Decomposition of gaseous ethyl acetate with spherical pellets of Fe-Pt/Al_2O_3 catalyst using a combustion method

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Abstract

The waste gases emitted from printing factories typically include volatile organic compounds (VOCs), such as ethyl acetate. In general, VOCs are decomposed by catalyst combustion methods, in which platinum catalysts are often employed. However, platinum is expensive and is a rare metal. In the present study, the development of an inexpensive iron-based catalyst was successfully achieved. The performance of the primitive iron catalyst was lower than the activity of commercially available platinum catalysts. Thus, a trace amount of platinum was added to the iron-based catalysts to improve the performance. Consequently, spherical pellets of the resulting Fe-Pt/Al_2O_3 catalyst exhibited optimal activity. Notably, the cost of the material was reduced by approximately 90%.

Keywords：Iron oxide, Spherical aluminum oxide, Combustion catalysts, VOCs, Platinum

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1 Introduction

As a consequence of extensive use of various kinds of organic solvents, gases emitted by painting and printing factories often include large amounts of volatile organic compounds (VOCs).1) Exposure to VOCs, such as toluene and ethyl acetate, can have detrimental effects on people's health, and the emission of these chemicals typically produces unpleasant smells.2-5) For this reason, the concentrations of VOCs in industrial emissions are regulated by law, and all factories must conduct waste gas treatments to keep the levels of VOCs below the specified standard concentrations.6-10) Catalytic combustion methods are typically utilized in printing plants for VOCs treatment.11-13) A platinum-based catalyst in the presence of alumina as a carrier is generally employed due to its good oxidizing performance.14,15) However, it is widely known that platinum is a rare and relatively expensive metal. Accordingly, the fact that platinum accounts for a significant amount of material costs and leads to an increase in the price of the catalyst is a major issue.16-18) Therefore, the development of catalysts using inexpensive metal and metal oxides have been actively conducted.19-23) In this study, we attempted to reduce the cost of VOCs combustion catalysts by using iron. We selected iron instead of platinum due to availability and low cost. The performance of the iron-based catalyst was evaluated by investigating ethyl acetate gas decomposition reaction and comparing the activity with a commercially available platinum catalyst. The iron catalyst was prepared using a general impregnation method. Initially, the developed catalyst exhibited a lower decomposition performance than the platinum catalyst. Consequently, we examined a new method for the production of a different iron-based catalyst. This approach involved oxidizing iron by hydrogen peroxide, followed by its attachment to an alumina ball surface as FeOOH. The performance of the catalyst produced by this method was somewhat improved; however, remained lower than that of the platinum catalyst. Since inadequate catalyst performance was obtained using just iron, further improvements were necessary. We subsequently investigated addition of a small amount of platinum to the iron catalyst. Ultimately, the performance of the catalyst-containing platinum exhibited activity equivalent to that of a commercially available platinum catalyst and importantly, the cost of the material was significantly reduced.

2 Experimental

2.1 Preparation of the iron-based catalyst

Fig. 1 shows the photographs of visual appearance of the iron-oxide catalyst and the iron-oxyhydroxide catalyst. The iron catalysts were prepared using two varying approaches. The first included the synthesis of the iron-based catalyst using a previously described impregnation method.24) Spherical aluminum oxide with a diameter of 5 mm was used as a catalyst carrier (Nikki-Universal Co.). The carriers (alumina balls) were immersed in a $FeSO_4$ solution whose concentration is 4.9wt.% and 11.7wt.% for 5 min. Subsequently, the carriers were dried at 100 °C in a dryer and baked at 500 °C in air, affording the desired iron-oxide catalysts (see Fig. 1a). The catalysts were prepared using two different a $FeSO_4$ solution concentrations, i.e., 4.9wt.% and 11.7wt.%.

