Evaluation of Thermal Catalytic Decomposition of Organic Compounds with TiO₂ by Packed-Capillary Gas Chromatography

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A novel method for evaluating the thermal catalytic decomposition of organic compounds on a solid acid catalyst was developed using a capillary gas chromatography-flame ionization detector (GC-FID) equipped with a packed-capillary column. The thermal catalytic decomposition of various organic compounds was investigated by introducing gaseous or liquid organic compounds into a heated test tube packed with TiO₂ particles. The resulting carbon monoxide (CO) and carbon dioxide (CO₂) in the test tube were determined in a conventional capillary GC system with a methanizer after separation on a packed-capillary column. In the packed-capillary GC system, several parameters affecting thermal catalytic reactions of various organic compounds were successfully evaluated, such as the type of the catalysts and the effect of catalytic temperatures. Finally, a sequential decomposition of organic compounds was confirmed in the heated reaction tube packed with TiO₂ particles.

Keywords Packed-capillary column, capillary gas chromatography, carbon dioxide, thermal catalytic decomposition

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Introduction

Decomposition of organic compounds with catalysts has been recently studied in many research fields; examples of such studies include photocatalytic decomposition with titanium(IV) oxide (TiO₂)1 and conversion of polymer or heavy hydrocarbons into light fuel.2 For the decomposition of the hydrocarbons, solid acid catalysts such as metal oxides1 and zeolite1 have been typically employed. As titanium(IV) oxide is one of the effective solid acid catalysts, various types of novel catalysts containing TiO₂ have been prepared.3 TiO₂ is also well known as a photocatalytic catalyst, where organic compounds are oxidized to CO₂ and H₂O on the surface of a TiO₂ catalyst at room temperature with UV irradiation.1

For the evaluation of the catalytic decomposition of organic compounds, the determinations of organic compounds and the generated CO₂ at the same time could be a reliable method. In order to determine CO₂, infrared detectors have been widely used.4 This method is suitable for continuous measurements of CO and CO₂; however, it is not suitable for the analysis of small amounts of gaseous samples, and inevitable interference from other gaseous compounds is also expected. The determination of these compounds by gas chromatograph (GC) is also one of the promising analytical methods, where a thermal conductivity detector (TCD) is often used after the separation typically by a packed column. However, it is not suitable for sensitive determination because of limited detectability of the TCD detector. Flame ionization detector (FID) has also been used for the determination of CO and CO₂ after the methanation reaction by a methanizer.5 In this technique, CO and CO₂ are reduced by hydrogen gas on the Ni catalyst in the methanizer, and the resulting reduced compound, methane, is then introduced into the FID. By using this method, these compounds can be determined at levels up to a few ppm. For the separation of CO and CO₂, a packed column having 3 - 4 mm i.d. is typically employed, and in this case, a GC system designed for the installation of these packed columns is necessary.

It is well known that a packed column has a unique retentivity and selectivity, although the resolution of a typical packed column is clearly lower than that of an open-tubular capillary column, and that the packed column is not suitable for a rapid temperature-programmed separation. Hence, a capillary GC system equipped with an open-tubular capillary column has been widely used in most recent GC analyses.6 Taking advantage of both the packed and open-tubular columns, our research group has developed a packed-capillary column for the determination of several complex mixtures in a conventional capillary GC instrument.7 This packed-capillary column consisted of a thin-walled stainless-steel capillary of 1.0 mm i.d. with packing material therein and two stainless-steel capillaries of 0.52 mm o.d. at the inlet and outlet of the column to directly connect to a conventional capillary GC system. This packed-capillary GC system showed good compatibility to the rapid temperature program, and it was further applied to the heart-cutting analysis of complex sample mixtures.8,9 Recently, we reported the determination of CO and CO₂ in a conventional capillary GC-FID system, where a packed-capillary column was introduced along with a commercially available methanizer designed for conventional packed columns of 3 - 4 mm i.d.10 On the basis of good compatibility of the packed-capillary...
column to the methanizer, this technique was applied for the evaluation of the photocatalytic decomposition of organic compounds on TiO$_2$ particles. The system allows for sensitive and rapid determination of small amounts of CO and CO$_2$ in a conventional capillary GC instrument without the need for any significant system modification.

In this study, a novel method for the evaluation of the thermal catalytic decomposition of organic compounds on a solid acid catalyst was developed in the packed-capillary GC-FID system with the methanizer. After loading of organic compounds into a heated test tube containing TiO$_2$ particles, the determination of the generated CO and CO$_2$ was carried out in the packed-capillary GC-FID. The amounts of the loaded organic compounds were also confirmed in another capillary GC-FID system. By the developed method, several thermal catalytic properties of a solid acid catalyst could be easily and quantitatively evaluated; the differences between catalysts, temperature dependence, sample dependence, and decomposition power under sequential loading of organic species.

