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A NEW COLUMN PACKING FOR THE SEPARATION OF CARBON MONO- AND DIOXIDE

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SUMMARY

Amberlyst, Nickel form, packed in a gas chromatographic column, was reduced at 180° for 6 h by hydrogen flowing at a rate of 150 ml/min. The resulting column of Amberlyst with the reduced active nickel metal was found to be suitable for separation of carbon mono- and dioxide. The properties of the column are discussed.

INTRODUCTION

The sulfonic acid cation exchanger, Amberlyst 15, has a macroporous structure similar to those of conventional adsorbents such as alumina and bone char[1]. In this work, Amberlyst is tested as a column packing for the separation of a gas mixture.

BRECK *et al.*[2] proposed the separation of carbon monoxide from gases using a molecular sieve with reduced iron and nickel or cobalt that absorbs carbon monoxide to form carbonyl compounds. The present authors prepared a column packed with the Amberlyst support with reduced active atomic nickel and found that the column was suitable for separation of carbon mono- and dioxide. The separation properties are investigated from the heat of adsorption of the gases on the new column packing.

The heat of adsorption of a gas is determined by GC from the familiar relationship[3]

$$\frac{t_R - t_{R,0}}{t_{R,0}} = K \cdot \frac{F_S}{F} = B\exp\left(\frac{-\Delta H_a}{RT}\right)$$

where $t_{R,0}$ and t_R are retention times of air and component, respectively, K is the partition coefficient, F and F_s are volume fractions of the mobile and stationary phases, respectively, B and R are constants, H_a is the heat of adsorption, and T is the absolute column temperature. It is seen from the above equation that the plot of log $\{(t_R - t_{R,0})/t_{R,0}\}$ *vs.* $1/T$ should be linear and that the heat of adsorption for an eluted gas could be derived from the slope of the plot for a given column.

EXPERIMENTAL

Column packing

The commercially available Amberlyst 15 is sieved to a fraction of 42–60 mesh. The resin is first washed with ethyl alcohol to remove impregnated toluene, and then with water, treated with an aqueous hydrochloric acid solution, dried by suction and heated at 110° for 8 h. 31.89 g of the dried H-form Amberlyst 15 are swelled in ethyl alcohol to prevent breakage, washed with water, and treated with an aqueous solution of nickel nitrate. The resulting Amberlyst in the nickel form is washed with water until the washings show no color reaction with dimethylglyoxime, and is dried by suction at 110° for 8 h. The weight of the nickel form resin is 37.44 g, and the calculated exchange capacity of the resin for nickel is 5.9 mequiv./g of dried resin.

Apparatus

The gas chromatograph used is a Shimadzu GC-1B with a thermal conductivity detector. Dried Ni-form, Amberlyst 15, 42–60 mesh, is packed in a stainless-steel column of 0.4 mm I.D. The length of the packing is 1.5 m. Hydrogen at a flow rate of 150 ml/min is employed to reduce the nickel ion to a metallic state at 180° for 6 h. After cooling, the column is used to separate gas mixtures. Helium is used as carrier gas.

Samples

Sample gases, namely carbon monoxide, carbon dioxide, and a mixture thereof, are prepared according to the conventional chemical methods from formic acid, calcium carbonate and oxalic acid. The concentration of carbon monoxide and/or carbon dioxide in the gas samples is indirectly determined by determining air in the sample by means of the calibration curve for air.