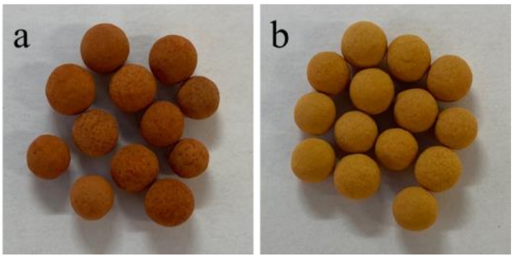

Fig. 1 The visual appearances of the iron-oxide catalyst (a) and the iron-oxyhydroxide catalyst(b)

In the second approach, the alumina balls were immersed in a $FeSO_4$ solution, to which hydrogen peroxide was added. The ionic iron species were oxidized by hydrogen peroxide to form iron compound on the surface of the alumina ball. Following oxidation, the carriers were dried at 100 °C in a dryer (see Fig. 1b). The X-ray diffraction (XRD) pattern of iron compound on the catalyst surface was recorded by the X-ray diffractometer (D8-Advance, Bruker). In addition, infrared (IR) spectra of iron compounds on the catalyst surface were recorded using the Fourier transformation infrared spectrophotometer (FT/IR-4100typeA, Jasco). The measured sample was prepared by scraping the outer surface of catalysts.

Furthermore, the catalysts were prepared by the addition of a small amount of platinum to the as-synthesized iron catalysts. The two types iron catalysts were immersed in a 0.1 g/L dinitrodiamine platinum nitrate solution (Tanaka Kikinzoku Kogyo, Japan) for 1 h. This resulted in the fixation of the majority of the platinum species in the solution to the catalysts. It is noteworthy that the platinum solution concentration was 20-fold lower than the amount of platinum required to produce a commercial catalyst (Nikki-Universal Co.). The commercially available platinum catalyst was evaluated using X-ray fluorescence analysis (Shimazu corporation, EDX-7000). It was found that approximately 1.7–2.2 g of platinum was attached to 1 L of the carrier. Subsequently, the immersed catalysts were dried at approximately 100 °C in a dryer, affording two types of Fe-Pt composite catalysts.

2.2 Evaluation of the catalytic activity

The evaluation of the catalyst performance for oxidative decomposition of gaseous VOCs was carried out using ethyl acetate gas at a concentration of 5000 ppm. The fixed bed reactor was used for the evaluation. The ethyl acetate gas was passed through a catalyst-containing heated furnace at a flow rate of 3 L/min. The air before and after passing through the catalyst was analyzed by gas chromatography (GC). The activity of a commercially available platinum catalyst, i.e., the standard for the catalytic performance, was assessed utilizing the same experimental system. The catalyst performance evaluation system is illustrated in Fig. 2. All piping consisted of silicone hoses. The air drawn by the pump was passed through silica gel to produce dry air exhibiting the relative humidity of 2–5%. A test gas mixture of air and ethyl acetate at a concentration of 5000 ppm was prepared by blowing dry air onto ethyl acetate in a test tube. The catalyst with height of 20 cm was in the quartz tube (a diameter of 26 mm and length of 500 mm.), which was heated using a ring furnace. The space velocity was approximately 424 /hr in the evaluation. The ethyl acetate gas was passed through the heated catalyst in the quartz tube from top to bottom. After passing through the sample, the gas was exhausted and analyzed by GC. The catalysts were heated at a temperature in the range of 250–400 °C. The concentration of gas was analyzed 5 times with the one temperature. The composition and specific surface area of the catalysts were measured by X-ray fluorescence analysis as well as using Brunauer-Emmett-Teller (BET) methods, respectively. Lastly, the surface structures were observed by scanning electron microscopy (SEM).

