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Application of a hydrogen storage alloy to the determination of trace impurities in high-purity hydrogen by gas chromatography

Group analysis of C_1, C_2 and C_3 hydrocarbons

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ABSTRACT

A hydrogen storage alloy was applied as an absorbent for hydrogen and as a catalyst for the hydrogenation of unsaturated hydrocarbons such as ethylene, propylene and acetylene for the determination of trace hydrocarbons in hydrogen by gas chromatography with photoionization detection. The hydrogen storage alloy was used at ambient temperature and under the pressure of the carrier gas. The conversion yields were 103% for ethylene to ethane, 77% for acetylene to ethane and 102% for propylene to propane and the detection limits were 0.01 ppm for methane, 0.02 ppm for ethane and 0.01 ppm for propane.

INTRODUCTION

Gas chromatography (GC) has been widely used for the determination of hydrocarbons components, as inherent impurities, in process gases such as hydrogen, nitrogen, oxygen and argon [1]. Photoionization detection (PID), which is based on the emission from a direct current discharge in helium gas, is a universally sensitive detection method [1] and has especially high sensitivity for inert gases [2]. We have reported in previous papers [3,4] that PID is suitable for the determination of trace amounts of inert gases such as nitrogen, argon, krypton and xenon. PID has a higher sensitivity to hydrocarbons such as methane, ethane and propane, which have lower ionization potentials than that of helium, and has a sensitivity similar to or higher than that of flame ionization detection (FID) [5].

However, in the determination of hydrocarbons such as methane, ethane and propane in hydrogen, it has been difficult to separate and determine directly and

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accurately trace amounts of the hydrocarbons below the parts per million level without reducing the proportion of hydrogen, as a major component, prior to introduction into the detector.

From the viewpoint of quality control of cylinder and/or bulk hydrogen gas, it is more practical to determine the total hydrocarbons in hydrogen in order to evaluate its purity; the carbon content in gases is a major concern in semiconductor manufacturing processes because the carbon may be deposited on the surface of water and influence the product yields of the device.

It is not necessary to determine individual hydrocarbon impurities, such as ethane, ethylene and acetylene, in hydrogen. If unsaturated hydrocarbons can be converted quantitatively into the corresponding saturated hydrocarbons, the gas chromatograms obtained will be simpler and the analysis time can be reduced. We found that unsaturated hydrocarbons could be converted quickly and very efficiently into saturated hydrocarbons by the use of a precolumn packed with a suitable hydrogen storage alloy (HSA), which was operated at room temperature and at the pressure of the carrier gas.

An HSA was used for the absorption of hydrogen, which is a major component of the sample gas, and also for the catalytic conversion of unsaturated hydrocarbons (*e.g.*, ethylene, acetylene and propylene) to the corresponding saturated hydrocarbons.

This paper describes a method for the group determination of C_1–C_3 hydrocarbons in hydrogen with the use of PID and the hydrogenation ability of an HSA at room temperature.

EXPERIMENTAL

Apparatus

A schematic diagram of the experimental apparatus is shown in Fig. 1. It consists of a gas sampler, a precolumn (hydrogen absorber) and a gas chromatograph (GC-263-30; Hitachi, Tokyo, Japan) with a photoionization detector. A precolumn was installed between the gas sampler (1.5 ml) and the stainless-steel analytical column (3 m × 3 mm I.D.), which was packed with active alumina (60–80 mesh). The precolumn (30 cm × 9.5 mm O.D. U-shaped stainless-steel tube) was filled with

