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Gas chromatographic separation of hydrogen isotopes on columns packed with alumina, modified alumina and sol–gel alumina

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ABSTRACT

The stationary phase of alumina adsorbents, prepared by different chemical processes, was used to study the separation behaviour of hydrogen isotopes. Three types of alumina, obtained by conventional hydroxide route alumina coated with silicon oxide and alumina prepared by internal gelation process (IGP), were used as packing material to study the separation of HT and T_2 in a mixture at various temperatures. The conventional alumina and silicon oxide coated alumina resolved HT and T_2 at 77 K temperature with different retention times. The retention times on SiO_2 coated columns were found to be higher than those of other adsorbents. However, the column filled with IGP alumina was found to be ideal for the separation of HT and T_2 at 240 K. The peaks were well resolved in less than 5 min on this column.

1. Introduction

Several methods of separating hydrogen isotopes have been reported in the literature [1–4]. With increased demand for the tritium as a result of greater emphasis for fusion research, the need for a method of separation and purification of tritium is of interest. Tritium is obtained on a large scale by cryogenic distillation of hydrogen isotopes at the boiling point of hydrogen. Gas chromatography with a cryogenic separation column is one of the most extensively used methods for the analysis of hydrogen isotopes [5–7] and column chromatography is also used for the separation of lighter elements [8]. It also could be used to recover small quantities of isotopically pure tritium from a sample feed in a batch process employing valve-switching technique [9]. Crystal structure, pore texture and chemical nature of the surface were largely dependent on the method of preparation of aluminium hydroxide and its subsequent dehydration. Several packing materials such as charcoal, alumina, molecular sieve 4A, 5A, 13X, etc. [10–16] have been used employing gas chromatography for the separation studies. We have already reported the separation of hydrogen isotopes employing vanadium oxide coated column [17]. The separation of HT and T_2 could be obtained on alumina and silicon oxide coated alumina at liquid nitrogen temperature. However, high porosity observed in alumina prepared by internal gelation process prompted us to study the separation of hydrogen isotopes on this alumina microspheres packed column. The microspheres packed column offered least resistance to gas flow as the particle size of this alumina was relatively large.

2. Experimental

2.1. Preparation of adsorbents

2.1.1. Preparation of alumina

Aluminium hydroxide was precipitated from the aqueous solution of aluminium nitrate (3 M) using ammonia. The precipitate was filtered and washed with distilled water. The precipitate was again homogenized with water and sprayed on a hot plate. Alumina of particle size 60 mesh size was filtered and used as column 1.

2.1.2. Preparation of silicon coated alumina

Alumina prepared as above was mixed with required quantity of tetraethoxy silane (TES). The particles were subjected to steam to hydrolyze TES and a fine coating of silicon hydroxide was obtained on alumina. The coated alumina was heated to 573 K for 3 h when a fine coating of silicon oxide was formed on alumina and is used in column II.

2.1.3. Preparation of porous alumina microspheres by internal gelation process (IGP)

The feed solution was prepared by gradually adding 10 °C cooled solution of hexamethylene tetramine (HMTA), urea, with continuous stirring to 10 °C cooled 3 M $Al(NO_3)_3$ solution taken in the required proportion. The shelf life was longer when the feed solution was stored at lower temperatures. The feed solution at 10 °C was forced through a SS capillary of 0.8 mm ID to convert it into

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Table 1
Specific surface area and pore volume of the micro porous alumina prepared by internal gelation process.

Adsorbent	Surface area (M^2/g)	Pore volume (cm^3/g)	Average pore radius (Å)
IGP-alumina	247	0.42	34
Alumina	205	0.21	20–60
SiO_2 coated alumina	153	0.15	20–50

droplet of about 1.6 mm diameter. These droplets were passed through a glass column filled with silicone oil (100 cst) maintained at 363 K, to convert them into solid gel particles. The gel particles were subjected to three contacts with CCl_4 to degrease them from silicone oil adhering to their surface. The washed spheres were dried in air and heated to 973 K before use in column III.

The microspheres were characterized out using X-ray diffraction and FTIR spectra. The morphology of the microspheres was obtained from the study of N_2 gas adsorption technique (BET method).

3. Results and discussion

The spherical alumina microspheres were obtained directly from 3 M aluminium nitrate solution using internal gelation technique [18].