**Experimental**

**Chemicals**

Standard gas of CO, CO$_2$, and alkanes, ethane (C$_2$) and n-butane (C$_4$), were purchased from GL Sciences (Tokyo, Japan). Alkanes, n-hexane (C$_6$), n-octane (C$_8$), n-decane (C$_{10}$), hexanol (C$_{6}$OH) and hexanal (C$_{6}$HO) were obtained from Tokyo Kasei Kogyo (Tokyo, Japan). Isoproxyloxy titanium and 2-propanol were obtained from Nacalai Tesque (Kyoto, Japan). Hydrochloric acid (HCl), glycerol, and rutile type TiO$_2$ particles with a diameter of 0.1 – 0.3 $\mu$m were obtained from Kanto Chemical (Tokyo, Japan). Polywax 500 (a polymer bead of polyethylene) was obtained from Toyo-Petrolite Co., Ltd. (Tokyo, Japan). Anatase TiO$_2$ particles with a diameter of 5 $\mu$m and 100 m$^2$/g surface area (TiO$_2$ (A)) was obtained from GL Sciences. A particulate TiO$_2$ (containing ca. 12% of rutile) having a diameter of 5 $\mu$m and 60 m$^2$/g surface area (TiO$_2$ (B)), and benzene were purchased from Wako Pure Chemical Industries (Osaka, Japan).

**Preparation of TiO$_2$ particles**

A particulate TiO$_2$ was prepared on the basis of procedures used in a previous study. First, 30 mL of a 6.0x10$^{-3}$ 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 isoproxyloxy titanium solution was dropped into the solution under magnetic stirring, and the solution was left to stand in the dark at room temperature for four days. The supernatant liquid was then transferred to another beaker, and stored again for seven days. The obtained precipitation was washed with pure water, where the 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 porous sphere particles having a diameter of 3 – 4 $\mu$m and the specific surface area was approximately 90 m$^2$/g (TiO$_2$ (C)).

**GC measurements**

In order to determine the organic compounds, CO and CO$_2$, two GC-FID systems (Shimadzu GC-2010 gas chromatographs, Kyoto, Japan) were used. A GC system equipped with an HR-1 fused-silica capillary column, 25 m × 0.25 mm with a 0.25 $\mu$m film thickness (Shinwa Chemical Industries, Kyoto, Japan), was used to confirm the amounts of organic compounds of alkanes from C$_3$ to C$_{10}$, benzene, C$_{6}$OH, and C$_{6}$HO. For the determination of CO, CO$_2$, and organic compounds of C$_3$ and C$_4$, a GC system equipped with an MTN-1 methanizer (Shimadzu, Kyoto, Japan) and a packed-capillary column, 1.0 mm i.d., 1.27 mm o.d., 1.0 m length, packed with Sunpak-A having a diameter of about 150 to 180 $\mu$m (Shinwa Chemical Industries), was used. The packed-capillary column has two stainless-steel capillaries of 0.3 mm i.d., 0.52 mm o.d., and 0.5 m length positioned at the inlet and outlet of the packed-capillary column for easy installation to a conventional GC injector and detector designed for typical capillary column connection. The injection temperature and FID temperature were both set at 250°C, and all the injections were operated in a split mode with a ratio of 5:1. The injection volume was 0.1 mL for both GC systems. As the carrier gas, He at head pressure of 150 and 200 kPa was used for conventional capillary GC and packed-capillary GC, respectively. The relative standard deviations of the peak areas for both GC systems were lower than 5.0% (n = 5). All the compounds measured in this study were quantified by the standard gaseous samples prepared in the gas sampling bag. The standard samples of CO, CO$_2$, C$_3$ and C$_4$ were prepared by the dilution of respective pure gas, while other compounds were prepared by evaporation in a vacuum glass vessel described in previous publications. The standard samples of CO, CO$_2$, C$_3$ and C$_4$ were prepared by the dilution of respective pure gas, while other compounds were prepared by evaporation in a vacuum glass vessel described in previous publications.