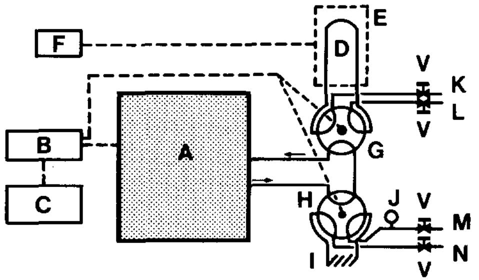

Fig. 1. Schematic diagram of the experimental apparatus. A = Gas chromatograph; B = interface; C = integrator; D = precolumn (HSA); E = heating block; F = thermo-controller; G, H = air-actuated six-port valves; I = sample loop; J = pressure transducer; K = hydrogen and helium gas inlet for HSA activation and purge; L = hydrogen and helium gas outlets; M = sample gas inlet; N = sample gas outlet; V = diaphragm stop valves (the arrow shows the direction of carrier gas flow).

a hydrogen storage alloy (HSA, 16–60 mesh) as described previously [4]. All fittings, such as the reducer and union tee (Nupro, Willoughby, OH, U.S.A.) were made of stainless-steel. This system can be programmed with a computerized integrator (C-R4A; Shimadzu, Kyoto, Japan) through an interface and is able to analyse and automatically report the results. Analytical results are computed by an absolute calibration method from the peak area. The operating conditions for the GC–PID system and the precolumn were as follows: oven temperature, 80°C; detector temperature, 100°C; carrier gas, helium at a flow-rate of 50 ml/min; discharge gas, helium at a flow-rate of 40 ml/min; discharge potential, 750 V; and precolumn temperature, room temperature (*ca.* 25°C).

Materials

The HSAs used, obtained from Japan Metals and Chemicals (Tokyo, Japan) are listed in Table I. The particle size of the pulverized HSA was initially in the range 16–60 mesh.

TABLE I

HYDROGEN STORAGE ALLOYS

HSA	Composition
HSA-1	$LaNi_{4.9}Al_{0.1}$
HSA-2	$MnNi_{4.5}Al_{0.5}$ [4]
HSA-3	$CaNi_5$

Reference gases were prepared by the gravimetric method and were supplied by Toyo Sanso (Tokyo, Japan). Most of the experiments to evaluate the applicability of the HSA as a hydrogenation catalyst were conducted with reference gases having the following compositions: (1) 10.0 ppm CH_4, 9.7 ppm C_2H_6, 9.6 ppm C_3H_8 in H_2; (2) 9.1 ppm C_2H_4, 9.5 ppm C_3H_6 in H_2; (3) 10.2 ppm C_2H_2 in H_2; and (4) 8.0 ppm C_2H_4, 9.3 ppm C_2H_6, 8.5 ppm C_2H_2, 8.9 ppm C_3H_6, 8.5 ppm C_3H_8 in He. High-purity helium (Toyo Sanso, [A] grade, 99.9999%) was employed as the carrier gas and discharge gas without further purification. The activation and regeneration of HSA were carried out with the procedure used previously [4], as shown in Table II.

RESULTS AND DISCUSSION

Selection of HSA

Several HSAs were examined to see if unsaturated hydrocarbons (*e.g.*, ethylene) can be converted completely into saturated hydrocarbons (*e.g.*, ethane). The chromatographic profiles obtained after passing through the precolumn, which were packed with different HSAs, are shown in Figs. 2–4. HSA-1 led to unasymmetrical and strongly tailing peaks for C_3 hydrocarbons, as shown in Fig. 2. HSA-2 and HSA-3 provided better peak shapes for C_2 and C_3 hydrocarbons. The quantitative results showed that the HSA-3 had an improved performance, *i.e.*, it could absorb much more hydrogen than HSA-2 without any loss of saturated hydrocarbons such as methane,

TABLE II

ACTIVATION AND REGENERATION PROCEDURES FOR PRECOLUMN FILLED WITH HSA-1–3

Activation steps	Regeneration steps
Precolumn turned to the activation position	Precolumn turned to the activation position
Evacuation (under vacuum for 30 min)	Evacuation (under vacuum at 140°C for 30 min)
Hydrogen absorption (at *ca.* 25°C, 6 atm for 30 min)	Precolumn turned back to the analytical position (heat at 180°C for 30 min)
Evacuation (under vacuum at 140°C for 30 min)	Precolumn cooled to *ca.* 25°C
Precolumn turned back to the analytical position (heat at 180°C for 30 min)	GC analysis
Precolumn cooled to *ca.* 25°C	
GC analysis	

ethane and propane and also could be successfully activated and regenerated by the procedures described previously [4]; HSA-3 provided better peak shapes, especially for propylene, than the other HSAs. The HSA-3 was therefore chosen for subsequent use.