The following reactions occur during the process of internal gelation technique:

$$(CH_2)_6N_2 + 6H_2O = 6CH_2O + 4NH_3 \quad (1)$$

$$Al(NO_3)_3 + NH_3 + H_2O = Al(OH)_3 + 3HNO_3 \quad (2)$$

This process of gelation where ammonia is generated internally needs to have very high aluminium molarity (near 3 M) with low free acid generation during the hydrolysis process as shown in reaction (2). Use of urea resulted in premature gelation. It was also observed that use of urea strongly influences the quality of alumina microspheres obtained in the process.

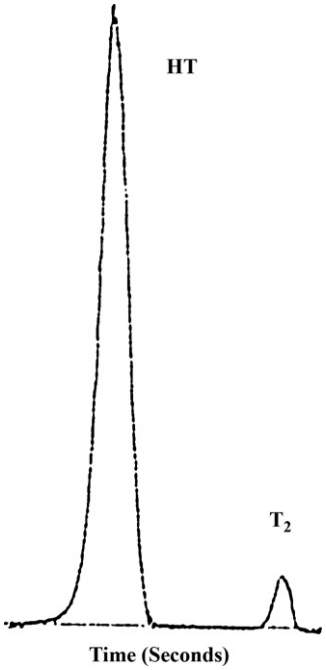

Fig. 1. Separation of HT and T_2 on column packed alumina prepared by hydroxide precipitation.

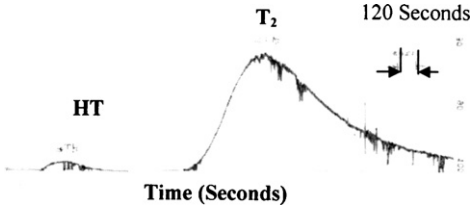

Fig. 2. Separation of HT and T_2 on column packed with SiO_2 coated alumina.

3.1. Surface area determination

In order to understand the morphology of the various particles nitrogen gas adsorption isotherms were studied for all the adsorbents. The alumina obtained by internal gelation process was found to have highest surface area and therefore offers strong adsorption at relatively low partial pressures. Surface area was determined by BET method using adsorption of nitrogen gas. The values of surface area and pore size determined for all the three types of adsorbents by this method are given in Table 1.

3.2. Studies of the separation of hydrogen isotopes

Separation of hydrogen isotopes was performed using columns of identical sizes packed with the adsorbents. The dimensions of all the columns were 3 m long and 1/8″ OD. All the adsorbents with similar particle size of 60 mesh were conditioned at a temperature of 573 K prior to the separation study.

3.3. Separation of HT and T_2 at 77 K temperature

The chromatographic facility was equipped with ion chamber as detector, as used previously on modified molecular sieve packed columns [12]. Separation of hydrogen isotopes on column 1 using helium as the carrier gas at a flow rate of 40 mL/min is shown in Fig. 1 while that observed with column-II is shown in Fig. 2. Symmetric peaks were obtained on alumina column-1 while skewed peaks were obtained on SiO_2 coated column-2. Both pure alumina and silicon oxide coated alumina columns (I and II of Table 1) resolved HT and T_2. Skewed nature of the peak and larger retention

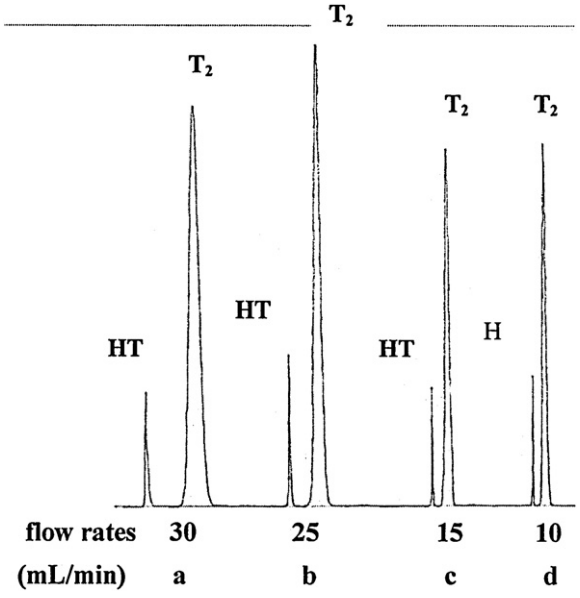

Fig. 3. Separation of HT and T_2 on column packed with alumina prepared by internal gelation process at flow rates (mL/min) of 10, 15, 25 and 30, respectively from right to left.

Table 2
Separation parameters for HT and T_2 on different columns.

