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Catalytic liquid-phase oxidation of acetaldehyde to acetic acid over a Pt/CeO₂-ZrO₂-SnO₂/γ-alumina catalyst

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ABSTRACT

Pt/CeO₂-ZrO₂-SnO₂/γ-Al₂O₃ catalysts were prepared by co-precipitation and wet impregnation methods for catalytic oxidation of acetaldehyde to acetic acid in water. In the present catalysts, Pt and CeO₂-ZrO₂-SnO₂ were successfully dispersed on the γ-Al₂O₃ support. Dependences of platinum content and reaction time on the selective oxidation of acetaldehyde to acetic acid were investigated to optimize the reaction conditions for obtaining both high acetaldehyde conversion and highest selectivity to acetic acid. Among the catalysts, a Pt(6.4 wt.)/Ce_{0.68}Zr_{0.17}Sn_{0.15}O_{2.0}(16 wt.)/γ-Al₂O₃ catalyst showed the highest acetaldehyde oxidation activity. On this catalyst, acetaldehyde was completely oxidized after the reaction at 0°C for 8 hr, and the selectivity to acetic acid reached to 95% and higher after the reaction for 4 hr and longer.

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Introduction

During the development of chemical industry in the past decades, industrial waste water has now caused a major environmental contamination according with an increase in the amount of chemical substance and water consumption. Especially, industrial liquid waste from chemical industry contains hazardous and refractory organic pollutants, leading to several problems for the environment and human health (Kim and Ihm, 2011; Mishra et al., 1995; Lei et al., 2007). Among them, acetaldehyde is soluble in water and is identified as a cancer-causing substance (Mohamed et al., 2008; Saleh et al., 2011). However, acetaldehyde is an indispensable organic compound and is often used as a solvent for paints and adhesives. Therefore, this compound is usually contained in a high level in industrial waste water from synthetic resin plants (Saleh et al., 2011). To protect our health and the environment, it is important to remove acetaldehyde in waste water as much as possible.

Liquid-phase oxidation using a heterogeneous catalyst is one of the most economical, environmental-friendly, and advanced purification methods for the treatment of refractory pollutants in industrial waste water (Kim and Ihm, 2011; Keav et al., 2014). Furthermore, benefits of using the heterogeneous catalysts are easy separation from the liquid reactants, readily-recoverable of the catalysis by calcination, and simple reaction in a serial manner, compared with those for the homogeneous catalysts (Demirel-Gülen et al., 2005; Prati and Rossi, 1998). In particular, selective air oxidation of acetaldehyde into useful acetic acid is one of the effective purification methods in the liquid phase (Venugopal et al., 1967; Wang et al., 1992; Suprun et al., 2006).

Although an electro-catalyst using Pt has been reported as one of the catalysts for liquid-phase oxidation of acetaldehyde to acetic acid and carbon dioxide, this catalyst suffers from low durability as well as insufficient activity (Kokoh et al., 2004). Some purification methods using photo-catalysis are also well known, but most of the photo-catalytic reactions

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require the ultraviolet light, which hardly exists in the solar spectrum and indoor illuminations. We think our catalyst could be a potent material for acetaldehyde elimination (Muñoz-Batista et al., 2014).

In this study, therefore, a Pt/CeO₂-ZrO₂-SnO₂/γ-Al₂O₃ catalyst was prepared for the selective oxidation of acetaldehyde to acetic acid in water. In this catalyst, the main oxidation catalyst is Pt and γ-Al₂O₃ is a catalyst support. The CeO₂-ZrO₂-SnO₂ solid solution works as a promoter to facilitate oxidation by supplying active oxygen from inside the bulk due to the oxygen storage and release properties (Yasuda et al., 2012). Accordingly, dependences of the amount of Pt and reaction time on the oxidation activity of acetaldehyde in water were investigated for the Pt/CeO₂-ZrO₂-SnO₂/γ-Al₂O₃ catalysts to realize high conversion and high selectivity to acetic acid simultaneously.

1. Materials and methods

1.1. Catalyst preparation

Commercially available granular γ-Al₂O₃ (DK Fine, Tokyo, Japan) was ground in a mortar and mechanically pulverized for 2 hr using a planetary ball-milling apparatus (Pulverisette 7, FRITSCHE GmbH, Idar-Oberstein, Germany). The fine γ-Al₂O₃ powder was used for a catalyst support.