Efficiency of hydrogenation

A series of experiments were conducted to evaluate the hydrogenation efficiency for converting C_1–C_3 unsaturated hydrocarbons at sub-parts per million levels in hydrogen into saturated hydrocarbons using activated HSA-3. The peak area for each

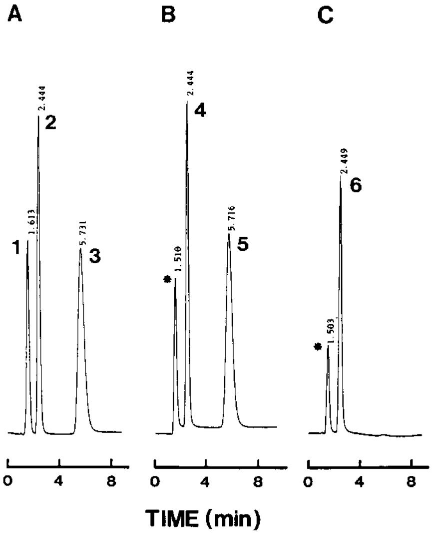

Fig. 2. Chromatograms obtained with HSA-1. (A) 1 = CH_4 (1.0 ppm); 2 = C_2H_6 (1.0 ppm); 3 = C_3H_8 (1.0 ppm). (B) 4 = C_2H_6 from C_2H_4 (1.0 ppm); 5 = C_3H_8 from C_3H_6 (1.0 ppm). (C) 6 = C_2H_6 from C_2H_2 (1.0 ppm). Asterisks show air peak.

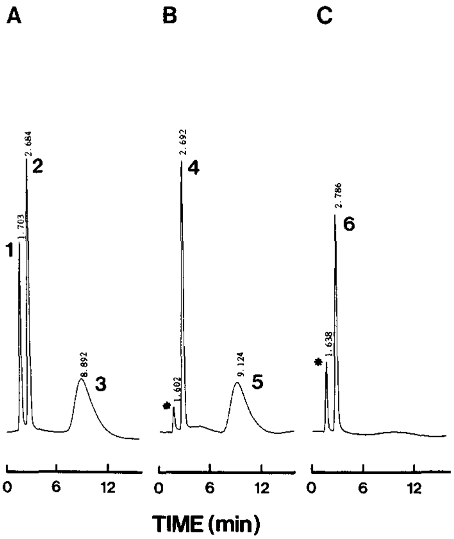

Fig. 3. Chromatograms obtained with HSA-2. A, B and C as in Fig. 2.

of the gases that passed through the precolumn was compared with that obtained without the precolumn; the sample gases used in both experiments were prepared by diluting the standard gas with high-purity hydrogen by the use of mass flow controllers.

The results showed that ethylene and propylene were completely converted into ethane and propane, respectively, within experimental error and acetylene was partially absorbed and converted into ethane with a constant hydrogenation ratio of

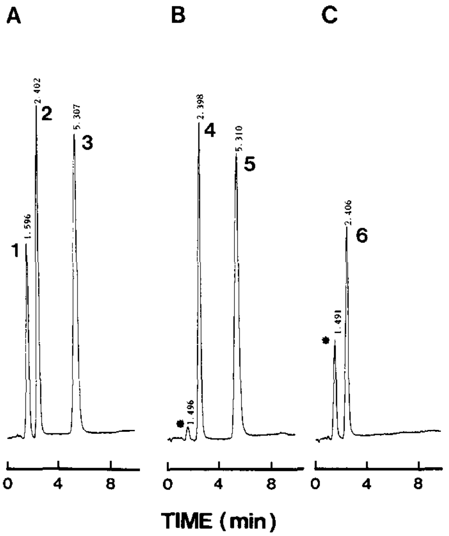

Fig. 4. Chromatograms obtained with HSA-3. A, B and C as in Fig. 2.