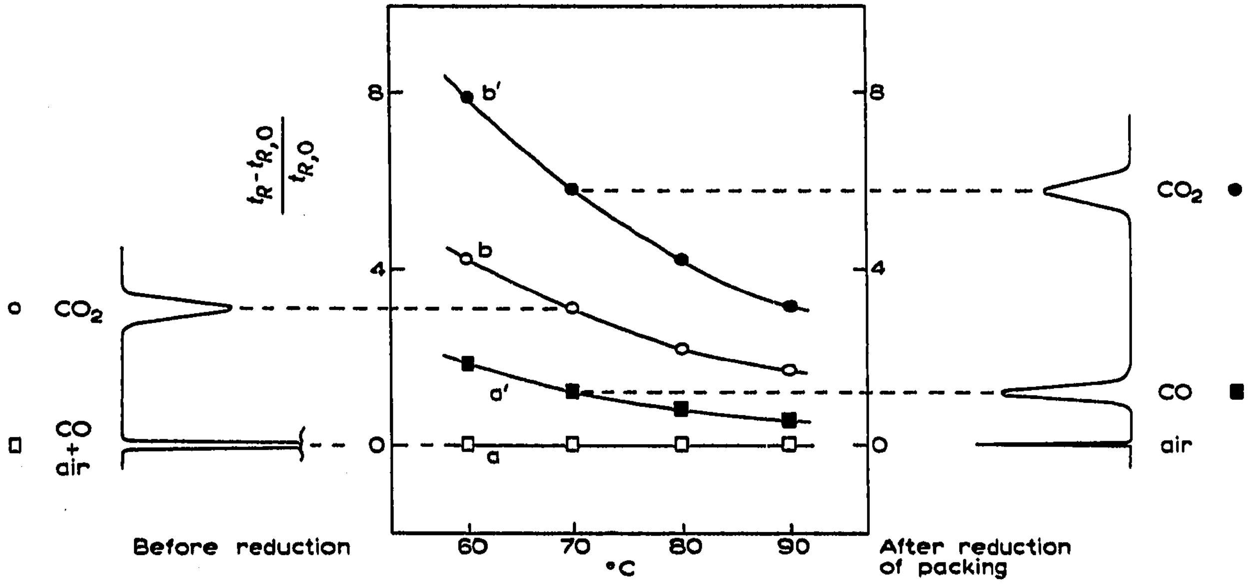

Fig. 1. The schematic gas chromatograms and the temperature dependences of the retention characteristics obtained before and after the reduction of the Ni-form Amberlyst 15 column, 42–60 mesh, 1.5 m long, 0.4 mm diameter. Flow rate of helium is 30 ml/min.

RESULTS AND DISCUSSION

Effect of nickel reduction

The gas chromatograms obtained before and after the reduction of the nickel column are shown in Fig. 1, together with the retention characteristics. Before the reduction, the dried Ni-form Amberlyst column is incapable of separating carbon monoxide from air, but separates carbon dioxide. After the reduction, however, the column excellently separates carbon mono- and dioxide from air.

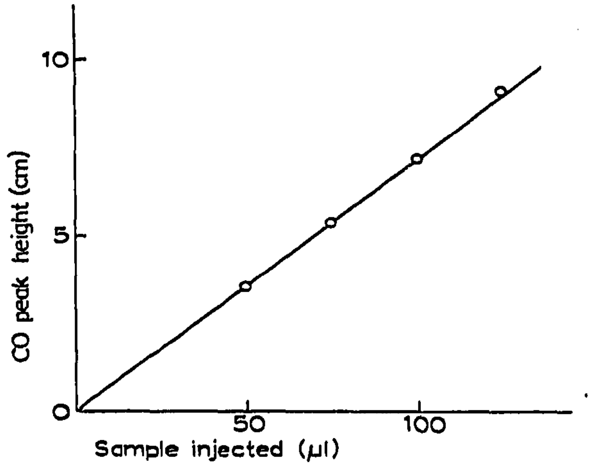

Fig. 2. Calibration curve for carbon monoxide. Column conditions are the same as given for Fig. 1. Column temperature is 70°. Sample: 66% CO + 34% air.

Proof that nickel carbonyl is not formed

It is now necessary to determine whether the separated peak in Fig. 1 is due to carbon monoxide itself or to nickel carbonyl. A sufficient amount of carbon monoxide, *viz.*, a 50-ml portion of a 30% carbon monoxide sample, is injected as a 0.4-ml portion, in succession, into the column of Amberlyst with reduced active nickel. The temperature of the column and detector is kept at 70°, and the cell current is cut off to prevent the possible decomposition of nickel carbonyl at the detector. The eluent gas is all trapped in a bubbler containing 6 ml of sulfuric acid, and the acid is neutralized with ammonia water before the solution is tested with dimethylglyoxime. No color of nickel dimethylglyoximate is developed. Thus, one may conclude that nickel carbonyl is not formed in the column. The analysis of the eluent gas by the molecular sieve 5A column also confirms that the second peak in Fig. 1 is due to carbon monoxide itself.

Calibration curve

Fig. 2 shows the calibration curve for the carbon monoxide. There is a good linearity between sample size injected and the peak height.