**Investigation of thermal catalytic decomposition by TiO$_2$**

TiO$_2$ particles of 0.3 g 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 then placed in an oven, where the top side (silicon septum) was positioned out of the oven as illustrated in Fig. 1A. Next, two needles were inserted into the test tube through the septum; one is served as the inlet for the air (oxygen 21% and nitrogen 79%) stream, and the other as the outlet for the air stream. Before the investigation of thermal catalytic properties of each catalyst, all the catalyst particles were heated at 300°C with air stream in the test tube to eliminate adsorbed CO$_2$ on the particles and to decompose organic compounds adsorbed on the particles. Then, these needles were removed from the test tube, followed by the loading of an adequate volume of organic compounds in the closed-mode test tube (Fig. 1A) at a certain temperature. As the organic compounds for the evaluation of the decomposition power of TiO$_2$ particles, two standard gases, C$_3$ and C$_4$, were used, while the headspace gas of C$_4$ (at 40°C) was also used. For C$_3$, C$_6$OH, C$_{6}$HO, and C$_{6}$HO, respective pure solvents were loaded into the test tube.
After loading each organic compound, the amount of the loaded organic compound was determined by conventional capillary GC, whereas the generated CO, CO₂, C₂ and C₄ were determined by a packed-capillary GC system.

For the investigation of the thermal catalytic properties during the sequential introduction of organic compounds, a flow-mode system was constructed, where 0.15 g of TiO₂ particles was packed into a home-made U-shaped glass tube as shown in Fig. 1B. To fix the TiO₂ catalyst, a small amount of quartz wool was also packed at each end of the packed TiO₂ particles. Both the inlet and outlet of the U-shaped glass tube were closed by silicon septa. To generate constant organic vapor stream, about 10 mL of C₆ was placed in a 50-mL glass vial having two silicon septa attached to the plastic cap of the vial. About 10 cm of a needle was immersed into the liquid C₆ to make sure that the needle tip just reached the bottom of the glass vial. A constant air flow was supplied through this needle, and the generated C₆ vapor flow was exited through another needle. The C₆ vapor flow was then directly introduced into the heated U-shaped glass tube containing TiO₂ particles. The outlet gas was exhausted from the other side of the U-shaped tube as shown in Fig. 1B. To measure the outlet gas, a needle attached to a gas tight syringe was also inserted to the U-shaped tube through the outlet side of the septum, followed by the analysis of the resulting gas in the two GC systems described above.

All the thermal catalytic degradations were measured at least three times, and similar profiles were confirmed at these repeatable measurements.

Results and Discussion
Investigation of thermal catalytic properties of TiO₂ in a closed system
The headspace gas of C₆ (0.1 mL) was introduced into the heated test tube with TiO₂ particles (Fig. 1A) at several different temperatures. At the decomposition temperature of lower than 150°C, thermal decomposition was not observed, where the amounts of CO or CO₂ in the test tube did not increase after the loading of C₆ into the tube for all the investigated three types of TiO₂ particles. The concentration of C₆ in the test tube decreased at all the investigated temperatures, probably due to the adsorption of C₆ onto TiO₂ particles especially at lower temperatures. Figure 2 shows variations of the concentrations of C₆, CO and CO₂ in the test tube at 200°C after loading of C₆. The concentration of C₆ rapidly decreased, while the concentrations of CO and CO₂ increased. In addition, the phenomenon could not be observed without TiO₂ particles. The results clearly indicated a thermal catalytic decomposition of C₆ on anatase-type TiO₂ particles as a solid acid catalyst. This could be due to the presence of many impurities or active sites in the catalyst. In the photocatalytic degradation of organic compounds on TiO₂ particles, CO was not generated, although certain amounts of CO were generated in this study. The ratio of generated CO and CO₂ were varied with decomposition temperature or organic compounds. The amounts of the loaded organic compounds did not agree with the amounts of the generated CO and CO₂. This is because the generated CO and CO₂ were adsorbed onto the TiO₂ particles. The conversion rates of the C₆ at several temperatures are shown in Fig. 3. At lower temperatures, the decrease of C₆ could be partly due to adsorption onto TiO₂ particles. The conversion speed for the C₆ increased with catalytic temperature, and at above 200°C, more than 99% of C₆ was converted within 20 min.
Thermal catalytic decompositions for several organic compounds were investigated at 200°C as shown in Fig. 4. The decomposition was not observed for C₂ (Fig. 4A) because the adsorption of C₂ onto TiO₂ could not occur due to high volatility. For C₆, slow decomposition was observed as depicted in Fig. 4B. Significant differences were not found for the decomposition profiles of C₆, C₈, C₁₀ and C₆OH (Fig. 4C). Slightly rapid decomposition was observed for C₆HO, as shown in Fig. 4D. A higher concentration of CO₂ was detected, although the concentration of C₆HO was quite low because of the rapid thermal catalytic decomposition.
The thermal catalytic decomposition ability of organic compounds for three types of different TiO₂ particles was compared at 250°C. The decomposition of organic compounds on TiO₂ particles (A) and (C) showed similar profiles, because these are pure anatase TiO₂ and they also have similar particle structures.
size and surface area. On the other hand, TiO2 (B) showed obviously slower decomposition, where the conversion rate of more than 95% was observed at 60 min after the loading of C6 at 250°C. The reason for this lower decomposition power could be the relatively smaller surface area and lower purity of the anatase TiO2. In fact, the rutile type TiO2 particles did not show any thermal catalytic decomposition of organic compounds even at a decomposition temperature of more than 250°C. In addition, the amounts of impurities or active sites in the catalysts could also affect the degradation of organic compounds.