A CeO₂-ZrO₂-SnO₂ (16 wt.%)/γ-Al₂O₃ composite was prepared by a co-precipitation method. The γ-Al₂O₃ support obtained above (2.11 g) was dispersed into a stoichiometric mixture of Sn(C₂O₄) (0.0775 g) and aqueous solutions of 1.0 mol/dm³ Ce(NO₃)₃ (1.7 cm³) and 0.1 mol/dm³ ZrO(NO₃)₂ (4.25 cm³), where the molar ratio of Ce:Zr:Sn was controlled to be 68:17:15. Then, an aqueous solution of 3.0 mol/dm³ nitric acid (20 cm³) was added into the fluid dispersion, and the mixture was stirred at room temperature for 30 min. The pH value was adjusted to 11 by the dropwise addition of aqueous ammonia (5%). After stirring for 12 hr at room temperature, the resulting precipitate was collected by filtration, washed several times with deionized water, and then dried at 80°C for 12 hr. The dried powder was ground in a mortar and then calcined at 600°C for 1 hr in an ambient atmosphere.

Finally, platinum was supported on the Ce_{0.68}Zr_{0.17}Sn_{0.15}O_{2.0} (16 wt.%)/γ-Al₂O₃ composite by impregnation of a platinum colloid stabilized with polyvinyl pyrrolidone (PVP). The amount of Pt on the catalyst was adjusted in the range of 5–10 wt.%. After impregnation, the solvent was evaporated at 180°C and the sample was dried at 80°C for 12 hr. The dried powder was ground in a mortar and then finally calcined at 500°C for 4 hr in an ambient atmosphere to obtain Pt(*x* wt.%; *x* = 5, 7, and 10)/Ce_{0.68}Zr_{0.17}Sn_{0.15}O_{2.0}(16 wt.%)/γ-Al₂O₃ (denoted as Pt*x*/CZSn16/Al₂O₃ hereafter) catalysts.

1.2. Catalyst characterization

The compositions of the Pt*x*/CZSn16/Al₂O₃ catalysts were analyzed with an X-ray fluorescence spectrometer (XRF, Supermini200, Rigaku, Tokyo, Japan). The crystal structures of the synthesized catalysts were identified by X-ray powder diffraction (XRD, SmartLab, Rigaku, Tokyo, Japan) using Cu Kα radiation (40 kV, 30 mA) in the 2θ range of 10–70°. The Pt particle size after the heat treatment at 500°C for 4 hr in air was determined using the following Scherrer equation:

$$D = \frac{k \times \lambda}{\beta \times \cos\theta} \quad (1)$$

where, *D* is the mean size of the crystalline domains, *k* is a dimensionless shape factor which is equal to 0.9, λ is the X-ray wavelength which is 0.154 nm for Cu-Kα, β is the full width at half maximum (FWHM), and θ is the Bragg angle. The Brunauer–Emmett–Teller (BET) specific surface area was measured at –196°C (Micromeritics Tristar 3000, Shimadzu, Kyoto, Japan) using N₂ adsorption.

The oxidation reaction of acetaldehyde in water was carried out in the air atmosphere in batch mode using a mechanically stirred 300 cm³ three-necked flask. An aqueous solution of 450 ppm acetaldehyde (10 cm³) was poured into the flask and the Pt*x*/CZSn16/Al₂O₃ catalyst (0.2 g) was loaded. The reactor was then cooled in an ice bath at 0°C. After the reaction for 2–8 hr, the catalyst was separated by centrifugation and the supernatant liquid was analyzed using gas chromatograph mass spectrometry (GCMS, GCMS-QP2010 Plus, Shimadzu, Kyoto, Japan) to evaluate the acetaldehyde conversion and the selectivity to acetic acid.

2. Results and discussion

The composition and BET specific surface area of the synthesized catalysts are summarized in Table 1. The sample compositions confirmed by the XRF analysis were in good agreement with the stoichiometric ratios within the experimental errors. The specific surface area of the γ-Al₂O₃ support was 248 m²/g after the heat treatment at 600°C for 2 hr, but it decreased to 151–162 m²/g after deposition of Pt and CZSn on the γ-Al₂O₃ support. The BET specific surface area also decreased with the increasing Pt amount, which might be just the result of the much larger density values of Pt than those of the oxide materials.

Fig. 1 shows the XRD patterns for the Pt*x*/CZSn16/Al₂O₃ (*x* = 5, 7, and 10) catalysts. The XRD patterns of the catalysts contain diffraction peaks of Pt, cubic fluorite-type oxide, and γ-Al₂O₃, and no crystalline impurities were observed. These results indicate that the objective catalysts were well

Table 1 – Composition and BET (Brunauer–Emmett–Teller) surface area of the catalysts.

