Rapid Temperature-Programmed Separation of Carbon Monoxide and Carbon Dioxide on a Packed Capillary Column in Gas Chromatography: Application to the Evaluation of Photocatalytic Activity of TiO₂

Ikuo UETA,^{*,†} Ayako MIZUGUCHI,^{*} Kazue TANI,^{*} Susumu KAWAKUBO,^{*} and Yoshihiro SAITO^{**}

^{*}*Department of Applied Chemistry, University of Yamanashi, Kofu 400-8511, Japan*

^{**}*Department of Environmental and Life Sciences, Toyohashi University of Technology, Toyohashi 441-8580, Japan*

Carbon monoxide (CO) and carbon dioxide (CO₂) were determined in a conventional capillary gas chromatography-flame ionization detector (GC-FID) by introducing a packed-capillary column and a methanizer. Due to good compatibility with rapid temperature-programmed operation of the packed capillary column, several volatile compounds, including CO and CO₂, were rapidly eluted along with satisfactory resolution and sample loading capacity. The limit of quantifications of CO and CO₂ were 5 and 3 ppm, respectively, with an injection volume of 0.5 mL. The developed system was then successfully applied to evaluating the photocatalytic decomposition of volatile organic compounds on titanium dioxide (TiO₂).

(Received February 14, 2013; Accepted April 13, 2013; Published June 10, 2013)

Introduction

Accurate and sensitive determinations of carbon monoxide (CO) and carbon dioxide (CO₂) are important for several research fields, such as environmental science,¹ biochemistry² and photocatalytic chemistry.³ Several analytical methods have been developed for the determination of CO and CO₂. Infrared (IR) detectors⁴ and electrochemical sensors⁵ are suitable for continuous measurements of these compounds; however, some of them are interfered by other gaseous compounds. In addition, these techniques are not suitable for the analysis of small amounts of gaseous samples.

Gas chromatographic (GC) methods have been employed for simultaneous determinations of complex mixtures.^{6,7} For the determination of inorganic gases, a thermal conductivity detector (TCD) is widely used; however, it is not suitable for the sensitive determinations, because the TCD is not able to detect concentrations below a few hundred ppm. In the GC method, a methanation reaction by a methanizer has usually been used for sensitive determinations of CO and CO₂ before flame ionization detection (FID).⁷ By introducing this technique, CO and CO₂ can be successfully detected at few ppm levels. In typical GC analysis, adequate sensitivities of target compounds are easily obtained, even if the sample injection volume is relatively small.

Complete separation of CO and CO₂ is necessary for accurate and precise determination in GC. In order to separate these permanent gases, a packed column has been typically used, because of its unique selectivity and retentivity as a GC stationary phase. In addition, a typical methanation reactor has been designed for connection to a conventional packed column

having a typical internal diameter of 3–4 mm. However, in recent GC analysis, a capillary GC system equipped with open-tubular capillary columns has been widely used for the determination of volatile organic compounds (VOCs) in samples.

Our research group has developed novel packed-capillary columns for the determination of several complex mixtures in a conventional capillary GC system.⁸ In these columns, a particulate stationary phase is packed into a thin-wall stainless-steel capillary of 1.0 mm i.d.; two stainless-steel capillaries of 0.52 mm o.d. are attached to the inlet and outlet of the column. Therefore, the developed column can be installed in a conventional capillary GC system without any modifications or adapters. Rapid temperature-programmed separation⁸ and heart-cutting analysis of complex sample mixtures⁹ have been investigated using the developed column.

In this study, CO and CO₂ were successfully determined in a conventional capillary GC-FID system based on the introduction of a packed-capillary column and a methanizer. After an evaluation of the developed system performance, the method was applied to an evaluation of the photocatalytic properties of titanium dioxide (TiO₂) for typical gaseous VOCs.

Experimental

Chemicals and materials

Standard gas of CO, CO₂ and alkanes from C₁ to C₄ were purchased from GL Sciences (Tokyo, Japan). Alkanes from C₅ to C₁₀, benzene and toluene, were obtained from Tokyo Kasei Kogyo (Tokyo, Japan). Isopropoxy titanium and 2-propanol were obtained from Nacalai Tesque (Kyoto, Japan). Hydrochloric acid (HCl) and glycerol were obtained from Kanto Chemical (Tokyo, Japan).

[†] To whom correspondence should be addressed.
E-mail: iueta@yamanashi.ac.jp

Fig. 1 Schematic illustration of the capillary GC system equipped with a packed-capillary column and a methanizer.

GC-measurements

GC-FID analyses were conducted using two Shimadzu GC-2010 gas chromatographs (Kyoto, Japan). The injection temperature and FID temperature were set at 250°C, and all of the injections were operated in a split mode with a ratio of 5:1. As the carrier gas, He at a head pressure of 200 and 150 kPa was used for packed-capillary column separation and fused-silica capillary separation, respectively. An MTN-1 methanizer (Shimadzu, Japan) was used for the determination of CO and CO₂. An HR-1 fused-silica capillary column, 25 m × 0.25 mm with a 0.25-μm film thickness (Shinwa Chemical Industries, Kyoto, Japan), was used to measure alkanes from C₅ to C₁₀, benzene and toluene.

