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[Letter]

Combustion of Toluene over Titanium(IV) Oxide Catalyst

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Combustion catalysts free from precious metals, such as platinum, for removal of volatile organic compounds were investigated. Common metal oxides (titanium(IV) oxide (TiO_2), alumina and silica) were selected as candidates for a catalyst for combustion of toluene at low concentrations. Complete conversion of toluene was not achieved even at 500°C without catalysts, although the ignition point of toluene is 480°C. TiO_2 exhibited the highest activity for combustion of toluene among representative metal oxides. Toluene was almost quantitatively converted to carbon dioxide (>99% yield) over TiO_2 under the condition of appropriate contact time at 500°C.

Keywords
Combustion catalyst, Titanium oxide catalyst, Volatile organic compounds, Toluene

1. Introduction

Volatile organic compounds (VOC) such as toluene have serious impacts on the environment and human health. It has been reported that toluene and formaldehyde are related to sick-house syndrome[1)]. Emission of VOC from factories into the atmosphere is now strictly regulated in Japan. When industrial wastes including medical wastes are degraded, large amounts of VOC are formed. Therefore, there is a need for effective and safe degradation methods for VOC as well as for medical wastes[2),3)]. Catalytic combustion method using supported platinum metal (Pt) is at present the most promising method for removal of VOC in low concentrations[4)~6)]. However, a Pt catalyst is generally deactivated within several years due to sintering of Pt particles and poisoning by sulfur contained in VOC and that from the environment. Replacement with a fresh catalyst increases the cost for maintenance. Rare elements such as the platinum group are produced in limited areas of the world and the supplies of these metals sometimes become unstable. Therefore, it is important to develop a new material made of a common and cheap element that has almost the same level of function (or performance) as that of a material made of a rare element. Research on transparent electrodes without using indium[7)] is typical case of "element strategy." Also, in the field of catalytic materials, especially supported precious metal catalysts such as Pt, rhodium and palladium, development of combustion catalysts free from precious metals is important. Supported gold catalysts[8)], manganese oxide-based catalysts, perovskite-type catalysts[9)] and hexaaluminate-based catalysts[10)] are combustion catalysts free from the precious metals, and some of these catalysts have been used as practical catalysts. However, it is necessary to investigate catalyst materials made of more common element(s) and having a simpler structure.

We chose titanium(IV) oxide (titania, TiO_2), active alumina and silica as the candidates for combustion catalyst of VOC because of several reasons as follows:1) They have large Klarke number. 2) They have been already used as catalyst materials in various fields. 3) They exhibit high stability toward chlorine or hydrogen chloride, which is important for combustion of chlorinated VOC. 4) They exhibit high thermal stability and possess large surface area. 5) Many samples

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"酸化チタン(IV)触媒によるトルエンの燃焼"
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having various physical properties are provided. 6) Moldings of these compounds are easily obtained. In this study, we selected toluene as a model compound of VOC and examined the combustion of toluene at a low concentration over TiO_2, alumina and silica.

2. Experimental

Degradation of toluene was carried out using a fix-bed, flow-type reactor. In a stainless reactor (SUS306, 29.4 mm in diameter, 355 mm in length, 240 cm^3 in volume), weighed sample was charged (air space in the reactor: 154 cm^3). Toluene (Wako Pure Chem. Ind., Ltd.) gas (mainly 2100 ppm) diluted with air was introduced to the reactor at 250-500°C with several flow rates (0.25-1.00 $dm^3 \bullet min^{-1}$). Concentrations of carbon dioxide (CO_2) and carbon monoxide (CO) in the outlet gas were continuously analyzed with a gas analyzer (Horiba, Ltd., PG-250). The concentration of toluene was determined with a gas chromatograph (Shimadzu Corp., GC-14A, PEG 1500 15% Chromosorb W, ϕ3 mm × 2 m).

Apparent carbon yields (Y_C) were calculated from the following Eq. 1:

$$Y_C = \frac{C_{CO} + C_{CO_2}}{7 \times C_T \times X_T/100} \times 100 \qquad (1),$$

where C_{CO} and C_{CO_2} are concentrations of CO and CO_2 in outlet gas, C_T is concentration of toluene in inlet gas and X_T is conversion of toluene.