Catalyst	Composition	BET surface area (m ² /g)	Pt particle size (nm)
Pt5/CZSn16/Al ₂ O ₃	5.4 wt.%Pt/16.6 wt.%Ce _{0.66} Zr _{0.18} Sn _{0.16} O _{2.00} /γ-Al ₂ O ₃	162	6.1
Pt7/CZSn16/Al ₂ O ₃	6.4 wt.%Pt/15.9 wt.%Ce _{0.64} Zr _{0.19} Sn _{0.17} O _{2.00} /γ-Al ₂ O ₃	155	8.0
Pt10/CZSn16/Al ₂ O ₃	9.3 wt.%Pt/15.2 wt.%Ce _{0.65} Zr _{0.19} Sn _{0.16} O _{2.00} /γ-Al ₂ O ₃	151	9.4

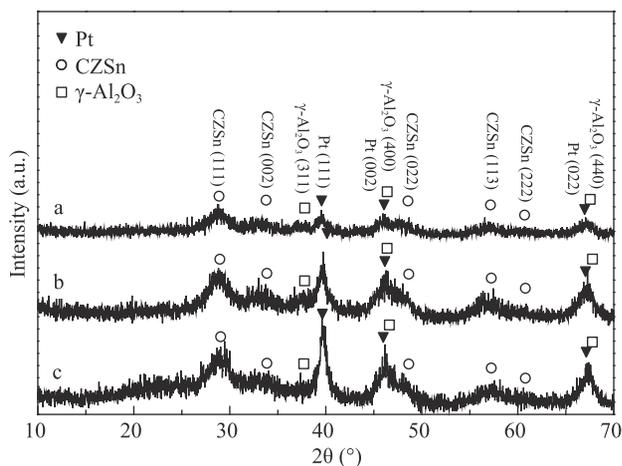


Fig. 1 – XRD (X-ray diffraction) patterns of the Pt x /CZSn16/Al $_2$ O $_3$ catalysts. (Line a) $x = 5$, (line b) $x = 7$, and (line c) $x = 10$. Pt x /CZSn16/Al $_2$ O $_3$ denoted Pt x /Ce $_{0.68}$ Zr $_{0.17}$ Sn $_{0.15}$ O $_{2.0}$ (16 wt.%)/ γ -Al $_2$ O $_3$ with the Pt content of x wt.%.

synthesized. The average sizes of the Pt particles evaluated from the Scherrer equation are also summarized in Table 1.

The results on the catalytic liquid phase oxidation of acetaldehyde using the Pt x /CZSn16/Al $_2$ O $_3$ ($x = 5, 7$, and 10) catalysts were tabulated in Table 2. The supernatant liquid after the reaction was analyzed using GC-MS. As a result, only acetaldehyde (starting material) and acetic acid (objective product) were detected, and accordingly, it is considered that carbon dioxide and water were by-products in the present cases.

The residual percentage of acetaldehyde (R) in Table 2 was calculated according to Eq. (2).

$$R = \frac{C_{\text{after}}}{C_{\text{before}}} \times 100\% \quad (2)$$

where, C_{after} and C_{before} are molar concentrations of acetaldehyde after and before the reaction.

The conversion of acetaldehyde after the oxidation reaction summarized in Table 2 was estimated by deduction of the residual percentage of acetaldehyde in the presence of the Pt x /CZSn16/Al $_2$ O $_3$ catalysts from that obtained in the blank test performed without a catalyst (the acetaldehyde solution only). In the blank test, the effect of vaporization is included.

Table 2 – Conversion of acetaldehyde and the formation rate of acetic acid using the catalysts after the reaction at 0°C for 8 hr.

Pt content (wt.%)	Residual percentage of acetaldehyde (%)		Conversion of acetaldehyde (%)	Formation rate of acetic acid (%)
	Blank	Pt x /CZSn16/Al $_2$ O $_3$		
5.4	97	27	70	64
6.4	97	12	85	81
9.3	97	17	80	75

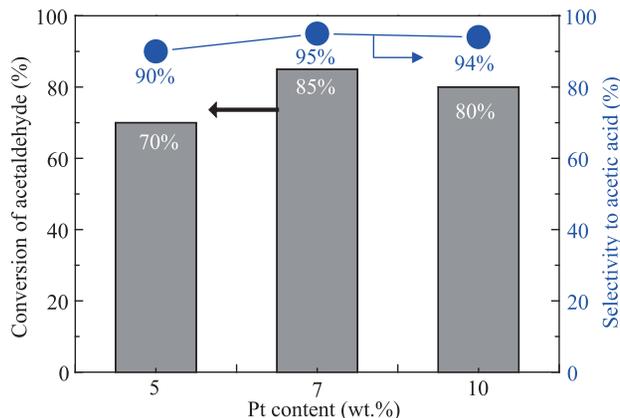


Fig. 2 – Pt content dependence of the acetaldehyde conversion and the selectivity to acetic acid after the reaction at 0°C for 4 hr.