The gas samples of CO, CO₂ and alkanes from C₁ to C₄ were separated using a packed-capillary column. The column was prepared by the same procedure as described previously.⁸ A stationary phase of Sunpak-A (Shinwa Chemical Industries) particles of between 100 and 80 mesh, corresponding to about 150 and 180 μm in diameter, was packed into a stainless-steel capillary of 1.0 mm i.d., 1.27 mm o.d., 1.0 m length. Then, two 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 for easy installation to a conventional GC injector and detector designed for the typical capillary column connection. The capillary GC system equipped with a packed-capillary column and a methanizer used in this study is illustrated in Fig. 1. The column outlet was connected to a tee-connector, and both of the separated CO and CO₂ were converted to CH₄, in a heated reactor tube packed with a Ni catalyst. The outlet of the methanizer was connected to a FID using a reducing union and a stainless-steel tube.

Preparation of TiO₂ particles for photo catalysts

TiO₂ particles were prepared based on a previous study,¹⁰ described as follows. First, 30 mL of a 6.0 × 10⁻⁵ M HCl solution, 1500 g of 2-propanol and 900 g of glycerol were placed in a beaker and mixed for 5 min under ultrasonication. Then, 60 mL of an isopropoxy titanium solution was dropped into the solution under magnetic stirring, and the solution was left standing in the dark at room temperature for 4 days. The supernatant liquid was then transferred to another beaker, and stored again for 7 days. The obtained precipitation was washed with pure water, and then a classification of particle size was also made. The particles were then washed with methanol, and finally heated for 24 h at 200°C. The obtained particles were

Fig. 2 Optimization of (A) H₂ flow rate and (B) methanation temperature for the methanation conditions of CO and CO₂. Conditions: sample concentration, 100 ppm each; injection volume, 0.5 mL; methanation temperature, (A) 440°C; H₂ flow rate, (B) 40 mL/min.

Table 1 LODs and LOQs for CO and CO₂

	CO	CO ₂
LOD, ppm	2.0	1.0
LOQ, ppm	5.0	3.0

Injection volume: 0.5 mL.

porous spherical particles having 3–4 μm diameter, and the specific surface area was approximately 90 m²/g.

Results and Discussion

Construction of a novel CO and CO₂ detection system

First, the methanation conditions of standard CO and CO₂ gas were optimized. CH₄ was also used as a reference. The flow rate of H₂ gas supplied from a tee-connector was investigated in the range from 10 to 50 mL/min. During this time, the flow rate of H₂ gas to FID was fixed at 10 mL/min. The rate was optimized by the obtained peak area of both CO and CO₂. As shown in Fig. 2A, the methanation reaction reached a plateau at more than 30 mL/min of H₂ gas. The smaller peak areas at a low H₂ flow rate could be due to a sensitivity change of FID that depended on the introduced H₂ volume. Therefore, 40 mL/min of H₂ gas was employed in following experiments. The temperature of the reaction tube packed with the Ni catalyst was also investigated. The maximum peak areas were obtained at above 400°C, as demonstrated in Fig. 2B; hence, a catalyst temperature of 440°C was chosen in this study. In Fig. 2, peak area of CO₂ is greater than that of CO. This is because a greater amount of CO₂ was included as an impurity in N₂ gas that was used for preparing standard gas samples.

The limit of detection (LOD) and the limit of quantification (LOQ) for CO and CO₂ were investigated under these optimized conditions. The results are tabulated in Table 1. The LOD of the method was identified to have a signal-to-noise ratio of 3, and the LOQ was determined to have a ratio of 10. As expected, the sensitivities for these compounds using the developed system are almost the same as that obtained by using a conventional packed column, because the number of theoretical plates for the packed-capillary column and a conventional packed column are the same. The upper LOQs for CO and CO₂ were more than 10%, and linear calibration curves were obtained with correlation coefficients greater than 0.99 for both

compounds from the LOQ to the upper LOQ. As described in a previous publication,⁸ the relative delay of the retention time from the theoretically estimated value was less than 4.6% at a temperature programmed rate of 40°C/min, using the packed-capillary column. A typical chromatogram for the determinations of CO, CO₂ and low molecular weight alkanes is shown in Fig. 3. Successful separation and determination of a mixture of

volatile compounds was obtained in the developed system with a rapid temperature program of 40°C/min without any significant peak broadening problem. In addition, no peak distortion was observed because of a high peak loading capacity of the packed-capillary column. The RSDs of the peak area for both compounds for a standard gaseous sample (500 ppm) were lower than 5.0% ($n = 5$).

Fig. 3 Typical chromatogram for the separation of volatile compounds. Conditions: column temperature, 40°C (1 min) to 200°C at 40°C/min; sample concentration, 100 ppm each; injection volume, 0.1 mL.

