Thermal desorption of normal paraffins from zeolite 5A

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Thermal desorption of normal paraffins from zeolite 5A has been studied by thermogravimetry. Normal paraffins studied range from C_8 to C_{18}. The desorption profiles for n-paraffins show well defined phases. For paraffins below C_{10} there are only two desorption phases corresponding to temperature ranges 353 K and 353–573 K. For paraffins higher than C_{10} a third phase in the temperature range 573–703 K emerges. The appearance of these phases has been explained in terms of interaction of paraffins with zeolite cavity and the dependence of these interactions on geometrical compatibility of paraffins and zeolite cavity.

INTRODUCTION

In addition to their uses for drying and purification purposes, zeolites are being increasingly employed[1] for bulk separations of closely related compounds. During the last decade, some of the major developments in this area have occurred and many more show good potential for the future. One such widely used process is separation of n-paraffins from non-linear hydrocarbons in kerosene by selective adsorption of the former on molecular sieve 5A. Normal paraffins are commercially important since these form raw materials for synthetic detergents, plasticizers and protein manufacture. Studies on adsorption and diffusion characteristics of lower paraffins in 5A are available [2–5] in the literature but are scanty for paraffins higher than decane. In practice, it is the higher paraffins (C_{10}–C_{18} range) which are of most interest. Further it has been reported[6] from diffusion studies of paraffins (C_2–C_{14}) on zeolite T that diffusivity exhibits a complicated dependence on carbon chain length. This is at variance with conventional transport in large pored adsorbents where diffusivity decreases monotonically with molecular weight. Vavlitis et al.[5] carried out sorption studies of n-pentane, n-octane and n-decane on 5A molecular sieve, but did not find any complicated dependence of diffusivities and have remarked that anomalously low diffusivities are expected for C_{12}–C_{14} paraffins in molecular sieve 5A.

Expecting that any such anomalous diffusivity dependence may be reflected in desorption behaviour of hydrocarbons, thermal desorption of n-paraffins ranging from n-octane to n-octadecane was carried out from molecular sieve 5A. Desorption measurements were carried out by thermogravimetry. Using a similar technique for desorption of water from molecular sieve 5A, existence of differently adsorbed water phases has been demonstrated[7,8].

EXPERIMENTAL

Studies were carried out employing TGA system 113

of Cahn Instruments. Molecular sieve samples were subjected to programmed heating using microprocessor Microcon 823 and a 'split shell' furnace and thermocouple K was used as a thermal probe. Samples were heated under high purity nitrogen atmosphere (60 ml min^{-1}) which was dried by passing through molecular sieve and anhydrous calcium chloride traps before being sent to the system.

Fresh molecular sieve 5A (commercial, from Linde) was activated at 623 K under nitrogen gas purge for 5–6 h. The activated sample was saturated with n-paraffins by keeping the sieve in hydrocarbon overnight. In the case of higher paraffins ($> C_{12}$) the adsorption was too slow at ambient temperature. Therefore the samples were warmed at 333–353 K for two hours to ensure saturated adsorption. The samples were then repeatedly washed with isooctane (which is not adsorbable by 5A) and dried to ensure complete removal of hydrocarbons from external or intercrystalline space. Approximately 30 mg of dried sample was subjected to a programmed heating (5 K/minute) from ambient to 703 K in the t.g.a. system. Weight loss and rate of weight loss at different temperatures were recorded (0.01 mg weight loss can be detected).

High purity samples of n-paraffin were used. Higher paraffins (C_{12}–C_{18}) were distilled 2–3 times and only the middle fraction taken. The level of binder in the zeolite was determined by comparing water adsorption capacities on this sample with the literature value[9] on 5A zeolite powder.

