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Focusing Review

Narrow Bore Packed Column Designed for Capillary Gas Chromatograph

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Abstract

A narrow-bore packed column (packed-capillary column) that designed for a direct installation in conventional capillary gas chromatographic (GC) system had been developed. In this column, particulate sorbents that employed in typical GC packed columns were packed into a stainless-steel capillary of 1.0 mm i.d. By attaching a pair of stainless-steel capillaries of 1.27 mm o.d. at both ends of the column, the packed-capillary column can be directly installed into the conventional capillary GC system. In this article, fundamental of the packed-capillary column developed by our research group is mainly reviewed, along with the various applications, such as column switching analysis and evaluation of catalytic property based on the determinations of CO and CO_2.

Key words: Packed-capillary column; Micro-packed column; Capillary gas chromatography

1. Introduction

Gas chromatography (GC) is a simple, rapid and precise technique for separation and determination of volatile compounds, and the method has been used in a wide variety of fields, such as environmental [1], biological [2,3] and food [4] analysis. For separation of complex sample mixtures, several types of columns have been developed [5]. Packed column has a high loading capacity and unique selectivity, and it is quite suitable for the separation of low-molecular-weight hydrocarbons and permanent gases [6,7]. Open-tubular capillary column has higher theoretical plates than the packed column, and it is widely used for the separation of typical volatile organic compounds (VOCs). In addition, capillary column can be suitable for a rapid temperature-programmed separation, as well as a good compatibility to a mass spectrometric detector (MSD). On the basis of the above advantageous features of the capillary column, most of the recent GC system has been designed for the connection of a capillary column, and therefore, a GC system adapted for a packed column is still needed when analyzing the mixtures containing permanent gases.

As a type of the packed-capillary columns, fiber-packed capillary column had been developed [8-13], where several heat-resistant synthetic fibers, such as Zylon and Technora, were longitudinally packed into a short fused-silica capillary or metal capillary. Short fiber-packed columns were applied to high temperature separations of relatively low-volatile compounds [14,15]. In addition the surface modified fibers were developed as the stationary phase in GC [16,17]. Recently, monolith-type GC capillary columns have been also developed [18,19].

In particle-packed column, downsizing of both the diameter of column and stationary phase particles have been investigated for increasing number of theoretical plates [20-24]. In these studies, particle sizes of lower than 10 μm were typically used. Based on these approaches the resolutions were clearly improved [25,26], although, at the same time, sample loading capacity was significantly

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decreased with a higher inlet pressure. Therefore, a specific instrument was necessary for the use of these packed-capillary columns in many cases.

Our research group has developed a packed-capillary column that packed with a particulate sorbent. As the sorbent the packing materials used in typical packed column was introduced for the separation of wide variety of volatile compounds in conventional capillary GC system without any modification of the system [27]. In this article, the packed-capillary column that recently developed by our research group is reviewed, including the fundamental of the packed-capillary column, the applications to the column switching analysis [28] and the evaluation of catalytic properties of titanium dioxide (TiO_2) based on the determination of carbon monoxide (CO) and carbon dioxide (CO_2) in capillary GC system [29,30].

2. Fundamental of the packed-capillary column

2.1. Development of a packed-capillary column

As the sorbent of the packed-capillary column, porous particles having 150 to 180 μm in diameter (80/100 mesh) that have been used in typical stationary phases in conventional packed column were introduced. In order to prepare the packed-capillary column, these particles were packed into a stainless-steel capillary of 1.0 mm i.d., 1.27 mm o.d., 1.0 m or 2.0 mm length. To prevent leak of the packed particles, small filters were attached to both ends of the packed section. Then, stainless-steel capillaries of 0.3 mm i.d., 0.52 mm o.d., 0.5 m length were attached to the inlet and outlet of the packed-capillary column as illustrated in Fig. 1. Hence, the packed-capillary column can be easily installed to a conventional capillary GC system without any system modification or an additional attachment. In addition, even though the head pressure using the packed-capillary column is the same as conventional packed column, the consumption of carrier gas volume is significantly lower than conventional packed column system. The packed-capillary column can also be easily installed to a conventional GC-MSD system.