Temp. (K)	Column filling	Sample size (μL)	Flow rate (mL/min)	Retention time		Resolution $\frac{t_{HT} - t_{T_2}}{(W1+W2)/2}$ R_s	Relative retention (t_{T_2}/t_{HT})
				HT	T_2		
196	Alumina (60 mesh)	100	40	1932	3380	7.31	1.7494
196	SiO_2 coated alumina	100	40	2478	4882	2.17	1.9701
240	IGP alumina	100	40	15	65	1.66	4.3333

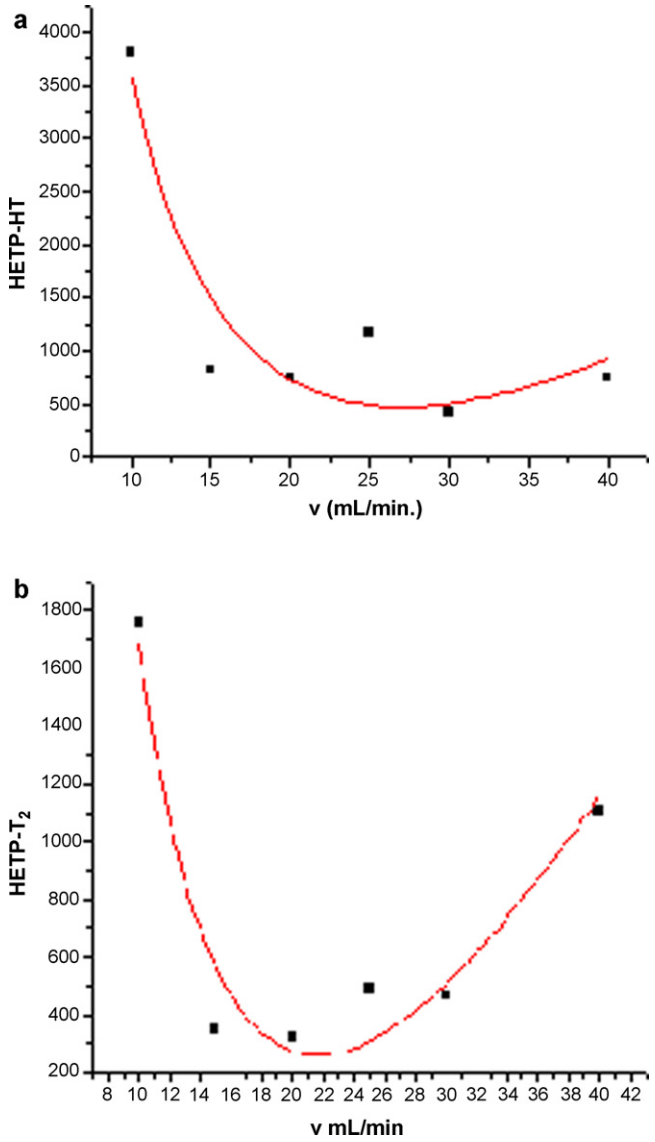

Fig. 4. (a) HETP as a function of flow rate for HT. (b) HETP as a function of flow rate for T_2.

times on column-2 indicate that SiO_2 coating on alumina resulted in stronger adsorption of gases on the solid surface compared to alumina in column-1 under similar experimental conditions.

Alumina prepared by internal gelation process was found to retain all the isotopes at temperature of 77 K. The behaviour of all the adsorbents for the separation of HT and T_2 on various columns used in the present study is given in Table 2.

Table 3
Variation of retention times for HT and T_2 on IGP alumina packed column-III at 240 K as a function of flow rate of the carrier gas helium.

Flow rate (mL/min)	Sample size (μL)	Retention time (HT) (s)	Retention time (T_2) (s)
10	300	71	328
15	300	48	178
20	300	30	138
25	300	24	99
30	300	18	76
40	300	15	65

3.4. Separation of HT and T_2 on column packed with IGP alumina

Since alumina prepared by internal gelation process retained hydrogen isotopic species at 77 K, the elution behaviour was studied at various elevated temperatures. It was found that a better separation could be achieved at 240 K for HT and T_2 with better retention times. The separation was studied as a function of flow rate and the chromatograms obtained are shown in Fig. 3 and the data are presented in Table 3. The optimum flow rate for efficient adsorption of HT and T_2 on the column was derived from van Deemter relation as shown in Fig. 4a and b. The average optimum flow rate was found to be 23 mL/min.

4. Conclusion

The separation behaviour of HT and T_2 was studied on alumina prepared from hydroxide route, alumina coated with SiO_2 and alumina prepared through sol–gel internal gelation process. The separation was found to be effective in alumina prepared from the gelation process.

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