RESULTS AND DISCUSSION

A typical thermogram for desorption of an n-paraffin (C_{11}) is given in *Figure 1*. The d.t.g. curve given in *Figures 2–5* shows several zones of desorption indicating that the nature of molecules in the adsorbed phase is varying. *Figures 2–5* give the d.t.g. curve for desorption of several paraffins (nC_8 to nC_{18}) from 5A molecular sieves. From these plots, it is apparent that for C_8 and C_9 n-paraffins there are two major broad peaks, while for higher than C_9 a third peak appears in the temperature range 573–673 K. The third peak
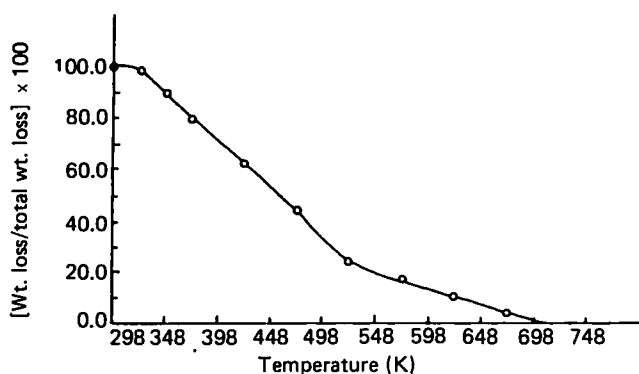
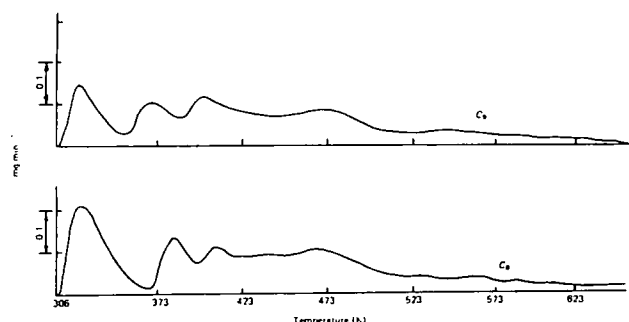**Figure 1** T.g.a. curve of n-undecane from molecular sieve 5A

Figure 2 D.t.g. curve of n-octane and n-nonane from molecular sieve 5A
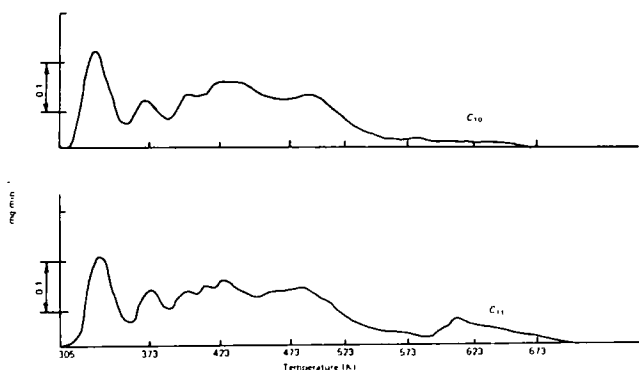

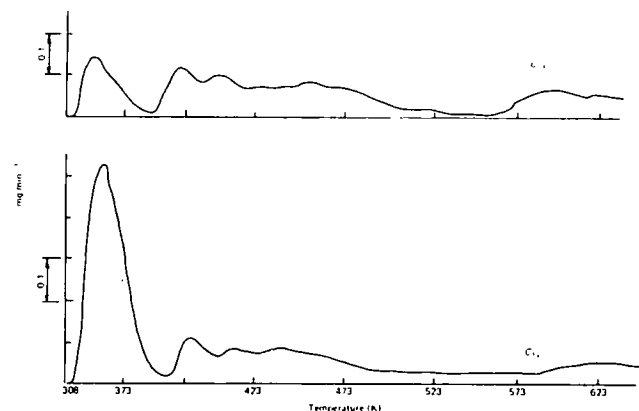**Figure 3** D.t.g. curve of n-decane and n-undecane from molecular sieve 5A

Figure 4 D.t.g. curve of n-tridecane and n-dodecane from molecular sieve 5A

becomes more prominent with an increase in the carbon number of n-paraffins. In *Table 1*, the temperature ranges corresponding to different peaks for all the hydrocarbons are presented. These temperature ranges do not differ much with carbon number.
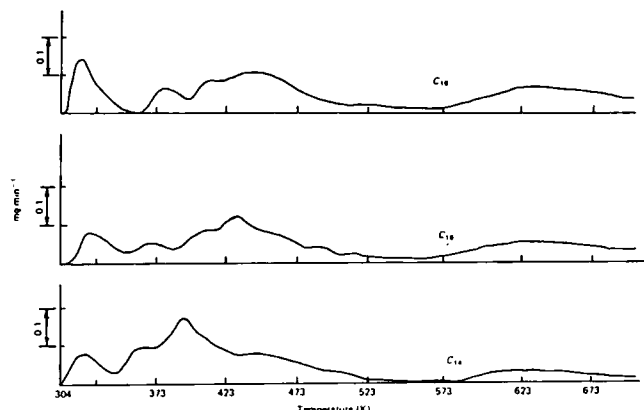