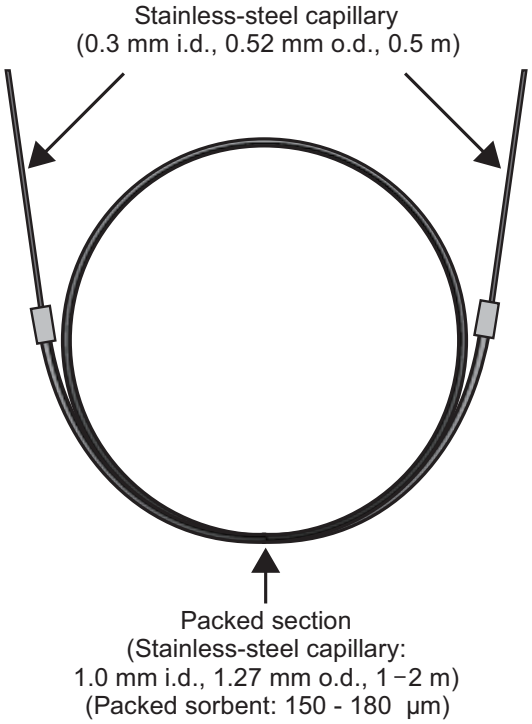

Fig. 1. Illustration of the packed-capillary column.

2.2. Evaluation of the packed-capillary column

Compatibility of the packed-capillary column to a temperature-programming separation was confirmed by a comparison with conventional packed column [27].

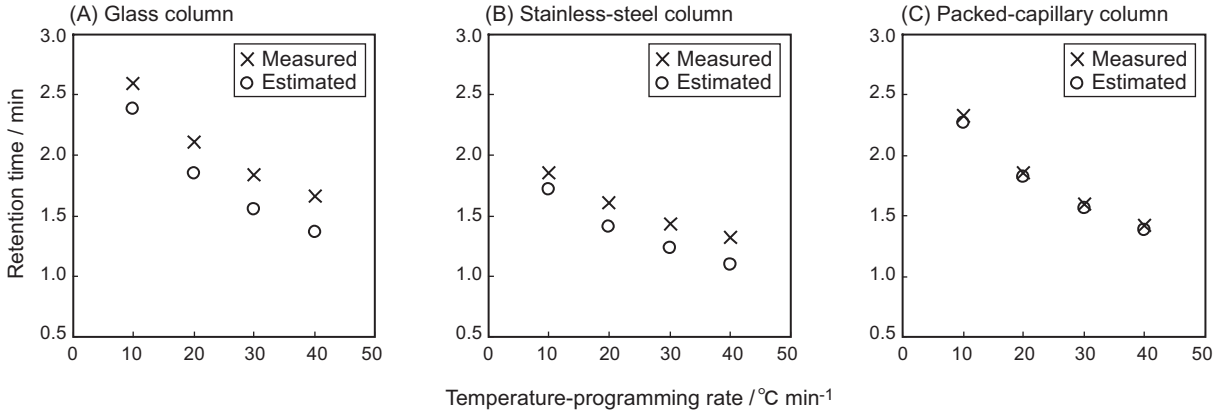

Fig. 2. Comparison of the estimated and measured retention data at temperature-programmed analysis. Column: (A) glass column of 3.2 mm i.d. × 1.1 m, (B) stainless-steel column of 3.0 mm i.d. × 1.0 m, (C) packed-capillary column of 1.0 mm i.d., × 1.0 m. Carrier gas liner velocity, N_2 7.5 cm/s. Modified from Fig. 1 in ref. [27] with permission.