103 ± 2%, 77 ± 3% and 102 ± 3% for C_2H_4, C_2H_2 and C_3H_6, respectively. Only acetylene, which has a carbon–carbon triple bond, showed a lower efficiency of hydrogenation than the other unsaturated hydrocarbons. Hence if a sample contains acetylene and other C_2 hydrocarbons, the analytical result obtained will be slightly lower than the real value. Fortunately, this will only slightly affect the determination of the purity of hydrogen as the impurity is present in mere trace amounts. In the 30 cm × 9.5 mm O.D. precolumn, over 120 ml of hydrogen could be absorbed; with a sample size of 1.5 ml, more than 80 samples can be analyzed.

Typical gas chromatogram

Typical gas chromatograms of gas mixtures in hydrogen obtained by a direct method (without the precolumn) and the present method (with the precolumn) are shown in Fig. 5. In the former chromatogram, a large hydrogen peak overlapped the peaks of later eluted components. Consequently, it was difficult and/or impossible to measure th peak areas of trace amounts of impurities accurately owing to the tailing of the large hydrogen peak. It takes more than 30 min untill the complete elution of hydrogen is achieved and the next analysis is possible. On the other hand, such a large hydrogen peak did not appear on the chromatogram obtained by the present method and also only saturated hydrocarbon peaks were eluted and an analysis could be finished within 10 min.

Reproducibility and detection limits

In order to evaluate the quantitative performance of the system, standard gas mixtures were repeatedly injected into the system. The results showed that the reproducibilities (relative standard deviation, $n = 5$–6) were 1.49, 0.76, 0.81, 0.34, 2.73 and 0.51% for CH_4 (1.04 ppm), C_2H_6 (1.01 ppm), C_3H_8 (1.04 ppm), C_2H_4 (0.98 ppm), C_2H_2 (1.08 ppm) and C_3H_6 (1.03 ppm), respectively. The detection limits, which were

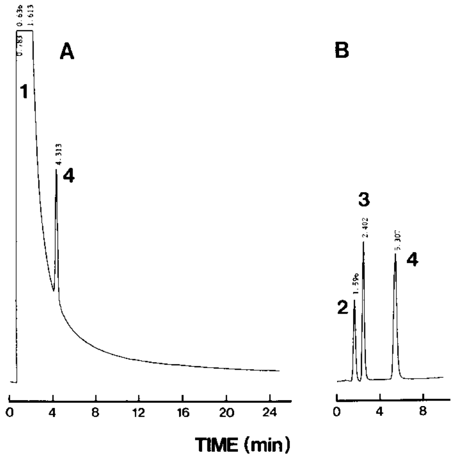

Fig. 5. Comparison between chromatograms obtained for C_1–C_3 hydrocarbons with and without the precolumn (HSA-3). Sample gas contains CH_4 (1.0 ppm), C_2H_6 (1.0 ppm) and C_3H_8 (1.0 ppm) in hydrogen. 1 = H_2; 2 = CH_4; 3 = C_2H_6; 4 = C_3H_8.

calculated from the minimum peak areas given by the integrator detection, were *ca.* 0.02, 0.01 and 0.01 ppm for CH_4, C_2H_6 and C_3H_8, respectively.

The calibration graphs were linear up to *ca.* 5 ppm in the concentration range examined. The relative sensitivities (methane = 100) were 174 ± 3 for ethane and ethylene, 127 ± 5 for acetylene and 247 ± 3 for propane and propylene, respectively.

In conclusion, the proposed procedure could be used to determine C_1–C_3 hydrocarbons down to the parts per billion level if the gas chromatograph is equipped with a highly sensitive detector such as a photoionization detector or a helium ionization detector [5].

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