeolite to act as a separating agent.

Zeolites are crystalline microporous solids which are widely used as sorbents, ion exchangers, catalysts and catalyst supports (Barrer, 1978). They are particularly interesting as sorbents due to their open structure consisting in some cases up to 50% of void space, organized into cavities and channels. The absorption properties of zeolites are determined by their crystalline structure particularly by the type and number of atoms in each unit cell and the dimensions of the pore openings of the adsorption cavities. They differ from those of conventional adsorbents (silica gel, activated alumina, activated carbon) due to the small size of the zeolite adsorption cavities, the uniform pore-size distribution, and the specific ionic properties of zeolites; the zeolite structure can be considered as positive charges concentrated on counterbalancing cations and negative charges distributed over the internal bonds of the $[AlO_4]^-$ units of the framework. As the adsorption properties of zeolites are strongly influenced by their chemical composition, they can be systematically varied by decationization, dealumination, introduction of certain elements (*Ge, P, B, Ga*) into the zeolite framework, and cation exchanges.

One of the thermodynamic functions used to characterize adsorption processes is the heat of adsorption, which reflects the energy of both adsorbate-adsorbent and adsorbate-adsorbate interactions taking place in the adsorbent. The energy of adsorbate-adsorbent interactions is a sum of dispersion energy (E_D), repulsion energy (E_R), polarization energy (E_P) and additionally the energy of the electrostatic interactions (E_E) (Barrer, 1978). In the case of zeolites the dispersion and repulsion energies (E_D, E_R), are given as the sum of all pair-wise interactions between atoms of the adsorbed molecule and either individual atoms of the zeolite framework or cations in the channel. The repulsion energy is dominant at small separation distances, whereas at large separations the contribution of the dispersion energy increases. The polarization energy E_P depends on the polarizability of the molecules involved in the interactions and the electrostatic field created by the oxygen ions of the interacting molecules or atoms.

In this work mordenite zeolite was modified by a range of double cation exchanges and the resulting modified zeolites were investigated for their ability to sorb the hexane isomers 3-methylpentane and 2,3-dimethylbutane. These two isomers are closely related in size as they both have the same kinetic diameter of 0.56 nm (Choudchary and Akolekar, 1989). In this work only heats of sorption have been investigated and measurement of the diffusion coefficients, which also affect the ability of the modified zeolites to act as good separating agents, is currently under investigation.

Experiment

In this particular work mordenite zeolite was modified by ion exchange (Klimczyk, 1994). All modifications were performed on the pelletized Na form zeolite (fraction 60–80 mesh) and led to the products listed in Table 1. The heats of adsorption of 2,3-dimethylbutane and 3-methylpentane on the studied zeolites were determined using gas chromatography, and applying the following equation (Dzhigit, 1979)

$$\log t_m(\text{cor.}) = C_o - [\Delta H/(2.303RT_c)] \qquad (1)$$

where ΔH is the heat of adsorption, R is the gas constant, T_c is the column temperature, t_m(corr.) is the corrected retention time of the adsorbate, and finally C_o is the constant. C_o is a function of the entropy of adsorption, the dimensions of

Table 1. Unit Cell Composition of the Zeolite Studies Determined by ICP-AES Analysis*

Abbreviation	Unit Cell Composition	M/Al
mor (Na, Li)	$Na_{5.0}Li_{3.0}Al_{8.0}Si_{38.0}O_{92.0}$	Na/Al = 0.68 Li/Al = 0.38
mor (Na, K)	$Na_{0.9}K_{7.1}Al_{8.0}Si_{38.0}O_{92.0}$	Na/Al = 0.11 K/Al = 0.89
mor (Rb)	$Rb_{8.0}Al_{8.0}Si_{38.0}O_{92.0}$	Rb/Al = 1.00
mor (Cs)	$Cs_{8.0}Al_{8.0}Si_{38.0}O_{92.0}$	Cs/Al = 1.00
mor (Na, Ba)$_a$	$Na_{2.1}Ba_{2.9}Al_{8.0}Si_{38.0}O_{92.0}$	Na/Al = 0.28 Ba/Al = 0.43
mor (Na, Ba)$_b$	$Na_{1.4}Ba_{3.3}Al_{8.0}Si_{38.0}O_{92.0}$	Na/Al = 0.19 Ba/Al = 0.43
mor (Na, Sr)	$Na_{3.6}Sr_{2.7}Al_{8.0}Si_{38.0}O_{92.0}$	Na/Al = 0.44 Sr/Al = 0.34
mor (Li, Na)	$Li_{1.0}Na_{7.0}Al_{8.0}Si_{38.0}O_{92.0}$	Na/Al = 0.90 Li/Al = 0.19
mor (Li, K)	$Li_{1.9}K_{6.0}Al_{8.0}Si_{38.0}O_{92.0}$	K/Al = 0.94 Li/Al = 0.26
mor (K, Ba)	$K_{3.5}Ba_{2.2}Al_{8.0}Si_{38.0}O_{92.0}$	K/Al = 0.46 Ba/Al = 0.25