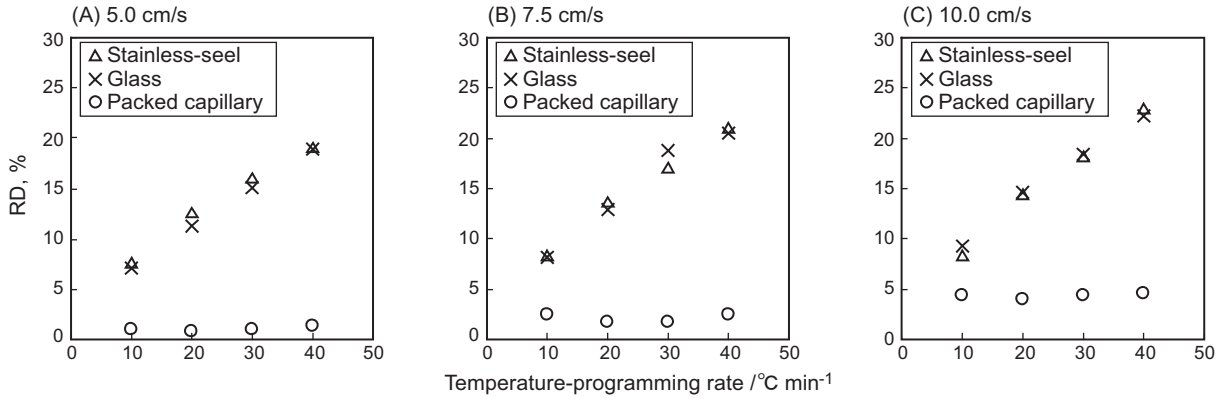

Fig. 3. Relative delay of the actual retention time from that estimated. Carrier gas liner velocity: (A) 5.0, (B) 7.5, (C) 10.0 cm/s. Column: glass column of 3.2 mm i.d. × 1.1 m, stainless-steel column of 3.0 mm i.d. × 1.0 m, and packed-capillary column of 1.0 mm i.d., × 1.0 m. Modified from Fig. 2 in ref. [27] with permission.

Compatibility to the temperature-programming was calculated based on the predicted retention time in a temperature-programming separation. The predicted retention time was estimated from the linear plot of van't Hoff plot, where the logarithmic retention factor (ln *k*) was plotted against the reciprocal absolute column temperature. Figure 2 shows estimated retention time and actual retention data of octane at various temperature-program rates for 2 types of packed columns and the packed-capillary column. As the sorbent, SE-30 (polydimethylsiloxane) 5%-coated Shimalite W (Shinwa Chemical Industries, Kyoto, Japan) was used for these columns, and the effect of the carrier gas

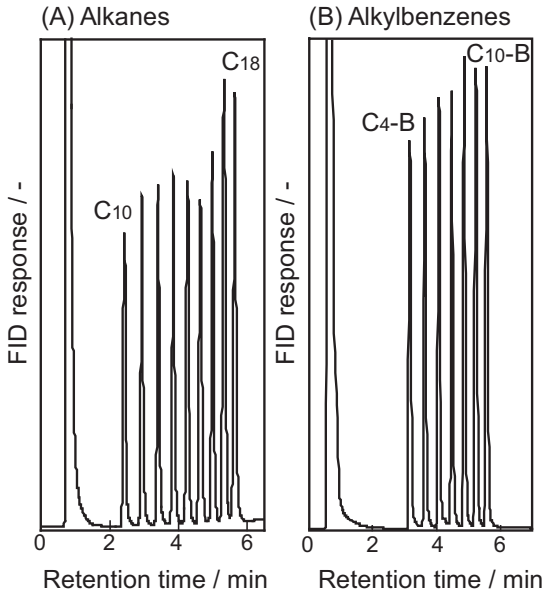

Fig. 4. Typical chromatograms for the separation of (A) alkanes and (B) alkylbenzenes on the packed-capillary column at rapid temperature programing. Stationary phase: SE-30 5% coated Shimalite W. Temperature program: (A) 100ºC (1 min) to 300ºC, (B) 40ºC (1 min) to 260ºC. Column head pressure: (A) 70 kPa, (B) 150 kPa. Sample: (A) alkane mixture containing 1.0% each from C_{10} to C_{18} in hexane, (B) alkylbenzene mixture containing 1.0% each from C_4-B to C_{10}-B in hexane. Injection: splitless injection of 1.0 μL. Modified from Fig. 3 and Fig. 4 in ref. [27] with permission.