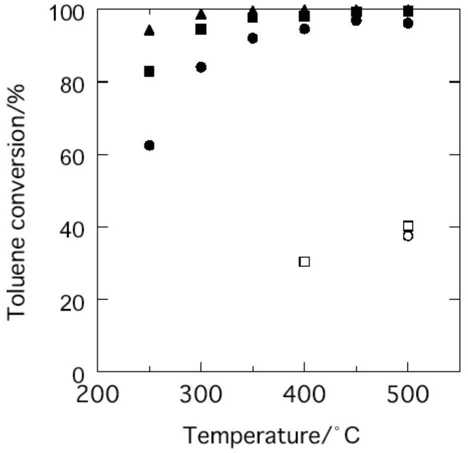
3. Results and discussion

Results of combustion of toluene over TiO_2, active alumina and silica with flow rate of 0.25 $dm^3 \bullet min^{-1}$ at 500°C are summarized in **Table 1**. Almost complete conversion of toluene (>99%) and 65 % of yield of CO_2 were obtained over TiO_2. A very small yield of CO_2 was obtained over active alumina, although the conversion of toluene was almost the same as that over TiO_2. Moreover, Y_C for active alumina was less than half of that for TiO_2, suggesting that acid sites of active alumina caused carbonization of toluene and deposition of carbon (coking). Less conversion of toluene and much larger yield of CO were obtained over silica. Result without a catalyst (blank test) is also summarized in **Table 1**. Low conversion of toluene was observed in the blank test, although the ignition point of toluene is 480°C. These results indicate that complete combustion of toluene is not achieved even in the presence of transition metals (or their oxides) of the stainless reactor at 500°C under the present conditions if the concentration of toluene is low. Low Y_C in the blank test indicates that large amounts of partially-oxidized product(s) of toluene and solid-type carbon were formed without a catalyst under the present conditions. These comparisons clearly show that TiO_2 exhibited the best result for combustion of toluene among common and simple metal oxides, although there has been little investigation of (thermo)catalysis of TiO_2

Table 1 Combustion of Toluene over Various Metal Oxides at 500°C[a)]

Metal oxide	C_T[b)] [ppm]	X_T[c)] [%]	Y_{CO_2}[d)] [%]	Y_{CO}[e)] [%]	Y_C[f)] [%]
TiO_2[g)]	2038	>99	65	5.3	70
TiO_2[g)]	1390	>99	>99	0.7	>99
Al_2O_3[h)]	2000	>99	27	0.1	27
SiO_2[i)]	1203	87	32	16	55
——[j)]	1696	55	14	5.5	36

a) Flow rate: 0.25 $dm^3 \bullet min^{-1}$. b) Initial concentration.
c) Conversion of toluene.
d) CO_2 yield. e) CO yield.
f) Apparent carbon yield calculated from the concentrations of CO_2 and CO and initial concentration and conversion of toluene.
g) Anatase-type, Sakai Chemical Industry Co., Ltd., SSP-G, 167 g.
h) Activated alumina, Nacalai Tesque, Inc., 160 g.
i) Silica, Nacalai Tesque, Inc., 129 g.
j) Blank test (No metal oxide).



Closed circles: 1.00 $dm^3 \bullet min^{-1}$, closed squares: 0.50 $dm^3 \bullet min^{-1}$, closed triangles: 0.25 $dm^3 \bullet min^{-1}$. Open circles and squares: blank tests (reactions without TiO_2) with flow rates of 1.00 and 0.50 $dm^3 \bullet min^{-1}$, respectively.

Fig. 1 Effects of Reaction Temperature on Conversion of 2100 ppm Toluene with Various Flow Rates

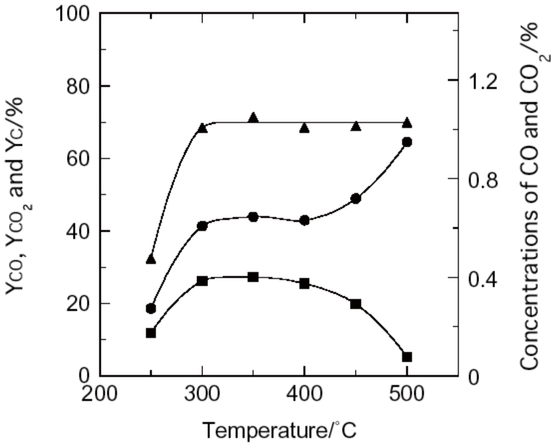


Fig. 2 Effects of Reaction Temperature on Yield of CO_2 (Y_{CO_2}, circles) and CO (Y_{CO}, squares) and Apparent Carbon Yield (Y_C, triangles) in Combustion of 2100 ppm Toluene at a Rate of 0.25 dm^3•min^{-1}

itself at high temperatures. It has recently been reported that polymers such as polycarbonate were degraded by thermocatalysis of TiO_2 at temperatures around 500°C$^{11)-13)}$.