Heat of absorption

The retention data of carbon mono- and dioxide obtained before and after the reduction of the Ni-form Amberlyst column are shown as a function of temper-

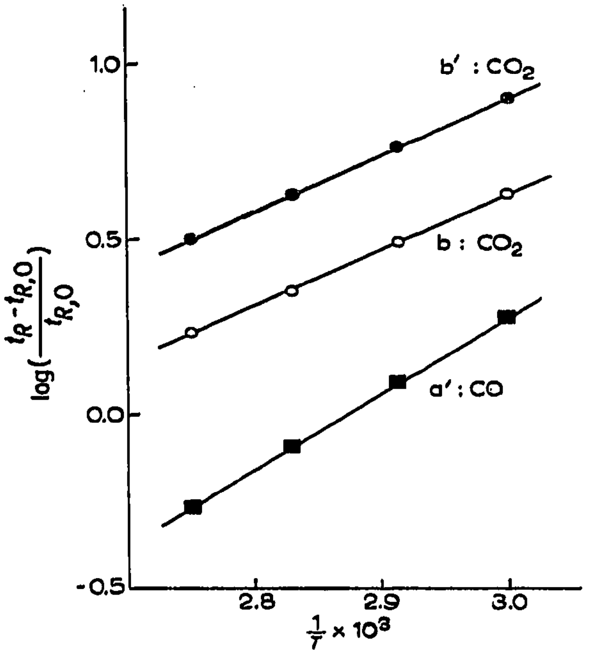

Fig. 3. Variation of logarithm of the corrected retention time relative to air with reciprocal of absolute temperature of the column. Closed and open circles correspond to the use of the Ni-form Amberlyst after and before the reduction of the nickel ion by hydrogen.

ature in Fig. 3. The slope of curve *a′* is $(2.17 \pm 0.07) \times 10^3$ at 95% confidence limits, thus the heat of absorption of carbon monoxide on the active nickel atom is (9.93 ± 0.32) kcal·mole^{-1}. The slopes of curves *b* and *b′* are $(1.60 \pm 0.05) \times 10^3$ and $(1.63 \pm 0.05) \times 10^3$, respectively. The difference in the two slopes cannot be regarded as significant. Therefore it can be concluded that carbon dioxide is not absorbed onto

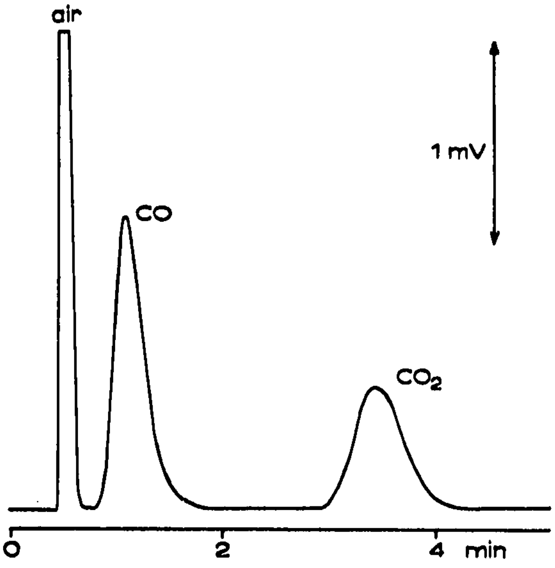

Fig. 4. The isothermal separation of carbon mono- and dioxide on the Amberlyst 15 column with reduced active metallic nickel. The column conditions are the same as given for Fig. 1. Column temperature 70°. 0.2 ml of the gas mixture of 20% CO, 20% CO_2 and 60% air is injected.

the active nickel metal. The heat of absorption of carbon dioxide on Amberlyst 15 is (7.46 ± 0.23) kcal·mole^{-1} which is similar to that obtained on the silica gel column by GREENE AND PUST[3].

Separation of carbon mono- and dioxide from air

Fig. 4 shows the isothermal separation of carbon mono- and dioxide. The sample gas is obtained by the decomposition of oxalic acid with sulfuric acid. It may be safe to say that carbon monoxide is retained by the active elementary nickel on the resin but carbon dioxide is retained by the molecular sieve structure of the Amberlyst. The separation power of the column is weakened by moisture, but it is easily restored by activating the column in a flow of hydrogen at 180° for 2–3 h.

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