Evaluation of the photocatalytic decomposition of VOCs on TiO₂

On the basis of the above-mentioned rapid and sensitive determination of CO and CO₂, the developed system was applied to an evaluation of the photocatalytic degradation of VOCs on TiO₂ particles. As the VOCs sample, alkanes of C₁ to C₁₀, benzene and toluene, were investigated. First, 0.3 g of synthesized TiO₂ particles were placed in a quartz test tube (12 cm length, 9.5 mm i.d.), and the test tube was closed by a silicon septum. The test tube was held horizontally, where the surface area of the TiO₂ particles (irradiation area of ultraviolet (UV)) was kept to constant. After loading VOC sample into the test tube, the peak area of the added VOC and CO₂ was measured at every 15 min for 60 min. Then, UV light (365 nm) was irradiated to the test tube. The results are given in Fig. 4, where the variations in the amounts of the representative VOCs loaded into the test tube are plotted along with that of CO₂, indicating significant adsorptions of all the VOCs onto TiO₂ after the injection of gaseous VOCs into the test tube. The amount of CO₂ remarkably increased upon the irradiation of UV light; at the same time, the VOCs also clearly decreased due to UV irradiation for all of the investigated compounds by photocatalytic oxidation on TiO₂. The amounts of the loaded VOCs did not agree with the amount of the increased CO₂. This is because the generated CO₂ was also adsorbed onto the TiO₂ particles. Typically, the photocatalytic property of a catalyst has been evaluated by using a flow-type reactor.^{11–13} However, for evaluating several properties of a catalyst, such as the adsorption of VOCs on the catalyst, and determining the photocatalytic

Fig. 4 Investigation of the photocatalytic degradation of VOCs on TiO₂ particles by the determination of CO₂ (cross) and VOCs (circle). Investigated VOCs: (A) ethane, (B) butane, (C) hexane, (D) octane, (E) decane, (F) toluene. Sample injection volume, 0.1 mL.

rate, the determination of both the VOC and CO₂ concentrations in a closed system could also be effective. Because the developed method requires only a small amount of a gaseous sample, it could be suitable for evaluating the photocatalytic property of a catalyst in a closed system.

Conclusions

A sensitive and rapid determination method for CO and CO₂ in a conventional capillary GC system was developed by introducing a packed-capillary column and a methanizer without any significant system modification. There are many potential requirements for an easy determination of CO or CO₂ with a small amount of the sample volume in many research fields; therefore, further applications of the method could be expected: such as the determination of atmospheric gas and combustion gas samples. The proposed method was also successfully applied to evaluating the photocatalytic property of TiO₂ particles for typical gaseous VOCs. The results indicated that the developed technique could be a relatively easy evaluation method of the photocatalytic property of catalysts. The method could also be suitable for this kind of the evaluation of several catalytic properties in a capillary GC system.

Acknowledgements

Part of this research was financially supported by a Grant-in-Aid for Scientific Research from the Japan Society for the Promotion of Science (JSPS). The authors acknowledge the

technical support of Prof. H. Okuzaki, Prof. N. Miyajima and H. Koizumi of University of Yamanashi.

References

1. W. Soon, S. L. Baliunas, A. B. Robinson, and Z. W. Robinson, *Clim. Res.*, **1999**, 13, 149.
2. L. Keck, C. Houeche, and U. Oeh, *Int. J. Mass Spectrom.*, **2008**, 270, 156.
3. A. Fujishima, X. Zhang, and D. A. Tryk, *Surf. Sci. Rep.*, **2008**, 63, 515.
4. M. B. Esler, D. W. T. Griffith, S. R. Wilson, and L. P. Steele, *Anal. Chem.*, **2000**, 72, 206.
5. M. Ando, *Trends Anal. Chem.*, **2006**, 25, 937.
6. J. B. Laurens, J. P. de Coning, and J. M. Swinley, *J. Chromatogr. A*, **2001**, 911, 107.
7. M. Kamiński, R. Katranowica, D. Jastrzębski, and M. M. Kamiński, *J. Chromatogr. A*, **2003**, 989, 277.
8. M. Inoue, Y. Saito, I. Ueta, T. Miura, H. Ohkita, K. Fujimura, and K. Jinno, *Anal. Sci.*, **2010**, 26, 687.
9. I. Ueta, K. Takahashi, and Y. Saito, *Anal. Sci.*, **2012**, 28, 953.
10. K. Tani and Y. Suzuki, *J. Chromatogr. A*, **1996**, 722, 129.
11. C. T. Brigden, S. Poulston, M. V. Twigg, A. P. Walker, and A. J. J. Wilkins, *Appl. Catal., B*, **2001**, 32, 63.
12. A. K. Boulamanti and C. J. Philippopoulos, *Atmos. Environ.*, **2009**, 43, 3168.
13. M. Hussain, N. Russo, and G. Saracco, *Chem. Eng. J.*, **2011**, 166, 138.