Accordingly, the rate of decrease in acetaldehyde in Table 2 indicates the result was surely caused by oxidation.

As seen in Table 2, the oxidation property of the Pt x /CZSn16/Al $_2$ O $_3$ catalysts was obviously recognized. High conversion ratios of 70% or more were obtained for all Pt x /CZSn16/Al $_2$ O $_3$ catalysts. Among the samples tested, Pt7/CZSn16/Al $_2$ O $_3$ showed the highest oxidation activity.

Fig. 2 depicts the dependences of the acetaldehyde conversion and the selectivity to acetic acid on the Pt content in the catalysts after the reaction at 0°C for 4 hr, where the selectivity (S) was calculated by Eq. (3).

$$S = \frac{C_{\text{acetic acid}}}{C_{\text{acetaldehyde}}} \times 100\% \quad (3)$$

where, $C_{\text{acetic acid}}$ and $C_{\text{acetaldehyde}}$ are the molar concentration of acetic acid obtained after the reaction and the molar concentration of acetaldehyde oxidized by the reaction. As seen in this figure, high acetaldehyde conversion and high selectivity were realized simultaneously over the Pt7/CZSn16/Al $_2$ O $_3$ catalyst. Accordingly, the optimum amount of Pt was approximately 7 wt.% in the present catalyst.

In addition, time course of catalytic activity for the Pt7/CZSn16/Al $_2$ O $_3$ catalyst was also measured at 0°C for 2, 4, 6, and 8 hr (Table 3). Fig. 3 shows the reaction time dependence of the acetaldehyde conversion and the selectivity to acetic acid. It clarifies that the oxidation of acetaldehyde proceeds continuously, and it was completely oxidized after the reaction for 8 hr.

Table 3 – Reaction time dependence of the acetaldehyde conversion and the formation rate of acetic acid after the reaction at 0°C using the Pt7/CZSn16/Al $_2$ O $_3$ catalyst.

Reaction time (hr)	Residual percentage of acetaldehyde (%)		Formation rate of acetic acid (%)
	Blank	Pt7/CZSn16/Al $_2$ O $_3$	
2	96	40	80
4	97	12	81
6	96	7	86
8	95	0	91

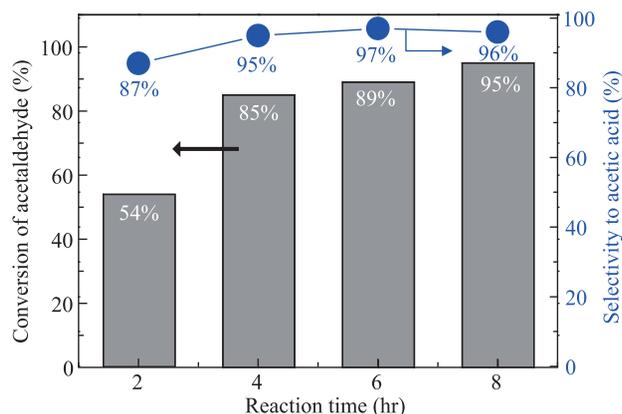


Fig. 3 – Reaction time dependence of the acetaldehyde conversion and the selectivity to acetic acid after the reaction at 0°C using the Pt7/CZSn16/Al₂O₃ catalyst.

The selectivity to the acetic acid reached 95% and even higher after the reaction for 4, 6, and 8 hr. The highest selectivity was obtained after the reaction for 6 hr, at which it reached 97%. These results mentioned above clearly demonstrate that the present Pt7/CZSn16/Al₂O₃ catalyst enables extremely efficient selective oxidation of acetaldehyde to acetic acid. Since the level of acetaldehyde in waste water is not so high, the concentration of produced acetic acid is also low. Accordingly, the economic viability is not so high from the viewpoint of acetic acid production. However, the aim of this study is not intended to the acetic acid production, but absolutely focuses on the wastewater purification. Therefore, the present catalyst is useful as a way to eliminate acetaldehyde in waste water effectively.