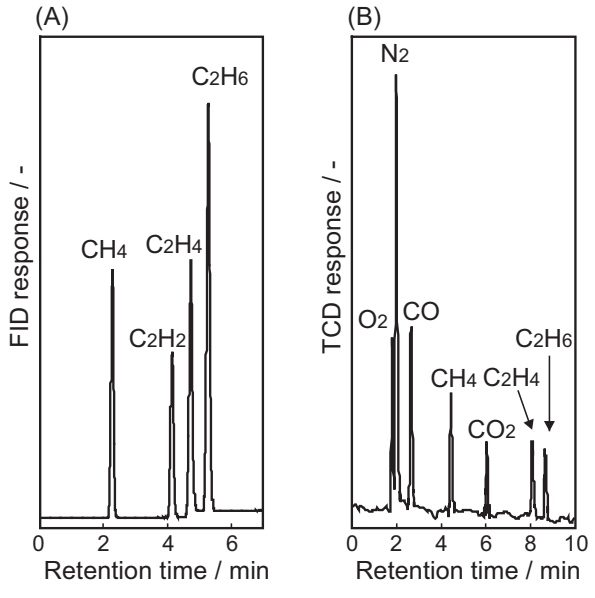

Fig. 5. Rapid temperature-programmed separations of (A) low-molecular weight hydrocarbons, (B) mixture of inorganic gases and low-molecular weight hydrocarbons. Stationary phase: Shincarbon ST (2 m). Temperature program: (A) 130ºC to 350ºC at a rate of 40ºC/min, (B) 20ºC (2 min) to 300ºC at a rate of 40ºC/min. Detector: (A) FID (350ºC), (B) TCD 310ºC. Carrier gas: (A) N_2 150 kPa, (B) He 150 kPa. Injection: splitless injection of 150 μL of standard gas samples. Modified from Fig. 5 in ref. [27] with permission.

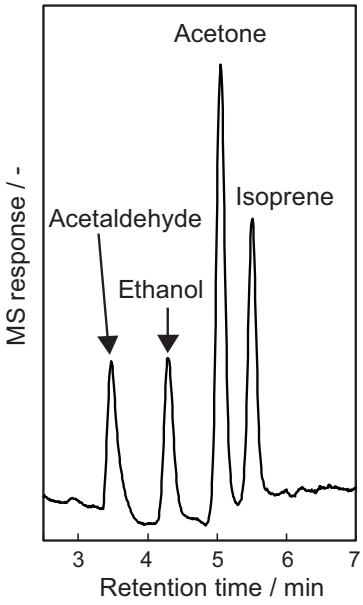

Fig. 6. Typical chromatogram for the separation of VOCs spiked human breath sample. Column: packed-capillary (SA). Temperature program: 100ºC (1 min) to 250ºC (1 min) at a rate of 30ºC/min. Determination: SIM (*m*/*z*: 44, 46, 58, 67 and 68). Sample concentration: *ca*. 1 v/v ppm each. Sample preparation: extraction of 50 mL of gaseous sample by a double-bed-type needle-type extraction device packed with Shincarbon ST and carbon molecular sieve.

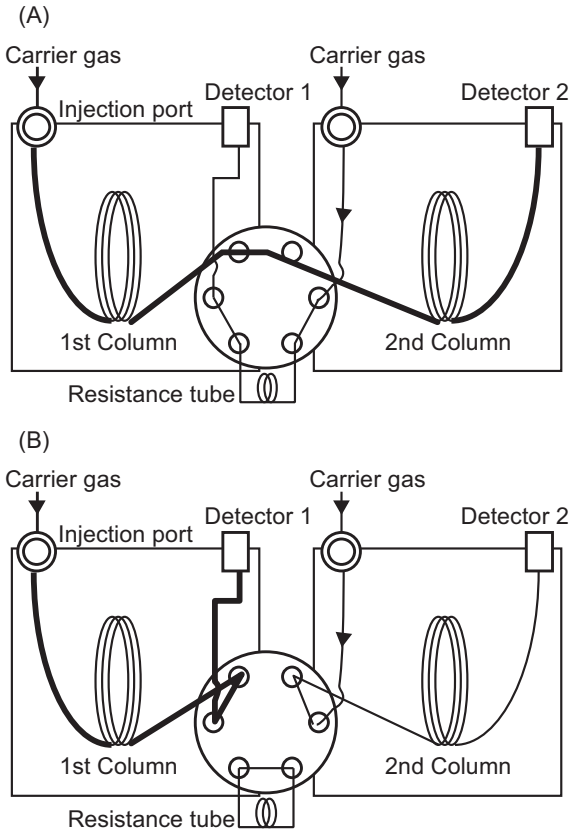

Fig. 7. Schematic illustration of the column switching system using two packed-capillary columns. (A) Sample loading to the second column, (B) separation of the first column or separation of two individual columns. Modified from Fig. 1 in ref. [28] with permission.