*Standard deviation 0.01.

the GC column, and the carrier gas flow rate. The corrected retention time t_m(corr.) represents the observed retention time corrected to 25°C and a pressure drop across the column according to Eq. 2:

$$t_m(\text{corr.}) = (t_m - t_o) \times T_c/298 \qquad (2)$$

where t_m is the observed retention time, and t_o is the retention time of a nonadsorbate in this particular study methane. The retention times of methane were constant at all temperatures (0.05 min), and the pressure drop across the column was negligibly small. The heats of adsorption of 2,3-dimethylbutane and 3-methylpentane on the modified forms of mordenite were determined from the slopes of the linear plots of $\log t_m$(corr) vs. $1/T_c$ according to Eq. 1.

GC experimental conditions

The carrier gas is helium; the temperature range is 300°C–350°C; the flow rate is 30 $cm^3 \cdot min^{-1}$; the sample volume is 2×10^{-4} cm^3; the column length is 53 cm; the internal diameter of column is 0.2 cm; and the weight of packing material (weight of pure zeolite) is 2.0 g.

Results

The calculated heats of adsorption of 2,3-dimethylbutane and 3-methylpentane on various zeolites, presented in Table 2, show that the adsorption of 3-methylpentane on these zeolites was always more exothermic than the adsorption of the dibranched hexane isomer. This was probably due to differences in the molecular structures of these two isomers. As 2,3-dimethylbutane is more spherical in shape than 3-methylpentane, it presents less surface area to the zeolite framework and hence the number of the interactions between atoms of this isomer and the atoms of the zeolite framework or

Table 2. Heats of Adsorption of 2,3-Dimethylbutane ($\Delta H_{2,3-}$) and 3-Methylpentane (ΔH_{3-}) on the Studied Zeolites*

Zeolite	$-\Delta H_{2,3-}$ kJ/mol	$-\Delta H_{3-}$ kJ/mol	$-\Delta H_{3-} - \Delta H_{2,3-}$ kJ/mol
mordenite (Na, Li)	75.59	78.78	3.2
mordenite (Na, K)	64.48	70.11	5.6
mordenite (Rb)	24.89	27.45	2.6
mordenite (Cs)	24.54	26.65	2.1
mordenite (Na, Sr)	39.23	41.47	2.2
mordenite (Na, Ba)$_a$	65.16	70.50	5.3
mordenite (Li, Na)	60.28	63.79	3.5
mordenite (Li, K)	34.55	38.70	4.2
mordenite (Na, Ba)$_b$	74.16	80.06	5.9
mordenite (K, Ba)	29.44	32.31	2.9

*Standard deviation 0.02.

cations present in the channels should be smaller than those of 3-methylpentane. As a consequence, the heat of adsorption, reflecting the energy of all possible adsorbate-adsorbent interactions, is lower for 2,3-dimethylbutane than that of 3-methylpentane.

As heats of adsorption obtained by means of the GC technique usually refer to a very low surface concentration of the adsorbed molecules, the adsorbate-adsorbate interactions can be neglected in favor of the adsorbate-adsorbent interactions. Hence, the heats of adsorption of the hexane isomers determined in this particular work are dependent upon the contribution of the dispersion energy, the repulsion energy, and the polarization energy of the adsorbate-adsorbent interactions. Moreover, as the polarizability of the saturated hydrocarbons is relatively low, the contribution of the dispersion energy should be predominant. As the dispersion energy of the adsorbate-zeolite interactions increases with a decrease in the separation distance between the interacting atoms, the substitution of Na^+ ions by larger cations of the same valency in mordenite should force the hexane isomers nearer the framework and hence increase the dispersion energy of the interactions. As a consequence, a larger heat of adsorption should be observed, provided that the cations are held in the main channel, which can accommodate the hexane isomers. However, in the studied systems the opposite effect was observed. Decrease in the size of the counterbalancing cation present in the zeolite channels in general led to an increase in magnitude of the heats of adsorption of both 2,3-dimethylbutane and 3-methylpentane. For example, in the case of (Na, Me) mordenites, where Me = Li, K, Rb, Cs, the heats of adsorption ($-\Delta H$) of 2,3-dimethylbutane and 3-methylpentane decreased in the following order: mordenite (Na, Li) > mordenite (Na, K) > mordenite (Rb) ≅ mordenite (Cs).