Figure 5 D.t.g. curve of n-tetradecane, n-hexadecane and n-octadecane from molecular sieve 5A

Table 2 presents the amount desorbed corresponding to different temperature ranges. From these values of weight loss the number of desorbed hydrocarbon molecule per unit cell of the molecular sieve was calculated and these are given in *Table 3*, using the unit cell composition[9] of dehydrated cell as [Ca_6 $(AlO_2)_{12}(SiO_2)_{12}$] For these calculations the amount of fresh adsorbent was obtained by subtracting the total desorbed amount from the initial weight of the saturated sample.

The d.t.g. profiles of higher ($> C_{10}$) normal paraffins have three clearly distinguishable phases. Phase I (353 K), which is more or less constant for each hydrocarbon, is most probably due to residual paraffins in the external surface and intercrystalline regions. Phase II (353–573 K), consisting of a series of fine peaks, represents desorption from internal surface. Phase III (573–703 K) is present in higher

Table 1 Temperature ranges corresponding to different phases for various hydrocarbons

Compound	Temperature (K)		
	Phase-I	Phase-II	Phase-III
n-Octane	306–375	375–703	–
n-Nonane	306–350	350–703	–
n-Decane	305–353	353–703	–
n-Undecane	305–353	353–573	573–728
n-Dodecane	308–373	373–573	573–703
n-Tridecane	304–358	358–563	563–703
n-Tetradecane	307–343	343–573	573–703
n-Hexadecane	303–373	373–553	553–703
n-Octadecane	308–368	368–553	553–703

Table 2 Amounts desorbed at different temperature ranges for various n-paraffins

n-Paraffin	Amount (mg)		
	Phase-I	Phase-II	Phase-III
C_8	0.97	3.32	–
C_9	0.67	3.98	–
C_{10}	0.85	4.33	–
C_{11}	0.75	3.68	0.95
C_{12}	1.17	4.02	1.22
C_{13}	0.66	2.49	1.33
C_{14}	0.34	2.74	1.45
C_{16}	0.55	1.66	1.95
C_{18}	0.75	1.48	2.23

Table 3 Number of desorbed hydrocarbon molecules per unit cell of the molecular sieve for different phases

| Compound	Phase-I	Phase-II	Phase-III
n-Octane	0.82	2.82	–
n-Nonane	0.46	2.76	–
n-Decane	0.54	2.76	–
n-Undecane	0.40	2.01	0.52
n-Dodecane	1.44	1.33	0.74
n-Tridecane	0.32	1.21	0.65
n-Tetradecane	0.16	1.28	0.68
n-Hexadecane	0.24	0.73	0.85
n-Octadecane	0.26	0.51	0.77

paraffins only. These profiles are in sharp contrast to the desorption from conventional microporous adsorbent, e.g. alumina as shown in *Figure 6*. This pattern is of the form expected of any microporous adsorbent, i.e. a narrow peak at low temperature region corresponding to the external surface or the macropores, followed by a broad band corresponding to the size distribution of the pores. Although the nature of interactions operating during adsorption of hydrocarbons on alumina and zeolites is similar, *viz.*, dispersion interactions, the presence of high temperature desorption phase II and phase III show that the energy involved is greater as the pore size approaches the dimension of the adsorbate molecules. This is clearly brought about by the desorption profile of hydrocarbon (C_{11}) from a large port molecular sieve, *viz.* 13 X as seen in *Figure 6*. The similarity in phase I and phase II between alumina and 13 X and the absence of phase III is particularly noteworthy.