liner velocity was also integrated. The results were clearly indicating a good compatibility of the packed-capillary column to a relatively rapid temperature-programming rate. Based on these results, relative delay (RD, %) were calculated as the ratio of difference between measured and estimated retention time to estimated retention time at respective column and temperature-programming rate. The RD values for each column at different liner velocities are plotted in Fig. 3. The RD value were slightly increased with increasing linear velocity, although compared to the conventional glass and stainless-steel columns, the packed-capillary column shows a quite short delay from the expected retention time, even at a fast temperature-programming rate of 40ºC/min. Typical chromatograms for the rapid temperature-programmed separation of mixture samples containing nine alkanes from decane (C_{10}) to octadecane (C_{18}) and seven alkylbenzenes from butylbenzene (C_4-B) to decylbenzene (C_{10}-B) at 40ºC/min with splitless injection are shown in Figs. 4A and 4B, respectively. These analytes were detected by a flame ionization detector (FID). The results demonstrated that rapid temperature-programmed separation at 40ºC/min could be possible with the packed-capillary column, where a satisfactory separation performance is maintained with a short analysis time without significant reducing the sample loading capacity as a packed column. Determination of low molecular weight hydrocarbons (Fig. 5A) and a mixture sample of inorganic gases and low molecular weight hydrocarbons (Fig. 5B) were accomplished by a packed-capillary column packed with an activated carbon particle as the sorbent, where the detections were made by thermal conductivity detector (TCD) and FID, respectively. The packed-capillary column has a good compatibility to MSD because of its lower carrier gas volume. Figure 6 indicates a typical chromatogram for the separation of VOCs spiked in a human breath sample in selected ion monitoring (SIM) mode. The analytes were extracted by a needle-type extraction device before the GC-MS analysis [31], showing a satisfactory sensitivity for typical VOCs.

3. Column switching analysis with packed-capillary column

3.1. Column switching analysis

As one of the applications of packed-capillary columns, column switching analysis was studied [28]. Two packed-capillary columns were connected in series *via* 6-port valve, as shown in Fig. 7, and the sample mixtures

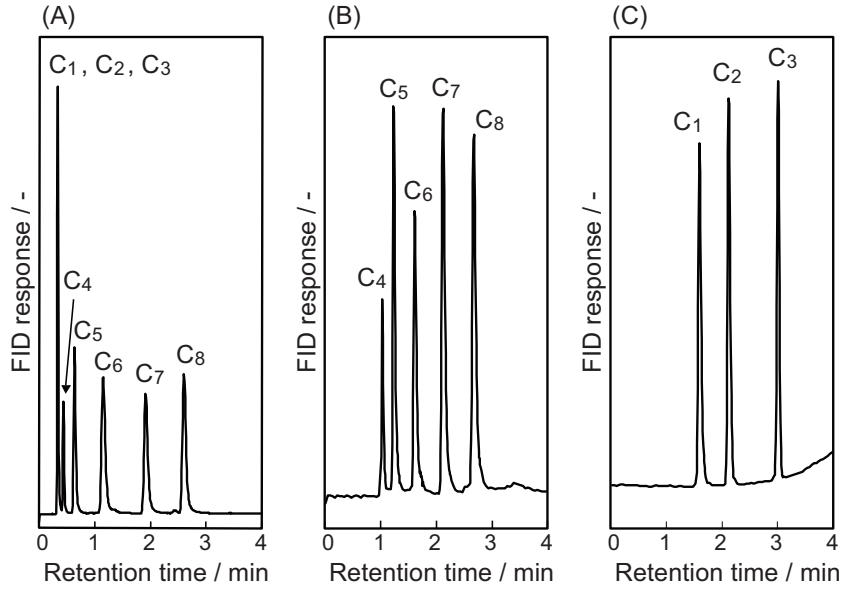

Fig. 8. Separation of an alkane mixture on (A) SE-30 column only, (B) SE-30 column as the first column in column switching separation, (C) SA column as the second column in column switching separation. Temperature program: (A) and (B) 35ºC (1 min) to 130ºC at 40ºC/min, (C) 100ºC (1 min) to 220ºC at 40ºC/min. Sample: 0.5 mL of gaseous alkane mixture containing *ca.* 1.0% each in N_2. Valve switching time: 61 s. Modified from Fig. 2 in ref. [28] with permission.