The decomposition of a solid hydrocarbon was also investigated in the test tube under an air flow condition. The flow rate of the air stream was fixed at 1.2 mL/min, and two needles were inserted into the test tube through the septum; one was inserted in the inlet of the air stream and another in the outlet of the air stream. To measure the concentrations of generated gas, a needle attached to a gas tight syringe was also inserted into the test tube. A polymer bead of Polywax 500 (9.0 mg) was placed into the test tube with TiO2 particles, and then, the test tube was heated at 225°C. At this temperature, the polymer bead was melted, although significant decomposition or evaporation was not observed without TiO2 particles because no increase of CO or CO2 was found. A burned residue was obtained during the heating of the polymer bead at more than 250°C. By heating the polymer bead with TiO2 particles, a significant increase in the concentrations of CO and CO2 was observed, suggesting the decomposition of the polymer. At the same time, some low-molecular weight hydrocarbons (C2 – C6) were generated. The peak having the largest area as hydrocarbons was assigned as benzene in gas chromatography–mass spectrometric (GC-MS) analysis. Figure 5 shows the variations of the concentrations of CO2 and benzene during the heating of Polywax 500 bead with TiO2 particles. The concentrations of these compounds gradually decreased because of the decomposition of the polymer bead. However, the color of TiO2 particles changed to brown in the decomposition process, suggesting that the TiO2 particles were overloaded by the 9.0 mg of Polywax. In fact, the brown color changed back to white after heating the particles with air stream at 300°C for more than 30 h. The result clearly demonstrated that a catalytic decomposition on TiO2 particles could be successfully proceeded in this setup as long as the appropriate amount of alkanes was loaded.

Sequential decomposition of organic compound

The developed method was applied to the evaluation of

![Fig. 4 Thermal catalytic decomposition profiles of several organic compounds. (A) C2, (B) C4, (C) C6, (D) C8HO. Decomposition temperature: 200°C.](image-url)
sequential thermal decomposition of organic compounds, where multiple loading of organic compounds was carried out in a closed mode, as shown in Fig. 1A. The headspace gas of C6 (0.1 mL) was injected into a heated test tube at 10 min intervals for 120 min. Variations of the concentrations of CO2 and C6 in this multiple loading are shown in Fig. 6. The loaded C6 rapidly decomposed due to thermal catalytic decomposition, although slightly decreased decomposition power was observed owing to the excess loading of C6.

Sequential decomposition of an organic compound on heated TiO2 particles was also investigated by introducing organic vapor flow in the flow-mode as illustrated in Fig. 1B. Figure 7 indicates the concentrations of CO2 and C6 at the outlet of the U-shaped glass tube. The concentration of CO2 was relatively lower than that in the closed-mode study due to the dilution by air stream, while the concentration of CO2 increased immediately after the loading of the organic vapor flow due to the decomposition of C6. At the same time, a small amount of C6 was also detected at the outlet of the U-shaped glass tube. This was probably caused by the incomplete packing of the TiO2 particles in the glass tube. However, the conversion rate of C6 reached more than 97%, where it was calculated based on the comparison of the amount of C6 in the inlet gas and the outlet gas of the U-shaped glass tube.

Conclusions

A novel evaluation method for thermal catalytic decomposition of organic compounds on a solid acid catalyst was successfully developed by a packed-capillary GC system. The amounts of CO and CO2 generated by the thermal catalytic decomposition reaction were easily and quantitatively determined in the developed system. Several experimental parameters for thermal decomposition were studied along with the application to the sequential decomposition of organic compounds on TiO2 particles. Various types of decomposition sample compounds were also studied in this work. These results clearly showed good applicability of the packed-capillary GC system for the evaluation of thermal catalytic decomposition properties of solid acid catalyst. For sensitive detection and determination of CO and CO2, the method only required a conventional capillary GC system that has higher applicability for the determination of various organic compounds. The repeatable use of the TiO2 particles was also confirmed, showing a catalytic ability of the material for the thermal decomposition of hydrocarbons. This technique could be further applied to the systematic evaluations of photocatalytic performance or thermal catalytic decomposition performance of the catalysts in the conventional GC instrument with packed-capillary column.

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