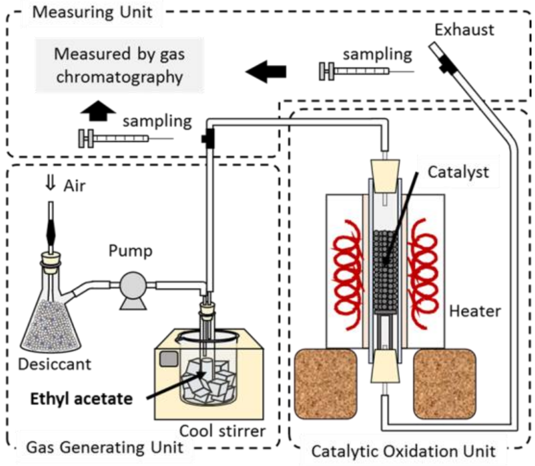

Fig. 2 The fixed bed reactor system for evaluation of catalytic activity

3 Result and discussion

3.1 Performance of the iron-oxide catalysts

The iron elemental content in the iron-oxide catalysts was measured by X-ray fluorescence analysis. We determined that the iron elemental content using the 11.7% $FeSO_4$ solution was 0.441 mg/cm^2, while the iron elemental content utilizing the 4.9% $FeSO_4$ solution was 0.245 mg/cm^2. The catalytic performance of the iron-oxide catalysts under the oxidation conditions is shown in Table 1. The ethyl acetate concentration after passing the catalyst is a mean value of 5 times analyzes. The catalyst activity was evaluated at 300 °C, 350 °C, and 400 °C. Examination of the gas after passing through the iron catalyst with the content of 0.441 mg/cm^2 revealed that 1905 ppm of ethyl acetate was detected at 300 °C, while at 350 °C, 70 ppm of the compound was noted. It is noteworthy that no ethyl acetate was detected at 400 °C; therefore, complete decomposition was suspected. Moreover, analysis of

Table 1 Characteristics of the Fe/Al_2O_3 catalyst

Supported amount of Fe(mg/cm^2)	**Oxidation method**	**Ethyl acetate concentration after passing the catalyst(ppm)**		
		Treatment temperature(℃)		
		300	**350**	**400**
0.441	**Baking at 500℃**	**1905**	**70**	**0**
0.245		**2775**	**23**	**0**
0.445	**Addition of H_2O_2**	**456**	**0**	**0**
0.270		**487**	**63**	**0**
Commercial platinum catalyst		**0**	**0**	**0**

the gas after passing through the iron catalyst with the content of 0.245 mg/cm^2 showed that 2775 ppm of ethyl acetate was noted at 300 °C, 23 ppm at 350 °C, and 2 ppm at 400 °C. Thus, the decomposition performance of ethyl acetate increased with increasing furnace temperature. In addition, the activity of the iron catalyst deposited with the content of 0.441 mg/cm^2 to decompose ethyl acetate was higher than that at the catalyst with the content of 0.245 mg/cm^2. Hence, we established that during the decomposition of ethyl acetate, the performance of the catalyst was enhanced with an increase in the iron content.

It was determined that the commercially available platinum catalyst completely decomposed ethyl acetate at 300 °C. On the other hand, iron catalysts require a temperature of 400 °C or higher. To improve the performance of the iron catalyst, we attempted to alter the method of oxidizing iron.

3.2 Changes in the catalytic activity following hydrogen peroxide oxidation

The performance of the iron catalyst, in which the iron was oxidized using hydrogen peroxide to produce iron oxyhydroxide on the catalyst surface is shown in Table 1. To compare the performance of the iron-oxyhydroxide catalyst with the iron-oxide catalyst, a sample of the former was prepared, and the amount of supported iron was measured by X-ray fluorescence analysis. It was found that the amount of iron in both types of catalysts was nearly the same. When the content of the iron element was 0.445 mg/cm^2, 456 ppm of ethyl acetate was detected after passing through catalysts at 300 °C. No ethyl acetate was detected at 350 °C or 400 °C. When the deposition amount of iron on the catalyst surface was at 0.270 mg/cm^2, 487 ppm of ethyl acetate was detected at 300 °C, whereas at 350 °C, 63 ppm was noted. Moreover, at 400 °C, no ethyl acetate was detected. Similarly to the case of iron-oxide catalysts, the decomposition of ethyl acetate increased with increasing the processing temperature of the electric furnace. In addition, the catalyst oxidation capacity of ethyl acetate improved with increasing iron content. The comparison of the performance of iron catalysts prepared using two different oxidation methods revealed that the activity of the catalyst oxidized employing hydrogen peroxide was superior.