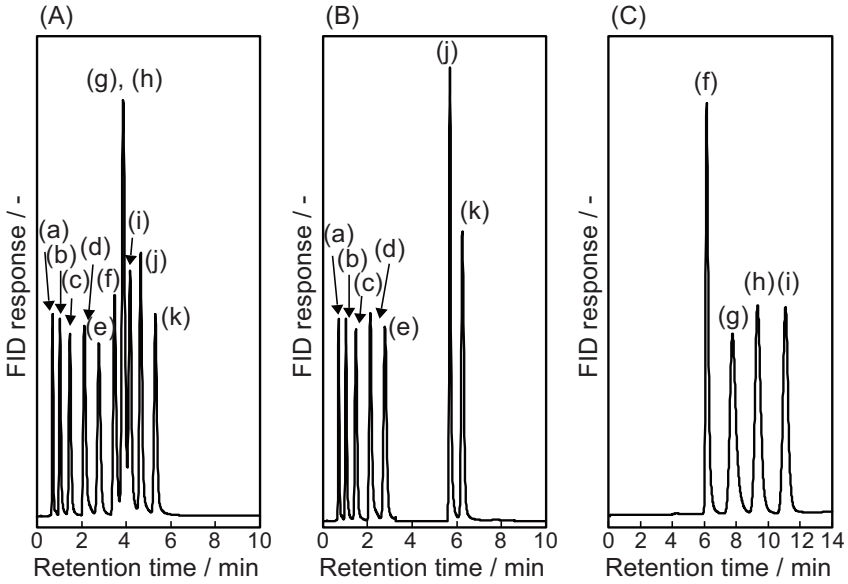

Fig. 9. Separation of a mixture sample in (A) SE-30 column only, (B) SE-30 column as the first column in heart cutting separation, (C) HR-20 M column as the second column in heart cutting separation. Temperature program: (A) and (B) 40ºC (1 min) to 120ºC at 20ºC/min, (C) 60ºC (6 min) to 150ºC at 10ºC/min. Sample: 1.0 μL of liquid mixture containing *ca.* 9% each of the following 11 organic solvent. Valve switching time: 200 s. Peaks: (a) hexane, (b) benzene, (c) heptane, (d) toluene, (e) octane, (f) ethylbenzene, (g) o-xylene, (h) styrene, (i) nonane, (j) propylbenzene, (k) decane. Modified from Fig. 5 in ref. [28] with permission.

containing the compounds having a wide range of volatility were separated with a simple valve switching operation. Figure 8A shows a typical chromatogram for the separation of a homologous mixture from methane (C_1) to octane (C_8) on a SE-30 coated Shimalite W packed-capillary column, where some components were co-eluted. Figures 8B and 8C indicate separations of the same mixture in a column switching system, where the second packed-capillary column packed with a stationary phase has a higher retentivity to highly volatile alkanes (Sunpack-A (SA)). A fraction including highly volatile alkanes was transferred to the second column after just passing through the first column (Fig. 8C), while the other components in the mixture were separated by the first column as found in Fig. 8B.

3.2. Heart cutting analysis

Upon the successful applications of the column switching analysis, a heart cutting analysis was also investigated in the developed system. Figure 9 shows a separation of a test sample mixture on a packed-capillary column. Incomplete separation was obtained for some compounds. Figures 9B and 9C illustrates a heart cutting analysis of the same sample mixture. With the heart cutting operation, a fraction including compounds incompletely separated in the first column was transferred to the second column (Fig. 9C), and the remaining two fractions were separated on the first column (Fig. 9B).

4. Applications for evaluation of catalytic properties of TiO_2

4.1. Determination of CO and CO_2

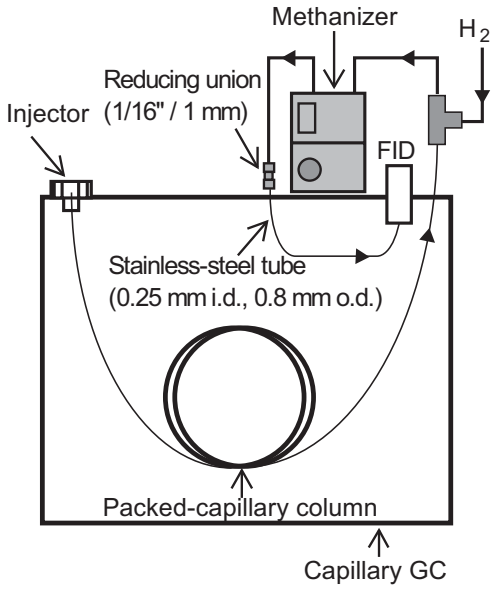

Fig. 10. Schematic illustration of the packed-capillary GC system with a methanizer. Modified from Fig. 1 in ref. [29] with permission.