The substitution of Na^+ cations by Rb^+ and Cs^+ cations into mordenite (Na) resulted in relatively low heats of adsorption of the hexane isomers. For comparison, the heats of adsorption of 2,3-dimethylbutane and 3-methylpentane on mordenite (Na, K) were about three times as large as those calculated for mordenite (Rb). The possible explanation of these results can be the influence of the polarization based interactions between the molecules of the hexane isomers and the cations present in the zeolite channels, (the charge densities of Rb^+ and Cs^+ are lower than those of Li^+ or Na^+ cations) combined with the repulsive type interactions. The

interactions based on the repulsive forces in the studied systems cannot be neglected, particularly when large cations such as Rb^+ and Cs^+ are present in the zeolite channels. The hexane isomers are relatively large in comparison to the mordenite pore size (the critical dimensions of both hexane isomers are 0.56 nm, while the main channels in mordenite are of size 0.65 nm$\times$0.70 nm) and in the presence of Rb^+ or Cs^+ ions, parts of the adsorbed hexane isomers, which are very close to the framework atoms, might be involved in the repulsive type interactions, lowering the heat of adsorption.

The determined heats of adsorption of 2,3-dimethylbutane and 3-methylpentane on the studied zeolites also prove that the heat of adsorption depends on the population of the counterbalancing cations. This is exemplified by the adsorption of 2,3-dimethylbutane and 3-methylpentane on mordenite (Na, Li), which gave larger values of $-\Delta H$ than mordenite (Li, Na) having less Li^+ cations. The more cations of high charge density, the higher the polarization energy of the interactions in the system. The adsorption of both 2,3-dimethylbutane and 3-methylpentane on the above mentioned zeolites is highly exothermic due to strong polarization type interactions caused by the presence of Li^+ cations of high charge density (2.21 e nm^{-3}) (Ball and Norbury, 1974).

The heats of adsorption of the hexane isomers determined in this work might also reflect the site locations of the cations in the zeolite pores. As an example, the calculated heats of adsorption of 2,3-dimethylbutane and 3-methylpentane on mordenite (Na, Sr) are much smaller than the heats of adsorption of these hexane isomers on mordenite $(Na, Ba)_a$, despite the fact that the charge density of Sr^{2+} (0.66 e nm^{-3}) (Ball and Norbury, 1974) is nearly twice as high as that of Ba^{2+}. On the basis of the polarization effects arising from the presence of the divalent cations, the heat of adsorption of 2,3-dimethylbutane and 3-methylpentane should be larger for mordenite (Na, Sr).

However Sr^{2+} cations, in contrast to Ba^{2+} cations, are more likely to be present in the side channels of mordenite (Breck, 1974) inaccessible to the hexane isomers (Klimczyk, 1994). Therefore, their influence on the adsorption processes is less significant than that of Ba^{2+} cations since only the cations present in the main channels of mordenite directly affect the dispersion type interactions between the molecules of the adsorbates and the zeolite by forcing the molecules of the hexane isomers closer to the zeolite framework and hence increasing the heat of adsorption.

Conclusion

The heats of adsorption of the hexane isomers on the modified forms of mordenite show that marked changes in adsorptive properties of this zeolite can be brought about by cation exchange of the original Na^+ ions. The sizes and charges of the replacing cations, as well as their population and site location in the zeolite, affect the adsorption properties.

Mordenite $(Na, Ba)_a$, mordenite $(Na, Ba)_b$, and mordenite (Na, K) gave the largest differences in the heats of sorption of the two hexane isomers, which suggest that they should be successful at separating 2,3-dimethylbutane and 3-methylpentane. This has been shown to be true only for mordenite (Na, K), whereas mordenites (Na, Ba) were unable to effect a satisfactory separation giving overlapping chromatographic peaks in the retention time data when the hexane isomers were studied in a mixture (Huddersman and Klimczyk, 1996). Mordenites containing Li^+ cations also gave relatively large differences in the heat of sorption of the two hexane isomers and are currently under further investigation.

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