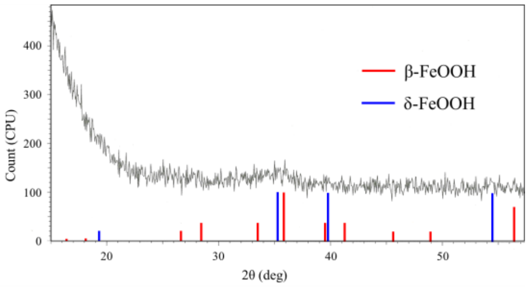

Fig. 3 X-ray diffraction pattern of the Fe compound coated on the iron-oxyhydroxide catalyst surface

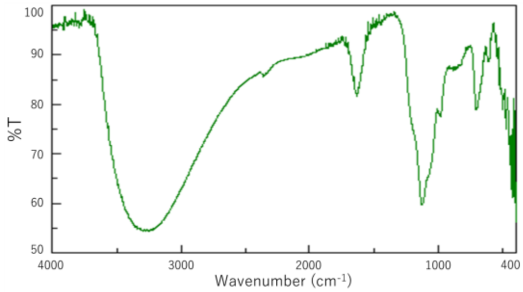

Fig. 4 The infrared spectra of the Fe compound coated on the iron-oxyhydroxide catalyst surface

According to Fig. 2b, the iron compound prepared by the second approach is yellowish brown.[25-28] For that reason, this iron compound is considered FeOOH. Fig. 3 shows the XRD pattern of iron compound on the catalyst surface. It is considered the amorphous peaks at $2\theta = 35.3°, 36°$ originated from δ-FeOOH and β-FeOOH.[29,30] Fig. 4 shows the IR spectra of the iron compound on the catalyst surface. Two absorption band observed around 705 and 847 cm^{-1} originated from β-FeOOH.[33] Furthermore, an absorption band observed around 1125 cm^{-1} originated from δ-FeOOH.[34] Considering these results from XRD pattern and IR spectra, the iron compound on the catalyst surface is identified the mixture of δ-FeOOH and β-FeOOH. When heated above 250 °C, iron oxyhydroxide (FeOOH) finally converts to iron oxide; therefore, heating does not change the iron content. However, the structure of the catalyst surface was altered by thermal decomposition of iron oxyhydroxide.

The SEM images of the two types of iron catalyst surfaces are illustrated in Fig. 5. Based on the SEM observation, the surface of the iron catalyst formed by baking at 500 °C was flat, while the surface of the iron catalyst oxidized with hydrogen peroxide was composed of numerous fine particles of approximately 0.1~0.5 µm and many pores of 1 µm.

To gain further insight, we subsequently

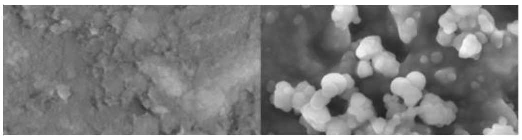

Table 2 Characteristics of the Fe-Pt/Al_2O_3 catalyst

Supported amount of Fe (mg/cm^2)	Oxidation method	Ethyl acetate concentration after passing the catalyst (ppm)		
		Treatment temperature (℃)		
		250	300	350
0.441	Baking at 500℃	1	0	0
0.245		Not measured	60	0
0.445	Addition of H_2O_2	0	0	0
0.270		0	0	0
Commercial platinum catalyst		5	0	0

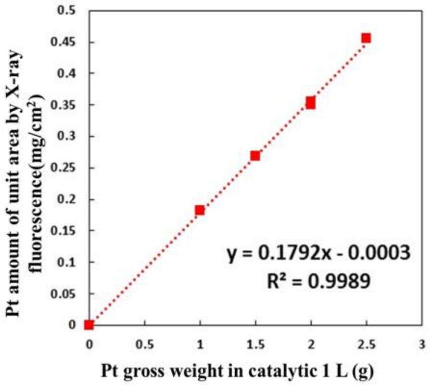

Fig. 6 Relationship between the platinum amount per unit area measured by X-ray fluorescence analysis and the gross platinum mass attached to 1 L of alumina pellets

measured the BET specific surface area of the catalysts. The specific surface area of the carriers (alumina balls) was 141 m^2/g. And the specific surface area of the heat-oxidized iron catalyst was established at 145 m^2/g, whereas the specific surface area of the iron catalyst oxidized with hydrogen peroxide was 171 m^2/g. These results were consistent with the SEM observation. Thus, it is considered that the iron catalyst prepared from oxyhydroxide exhibited a large specific surface area, and thus the dispersion effect is high, which is an advantageous property for catalytic reactions.[35-37] Furthermore Because of having many pores, contact efficiency between the iron catalyst oxidized with hydrogen peroxide and reaction gas increased. Thus, it is considered that the catalyst performance has improved.[38,39]