3. Conclusions

Pt(x wt.)/Ce_{0.68}Zr_{0.17}Sn_{0.15}O_{2.0}(16 wt.)/γ-Al₂O₃ catalysts were prepared for the purification of acetaldehyde in water by the oxidation to useful acetic acid. The catalysts were successfully synthesized by co-precipitation and wet impregnation methods. The dependence of Pt content on the catalytic oxidation of acetaldehyde elucidated that the optimum amount of Pt was 6.4 wt.% to promote the acetaldehyde oxidation. On this catalyst, acetaldehyde was completely oxidized after the reaction at 0°C for 8 hr, and the selectivity to acetic acid was 95% and higher after the reaction for 4 hr and longer. The highest selectivity of 97% was obtained after the reaction at 0°C for 6 hr.

REFERENCES

- Demirel-Gülen, S., Lucas, M., Claus, P., 2005. Liquid phase oxidation of glycerol over carbon supported gold catalysts. *Catal. Today* 102–103, 166–172.
- Keav, S., de los Monteros, A.E., Barbier Jr., J., Duprez, D., 2014. Wet air oxidation of phenol over Pt and Ru catalysts supported on cerium-based oxides: resistance to fouling and kinetic modeling. *Appl. Catal. B Environ.* 150–151, 402–410.
- Kim, K.H., Ihm, S.K., 2011. Heterogeneous catalytic wet air oxidation of refractory organic pollutants in industrial wastewaters: a review. *J. Hazard. Mater.* 186 (1), 16–34.
- Kokoh, K.B., Hahn, F., Belgsir, E.M., Lamy, C., Andrade, de A.R., Olivi, P., et al., 2004. Electrocatalytic oxidation of acetaldehyde on Pt alloy electrodes. *Electrochim. Acta* 49 (13), 2077–2083.
- Lei, L.C., Gu, L., Zhang, X.W., Su, Y.L., 2007. Catalytic oxidation of highly concentrated real industrial wastewater by integrated ozone and activated carbon. *Appl. Catal. A Gen.* 327 (2), 287–294.
- Mishra, V.S., Mahajani, V.V., Joshi, J.B., 1995. Wet air oxidation. *Ind. Eng. Chem. Res.* 34 (1), 2–48.
- Mohamed, A.A., Mubarak, A.T., Marestani, Z.M.H., Fawy, K.F., 2008. Highly sensitive and selective catalytic determination of formaldehyde and acetaldehyde. *Talanta* 74 (4), 578–585.
- Muñoz-Batista, M.J., de los Milagros Ballari, M., Kubacka, A., Cassano, A.E., Alfano, O.M., Fernández-García, M., 2014. Acetaldehyde degradation under UV and visible irradiation using CeO₂-TiO₂ composite systems: evaluation of the photocatalytic efficiencies. *Chem. Eng. J.* 255, 297–306.
- Prati, L., Rossi, M., 1998. Gold on carbon as a new catalyst for selective liquid phase oxidation of diols. *J. Catal.* 176 (2), 552–560.
- Saleh, T.A., Gondal, M.A., Drmash, Q.A., Yamani, Z.H., Yamani, A.A., 2011. Enhancement in photocatalytic activity for acetaldehyde removal by embedding ZnO nano particles on multiwall carbon nanotubes. *Chem. Eng. J.* 166 (1), 407–412.
- Suprun, W.Y., Kießling, D., Machold, T., Papp, H., 2006. Oxidation of acetaldehyde and propionaldehyde on a Vo_x/TiO₂ catalyst in the presence of water vapor. *Chem. Eng. Technol.* 29 (11), 1376–1380.
- Venugopal, B., Kumar, R., Kuloor, N.R., 1967. Oxidation of acetaldehyde to acetic acid in a sparger reactor. *Ind. Eng. Chem. Process. Des. Dev.* 6 (1), 139–146.
- Wang, S.Q., Zhang, R.F., Wang, J.C., 1992. Mathematical model of the process for the oxidation of acetaldehyde to acetic acid. *Comput. Ind. Eng.* 18 (2), 213–219.
- Yasuda, K., Yoshimura, A., Katsuma, A., Masui, T., Imanaka, N., 2012. Low-temperature complete combustion of volatile organic compounds over novel Pt/CeO₂-ZrO₂-SnO₂/γ-Al₂O₃ catalysts. *Bull. Chem. Soc. Jpn.* 85 (4), 522–526.