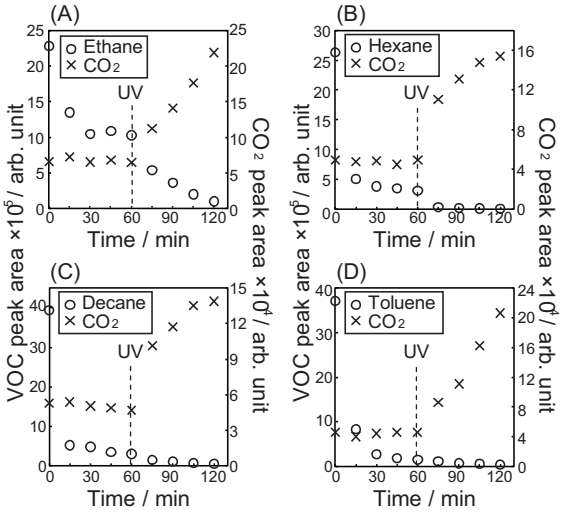

Fig. 11. Schematic illustration of the packed-capillary GC system with a methanizer. Modified from Fig. 1 in ref. [29] with permission.

In order to determine inorganic gases, such as CO and CO_2, TCD is widely used. However, it is not suitable for the sensitive determination. A methanation reaction by a methanizer has usually been used for sensitive determination of CO and CO_2 before the FID detection [32]. For the separation of these permanent gases, a packed column has been typically employed. In addition, a typical methanation reactor was designed only for the connection to a conventional packed column.

The packed-capillary GC system was applied to the determination of CO and CO_2 in a conventional capillary GC-FID system by introducing a methanizer as illustrated in Fig. 10. The column outlet was connected to a tee-connector, and both of the separated CO and CO_2 were converted to CH_4 in a heated reactor tube packed with a Ni catalyst (methanizer) [29]. The limit of quantifications (LOQ) of CO and CO_2 with injection volume of 0.5 mL of the sample gas were 5.0 and 3.0 ppm (v/v), respectively. By introducing this system, simultaneous and sensitive determination of CO, CO_2 and low molecular weight hydrocarbons were accomplished in a conventional capillary GC-FID without any modification.

4.2. Evaluation of photocatalytic activity of TiO_2

Evaluation of the photocatalytic degradation of VOCs on TiO_2 particles was carried out using the packed-capillary GC-FID system [29]. First, synthesized anatase-type TiO_2 particles were placed in a quartz test tube, and the test tube was closed by a silicon septum. Then, gaseous VOC was loaded into the test tube. The validations of the added VOC and CO_2 in the test tube are shown in Fig. 11. The ultraviolet (UV) light (365 nm) was irradiated to the test tube after 60 min from the loading of the VOC. The gas samples of CO_2, ethane and butane were detected in a packed-capillary GC equipped with a methanizer. Hexane, octane, decane and toluene were determined by another capillary GC system equipped with a HR-1 fused-silica capillary column. The VOCs loaded in the test tube were decreased with time due to the adsorption onto TiO_2 particles. The amount of CO_2 was remarkably increased upon the irradiation of UV light; at the same time, clear photocatalytic degradation of VOCs on TiO_2 was confirmed by decreasing of VOCs upon irradiation of UV light.

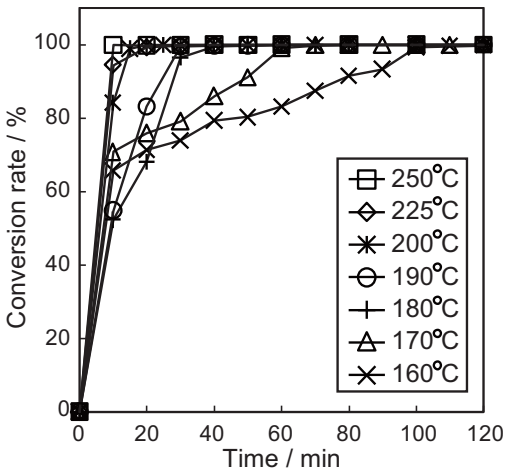

Fig. 12. Conversion rate of hexane at different catalytic temperatures. Modified from Fig. 3 in ref. [30] with permission.