The series of peaks present in phases II and III presumably arise out of different geometric location of the adsorbed hydrocarbon molecule in the zeolite cavities. Zeolite A has a pore system consisting of a nearly spherical supercage[9], 11.4 Å in diameter, separated from another similar cage by an 8-ring aperture or 'window' having a diameter of 4.2 Å. Each supercage is surrounded by 8 smaller cavities (6.6 Å diameter) which is entered by an aperture of 2.2 Å. Thus the 'walls' of zeolite supercage mainly consist of alternative oxygen-ring apertures and Si(Al)–O–Al(Si) linkages. Adsorption of normal paraffins takes place in supercages only by entry through the 8-membered apertures. When the $-CH_2-$ group of a hydrocarbon is situated close to the wall, the interaction energy is significantly higher[10,11] (-12.4 kJ mol^{-1}) than when located in the centre of

Figure 6 D.t.g. curve of n-undecane from molecular sieve 13 X and alumina

the cavity (-7.4 kJ mol^{-1}). It is to be expected that at lower loading the adsorbable molecule will take an orientation by which all the $-CH_2-$ groups will lie close to the Si–O or Al–O linkages. With an increase in loading, however, the molecules will orient themselves in order to accommodate the maximum number of molecules which, during thermal desorption, give rise to closely spaced peaks in the d.t.g. curve.

This still does not satisfactorily explain the origin of phase III which is present in n-paraffins with chain length greater than C_{10} in molecular sieve 5A. This phase is absent also in the case of 13 X, irrespective of carbon chain length. It has been shown[9,12] that for paraffin adsorption the greatest interaction is between oxygen atoms of the 8-membered ring and methyl group when the methyl group is located in the centre of the former. It is therefore, reasonable to assume that the highest interaction of the paraffin molecule in zeolite will be when the configuration is such that the molecule is lying close to the curved 'wall' of the spherical cavity of the zeolite, with its 'head' and 'tail' methyl groups positioned in the centre of the 8-membered apertures diagonally facing each other. It can be shown that such an orientation in 5A requires a chain length of at least 15 Å which corresponds to nC_{10} paraffin number. With an increase in chain length only the number of molecules occupying such an orientation within the zeolite increases and not the interaction energy. This fact adequately explains the observation that in the d.t.g. curve with increase in chain length, the position of phase III does not appreciably change, but that this peak becomes progressively more prominent. Further, the absence of this phase in the case of nC_{11}–13 X system supports this proposition.

The number of molecules of paraffins which can be packed in the supercages depend on the carbon chain length (*Table 3*). These values are compared with the estimated number which can be accommodated in a supercage of A-type zeolite assuming (a) a molecular volume estimated from the critical diameter and the carbon chain length (b) a molecular volume derived from the liquid density (*Table 4*). It is observed that paraffins beyond C_{14} (having a carbon chain length of about one and a half times the diameter of the zeolite cavity) the molecular packing in the cavity is closer than in the liquid state and approaches the maximum close packing. For longer carbon chains, such a close packing is not possible and is found to be even lower than existing in the liquid state. It is quite
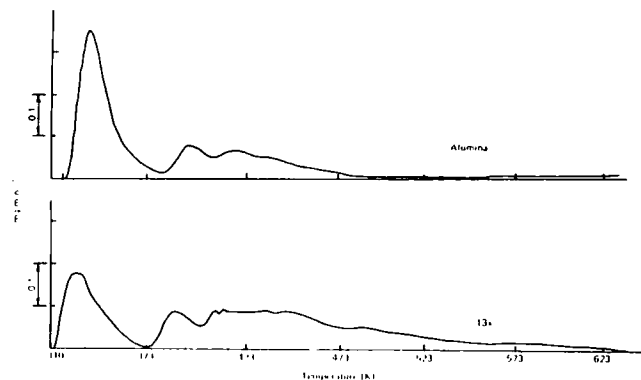
Table 4 Comparison of number of molecules per unit cell determined by t.g.a. with estimated values

n-Paraffin	Number of molecules per unit cell of zeolite		
	t.g.a.	From liquid density	From molecular geometry
C_8	3.1	2.8	3.2
C_9	2.7	2.6	2.9
C_{10}	2.7	2.4	2.7
C_{11}	2.5	2.2	2.5
C_{12}	2.3	2.1	2.3
C_{13}	1.9	1.9	2.2
C_{14}	2.0	1.8	2.1
C_{16}	1.6	1.6	1.8
C_{18}	1.3	1.4	1.7

probable that when the cavities are fully saturated molecules shorter than C_{14} tend to coil around and occupy the same cavity leading to the closest packing, while longer chains might need to occupy more than one cavity, thereby diminishing the extent of close packing due to steric factors.

ACKNOWLEDGEMENT

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