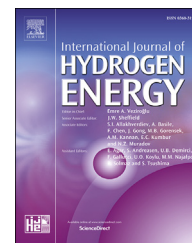




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An insight into hydrogen isotopic separation on iron-alumina and chromium-alumina as stationary phase in gas chromatographic method

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ABSTRACT

In gas chromatographic separation of hydrogen isotopes iron-alumina as a stationary phase is conventionally used. Further, Chromium-alumina as an alternative stationary phase has also been mentioned in the literature. In this present study, a detail comparative study of both the stationary phases in terms of their hydrogen isotope separation ability has been carried out. This study shows that chromium-alumina is better alternative than iron-alumina which might be attributed to its improved resolution, higher column efficiency, easy mode of preparation and shorter retention time along with equally simple regeneration procedure for regaining the performance of column material. To understand the basis behind their difference in ability of hydrogen isotope separation, hydrogen adsorption/desorption phenomenon at experimentally condition along with different surface related properties of both stationary phases have been evaluated. These experimental findings have been correlated with hydrogen isotope separation ability in terms of its retention time and resolution obtained during hydrogen isotopic separation and it illustrates the fact that hydrogen adsorption/desorption phenomenon is one of the governing factor in deciding the performance of the column materials.

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Introduction

In general, separation of any isotopes is relatively difficult due to their identical electronic structure. Further, were as in case of hydrogen isotopes an additional presence of isomers (ortho & para) complicates the isotopic separation process more. However the retention time of ortho hydrogen is different from that of para hydrogen and hence they get separated at $-197\text{ }^{\circ}\text{C}$. But the ortho hydrogen peaks usually overlaps with the HD peak and to overcome this, transition metals are used

to catalyze ortho-para conversion, thus enabling exact quantification of HD isotopes. The hydrogen adsorption on alumina at room temperature is insignificant and hence separation is carried out at liquid nitrogen temperature. One of the major drawbacks of this cryogenic separation technique is comparatively higher retention time resulting in longer analysis time required for carrying out one set of experiments. Hydrogen isotopes separation, quantification and storage are one of the most crucial works involved in nuclear industry and for future fusion technology. Several methods such as mass-

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spectrometry [1], nuclear magnetic resonance spectroscopy [2,3], gas chromatography (GC) [4,5] and frontal displacement chromatography [6] have been used for analyzing hydrogen isotopes. However gas chromatographic separation of hydrogen isotopes in cryogenic column coupled with TCD detector is one of the most extensively used methods [7–12]. This method is simple and reliable for analyses of hydrogen isotopes from the view point of accuracy of results, reproducibility and ease of operation. In fact, construction and maintenance of instrument is comparatively simpler and user friendly. Besides this, since it is non-destructive in nature, this technique can be extended to separate and store heavier hydrogen isotopes having very low abundance from hydrogen isotopic gas mixture.

For the analyses of hydrogen isotopes, gas chromatograph with different column material (stationary phase) has been proposed in literature [13–18] and a few among these are been used for analyses of hydrogen isotopes in laboratories. The commonly used stationary phase materials are alumina and alumina coated with different transition metals (Fe, Cr, Mn, Ni etc). The Iron-alumina stationary phase is generally used; however loading iron on alumina involves tedious process of neutralization step with ammonium hydroxide. Among various column materials based on alumina reported in the literature [19–25], chromium-alumina column material is compared with iron-alumina for hydrogen isotopic separation and a comprehensive comparison study covering their retention time, resolution and the column efficiency of these two stationary phases (column materials) is carried out, this will ease in selecting stationary phase to be used between them for carrying out hydrogen isotopic separation.

Two Alumina base column materials coated with iron and chromium are prepared for the comparative studies. The experiments are carried out at cryogenic condition to evaluate resolution, efficiency and retention time. These prepared column materials are characterized by using XRD, SEM and BET techniques. The hydrogen adsorption and desorption isotherm of the column materials have also been determined. This paper compares the performance of prepared columns and correlates them with their corresponding surface related properties along with its hydrogen adsorption/desorption phenomenon occurring on these stationary phases.

Experimental

The gas chromatograph used in these experiments is **G.C 1000 CIC India make model** consisting of sample injection system, helium gas purifier unit, analytical column port which is modified for immersion of column in liquid nitrogen Dewar flask and associated electronics, consisting of data acquisition and processing was performed with a chromatography software through an advanced computer interface. Sample gas used in these experiments is prepared by mixing deuterium gas generated by electrolysis of heavy water using deuterium generator with high purity hydrogen gas in proportionate volume. The Gas mixture comprising of H₂, HD & D₂ in mole percentage of 84.5, 1 & 14.5 mole (%) respectively is obtained and is used to test the prepared column material. Method of preparation of column materials is as follows.

Preparation of stationary phase

Two stationary phases, Iron-alumina and Chromium-alumina (80–100 mesh size) are prepared by loading 6.5 (Wt %) iron and chromium respectively. Before preparation, alumina used for loading is crushed and screened through series of standard screens to obtain alumina particles of 80–100 mesh size.

Iron alumina stationary phase

Twenty grams of alumina (80–100 mesh size) is added with stirring to 100 cm³ of 1.8 M FeCl₃ in 10.0 (M) hydrochloric acid (alumina has been previously activated at 500 °C for 16 h). The mixture is allowed to settle for 1 h and excess of FeCl₃ is decanted, 100 cm³ deionised water is added, followed by slow addition of ammonium hydroxide – 6.0 (M), with continuous stirring till the pH-7 is attained. Precipitate material is allowed to settle and the excess solution is decanted. Precipitate is then filtered and dried in oven at (120 °C) for 24 h and filled in S.S tube (length: 2 m; dia: 2.3 mm) and coiled spirally. This iron-alumina column is then regenerated at 120 °C for 8 h under helium gas before hydrogen isotopic gas mixture analyses.

Chromium-alumina stationary phase

Twenty grams of alumina (80–100 mesh size) activated at 500 °C for 16 h. The activated alumina is slowly added to chromium trioxide aqueous solution 6.7% (m/v). The mixture is continuously stirred for three hours by magnetic stirring and allowed to settle down; excess liquid is removed by decantation. Residue obtained is dried and chromic acid is reduced in stream of hydrogen gas at 350 °C with a flow of hydrogen at a rate of 20 cm³/min the colour of residue changes from yellow to green indicating completion of reduction process, the residue obtained is filled in S.S tube (length: 2 m; dia: 2.3 mm) and coiled spirally. This chromium-alumina column is reactivated at 145 °C under helium gas flow before carrying out analysis of hydrogen gas mixture.

Experimental conditions

Experimental set up as shown in Fig. 1, consisting of gas purification unit for mobile phase helium gas, G.C 1000 CIC India make gas chromatograph is used for testing both stationary phases (Iron-alumina and chromium-alumina) packed in S.S. tubes and coiled into spiral coil of identical dimension. Prior to analyses both columns are regenerated in situ in G.C oven at 140 °C for 10 h with helium gas. The Experimental conditions as listed in Table 1 are maintained constant for both the analytical columns and feed gas sample is injected in column at constant flow rate of 4 ml/min through online sample injection system.

Characterization and measurement of hydrogen adsorption of column material

BET surface area and hydrogen adsorption of prepared column materials is estimated by nitrogen adsorption at –197 °C and to determine their hydrogen adsorption capacity **Thermo make sorptomatic 1990** instrument is used. It is a volumetric method applied for measurement of adsorption isotherm. The

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