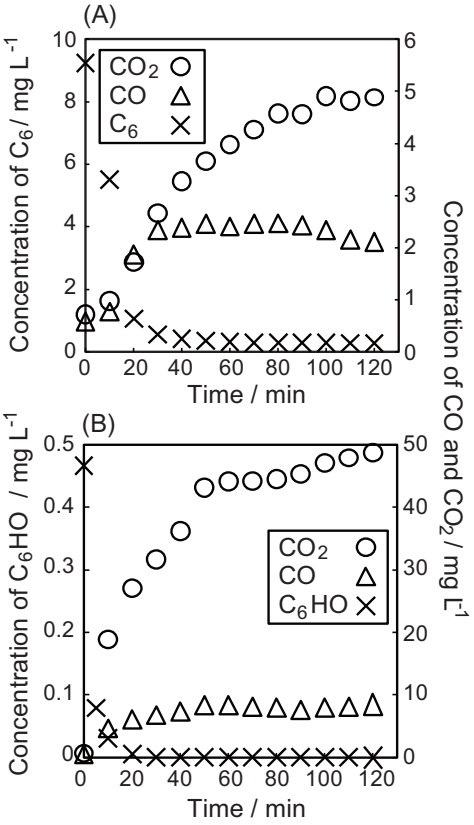

Fig. 13. Thermal catalytic decomposition profiles of (A) hexane and (B) hexanol. Decomposition temperature: 200ºC. Modified from Fig. 2 and Fig. 4 in ref. [30] with permission.

4.3. Evaluation of thermal catalytic decomposition with TiO_2

The method for the determination of CO and CO_2 in the packed-capillary GC was further applied for the evaluation of the thermal catalytic decomposition of organic compounds on TiO_2 particles as a solid acid catalyst [30]. Gaseous or liquid organic compounds were introduced into a heated test tube with TiO_2 particles therein, and the thermal catalytic decomposition was investigated. At the decomposition temperature of lower than 150ºC, thermal decomposition was not observed, where the amounts of CO or CO_2 in the test tube were not increased after the loading of organic compounds into the test tube. The conversion rates of the hexane at several temperatures are shown in Fig. 12. The conversion speed was clearly increased with catalytic temperature, and at temperatures above 200ºC, more than 99% of hexane was decomposed within 20 min. The thermal catalytic decomposition was not observed for methane and ethane, because the adsorption of these compounds onto TiO_2 was not occurred due to their high volatility. Thermal catalytic decomposition profile for hexane is shown in Fig. 13A. The compounds of hexane, octane, decane and hexanol showed quite similar decomposition profiles, although a slightly rapid decomposition was observed for hexanal (C_6HO) as shown in Fig. 13B.

The decomposition of a solid hydrocarbon was also investigated, where a polymer bead of Polywax 500 (Toyo-Petrolite Co. Ltd. (Tokyo, Japan)) was heated with TiO_2 particles at 225ºC in a test tube. By heating of the polymer bead with TiO_2, CO and CO_2 were significantly increased, at the same time, some low molecular weight hydrocarbons (C_2-C_6) were generated. The peak having the largest peak area was assigned as benzene.

A sequential thermal decomposition of organic compound was investigated by introducing of hexane vapor flow into a heated U-shape test tube with TiO_2 particles therein. There results indicated sequential thermal decomposition of hexane on TiO_2 particles was obtained up to at least 6 hours, and the conversion rate of introduced hexane was more than 97%.

5. Conclusions

It has been demonstrated that the developed packed-capillary column offers the benefits of typical packed column, such as large sample loading capacity and unique selectivity. The packed-capillary column can be directly installed to a conventional capillary GC system. A rapid analysis of complex sample mixture can be carried out with the developed packed-capillary column, because of a good compatibility to a rapid temperature-programmed elution. The packed-capillary GC was further applied to the column switching and heart cutting analysis with a set of two packed-capillary columns.

Sensitive and rapid determinations of CO and CO_2 in a conventional capillary GC were also developed by introducing the packed-capillary column and a methanizer. The method was successfully applied to the evaluation of the photocatalytic and thermal catalytic properties of TiO_2 particles. More applications of the method for the evaluation of several catalytic properties in a capillary GC system could be expected in the near future.

In order to obtain a more sensitive determination of volatile compounds, the hyphenation of packed-capillary GC with an appropriate sample preparation technique [33-36] and with MSD could be expected.

Acknowledgements

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