The effects of reaction temperature on conversion of toluene with various flow rates (1.00, 0.50 and 0.25 dm^3•min^{-1}) over TiO_2 are shown in **Fig. 1**. For comparison, results of blank tests (reactions without TiO_2) are also shown. Conversions of toluene without TiO_2 at 500°C were 38% and 40% with flow rates of 1.00 and 0.50 dm^3•min^{-1}, respectively. In the presence of TiO_2, more than 60% of toluene was converted at 250°C at all flow rates. Conversion of toluene was increased by elevating the reaction temperature, and the conversion exceeded 90% at 400°C, 300°C and 250°C when the flow rates were 1.00, 0.50 and 0.25 dm^3•min^{-1}, respectively. Since conversion of more than 96% was achieved at 500°C under all reaction conditions, it is concluded that TiO_2 has some effect on reaction of toluene.

Effect of reaction temperature on yields of products and Y_C with a flow rate of 0.25 dm^3•min^{-1} is shown in **Fig. 2**. Yields of gaseous products, CO_2 and CO, were low (19% and 12%, respectively) at 250°C, though the conversion of toluene was relatively high (94%). Very low Y_C (32%) at 250°C suggests that a non-volatile product(s) was formed at that temperature. An intermediate compound(s) such as benzoic acid or maleic anhydride having a high boiling point was probably formed by partial oxidation of toluene and deposited on the surface of TiO_2 and around the exit of the reactor used in this study. However, since analysis of compounds having high boiling temperatures is generally difficult, identification and quantitative analysis of the intermediate(s) is now in progress.

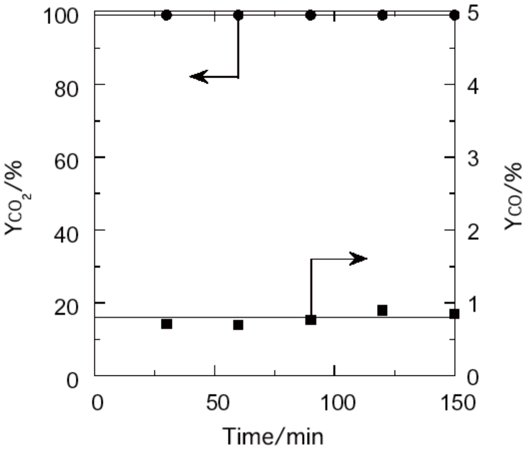


Fig. 3 Time-dependency of Yields of CO_2 (circles) and CO (squares) in Combustion of 1390 ppm Toluene under the Condition of a Flow Rate of 250 dm^3•min^{-1} at 500°C

When the reaction temperature was elevated to 300°C, yields of CO_2 and CO were increased and Y_C was improved (68%), indicating that successive oxidation of the intermediate to CO and CO_2 occurred at this temperature. Product distribution was almost the same in the temperature range of 300 to 400°C. The yield of CO was decreased and the yield of CO_2 was increased at 450°C. These results indicate that reaction rate for oxidation of CO to CO_2 was increased at this temperature. At 500°C, oxidation of CO to CO_2 was further accelerated and most of the gaseous product was CO_2, *i.e.*, selectivity of CO_2 in gaseous products reached 92%. Y_C increased up to 300°C. However, Y_C remained almost the same (70%) up to 500°C. Since the intermediate(s) with a high boiling point was probably degraded at around 400-500°C, the low Y_C at these temperatures is attributable to formation of a solid-type carbon such as soot. It has been reported that temperature for self-combustion of solid-type carbon in the presence of oxygen was higher than 650°C and that the combustion temperature over a catalyst having an excellent oxidation activity is around 570°C$^{14)}$. Therefore, since solid-type carbon was partially formed from toluene under the present reaction conditions and was emitted out of the system without being oxidized, Y_C was decreased.

The rate of CO_2 formation over TiO_2 at 500°C was calculated to be 0.62 μmol•min^{-1}•g-TiO_2^{-1}. The maximum concentration of toluene for 100% yield of

CO_2 was estimated to be *ca*. 1300 ppm based on the assumption that the rate of CO_2 formation was independent of the initial concentration of toluene. The results are also shown in **Table 1**. As expected, 1390 ppm of toluene almost quantitatively converted to CO_2 over TiO_2 under the same flow rate. Time-dependency of combustion of toluene under the same condition is show in **Fig. 3**, indicating that mineralization of toluene to CO_2 over TiO_2 continuously occurred within the reaction period (2.5 h) examined in this study.

In conclusion, in the course of research on "element strategy" for a combustion catalyst, we focused on TiO_2 alumina and silica, which are abundant as a resource and have simple composition, and examined combustion of toluene over these metal oxides. Among them, TiO_2 exhibited the highest activity for combustion of toluene. Toluene was almost quantitatively mineralized to CO_2 (>99% yield of CO_2) under the condition of appropriate contact time at 500°C.

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