3.3 Improvement of the iron catalyst performance by the addition of trace platinum

The Fe-Pt catalysts were obtained by adding a small amount of platinum to the two types of iron catalysts. The performance of the prepared catalysts is shown in Table 2.

It was found that the Fe-Pt catalysts (impregnation method) prepared by the addition of trace platinum completely decomposed ethyl acetate at 300 °C (high iron content catalyst) and at 350 °C (low iron content catalyst). Furthermore, the Fe-Pt catalyst obtained by adding trace platinum to the iron-oxyhydroxide catalyst decomposed ethyl acetate at 250 °C, regardless of the Iron content. Notably, the performance of this Fe-Pt catalyst was shown to outperform the characteristics of commercially available platinum catalysts. Moreover, the Fe-Pt catalyst prepared by the addition of platinum to the iron-oxide catalyst containing a large supported amount as well as the catalyst obtained by adding platinum to the iron-oxyhydroxide catalyst exhibited analogous performance to the commercially available platinum catalyst. We suspect that this is a consequence of the addition of a small amount of platinum to the iron catalyst, which promoted the catalytic activity of iron. Platinum is known to display strong dehydrogenating effects on hydrocarbon molecules.[40] Thus, the presence of platinum results in dehydrogenation and activation of ethyl acetate. Subsequently, iron catalyzes the decomposition of ethyl acetate activated by platinum. Therefore, it is considered that the decomposition proceeds more easily using both catalysts than with iron alone. The amount of the supported platinum was also measured by X-ray fluorescence analysis. We determined that the platinum content of the commercially available platinum catalyst was 0.333 mg/cm^2, while the platinum content of the Fe-Pt catalyst was in the range of 0.014–0.016 mg/cm^2.

The relationship between the platinum amount per unit area measured by X-ray fluorescence analysis and the total platinum mass attached to 1 L of spherical alumina pellets is demonstrated in Fig. 6. As it can be seen, the platinum content in the Fe-Pt catalyst at 0.014–0.016 mg/cm^2 corresponds to approximately 0.1 g of platinum attached to 1 L of the alumina pellets. Furthermore, the platinum content of this Fe-Pt catalyst is approximately 1/20 that of a commercially available platinum catalyst, the catalytic performance is enhanced. Importantly, the material costs were reduced by approximately 90%. Based on the results of our study, the cost of the combustion catalyst was significantly reduced by utilizing the described catalytic system consisting of iron and trace platinum.

4. Conclusion

The performance of the developed iron-based catalysts was evaluated using ethyl acetate gas decomposition reaction and compared with a commercially available platinum catalyst. The activity of the iron-oxide catalyst obtained utilizing a general impregnation method was lower than that of the commercially available platinum catalyst. Based on this result, we searched for a new approach for producing a more efficient iron catalyst. The iron was oxidized by hydrogen peroxide and attached to an alumina surface as FeOOH. The performance of the iron-oxyhydroxide catalyst prepared in this way considerably improved; however, it was not as high as the activity of commercially available platinum catalysts. Since the catalyst performance using just iron was inadequate, it was necessary to make further improvements. Hence, we prepared Fe-Pt catalysts by the addition of a very small amount of platinum to the iron catalysts. As a result, it was found that the catalyst performance was enhanced to the level of commercially available platinum. Ultimately, the mass of platinum used was reduced to approximately 1/20 of that of commercially available platinum catalysts, and the overall cost of the VOCs decomposition and combustion catalysts was greatly reduced.

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