Preparation and catalytic property of zirconia-system composites consist of Zr–O material derived from zirconium oxy-acid salts

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Catalysts based on Zr–O material were prepared from zirconium oxychloride and zirconium oxynitrate with ultrasonication. The deposited Zr–O materials were not detected by XRD because of amorphous phase of an oxygen deficient type zirconia. The obtained zirconia based composite showed higher catalytic performance for oxygen addition activity than Pd based composite for the combustion of carbon. However, the obtained zirconia based composite showed the less catalytic performance for dehydrogenation reaction activity than Pd based composite for the combustion of methane. This zirconia based catalyst is expected to use for the electrode material of the fuel cell that needs restraint of the carbon deposition.

Key-words : Zirconia, Catalyst, Ultrasonication, Oxygen addition activity

1. Introduction

Platinum group metal (PGM) is used for catalyst in various industrial fields. Since PGMs are rare resources, substituting materials of PGM are desired. The candidate of substituting material of PGM is an oxide-based non-noble metal catalyst and carbon alloy catalyst. Many works were carried out in this field.⁵–⁷ Among them, there is a report that graphene on carbon nanotube has greatly contributed to catalytic activity⁸ and Co/CoO nano particles on carbon functioned as an oxygen reduction catalyst⁹. In addition, there is a report that CuZrGaO catalyst directly produced hydrogen and carbon dioxide from methane.⁶ It is thought that the catalytic activity of these catalysts developed by miniaturization of catalyst.

The catalyst particle is expected to develop the specific function such as Au nano particle¹⁰ by reducing of particle size. This phenomenon is explained by the change of chemical reaction following the increase of the active surface atom. Furthermore, the material that is reduced to ultimate size is a cluster. Castleman et al. reported that two atomic clusters of WC, ZrO and TiO have a similar electronic state with Pt, Pd and Ni, respectively.⁵,⁹ This suggests that the catalytic function similar with Pt or Pd can be provided if WC or ZrO cluster like structure realizes on the fine particle surface of WC or ZrO. However, it is necessary to develop fine particles of WC and ZrO by simpler and easier method because the cluster has difficulty in large-scale usage as catalyst.

There are many manufacturing methods to obtain ceramic fine particle, however, the method of directly deposition on catalyst support is the most suitable for catalyst. One is a method using deposition assisted by the ultrasonication. About fine particle synthesis using a ultrasonication, there are reports for magnetite fine particle¹⁰ and iron hydroxide fine particle.¹¹ In addition, there are some reports that deposition of manganese oxide on carbon by using ultrasonication. The performance of the rechargeable battery improved when this manganese oxide/carbon hybrid was used to anode material in the lithium ion battery.¹²,¹³ And, the performance of electrostatic capacitance increased when this manganese oxide/carbon hybrid was used for the capacitor material.¹⁴ The fine particle deposition method using the ultrasonication is an important manufacturing technique to attract attention as the low energy process. In this paper, Zr–O fine particle was hybridized with activated carbon or activated alumina by using ultrasonication and catalytic properties of obtained composites were evaluated.

2. Experimental

2.1 Sample preparation and characterization

Zirconium oxychloride octahydrate (ZrOCl₂·8H₂O) and zirconium oxynitrate dehydrate [ZrO(NO₃)₂·2H₂O] were used as Zr source. Activated carbon (AC: Kanto Chem.) and activated alumina (AA: Nacalai Tesque) were used as a catalyst support when the Zr–O material used for catalyst. By dissolving Zr sources in deionized water, ZrOCl₂ solutions of 0.01–2.0 M and ZrO(NO₃)₂ solutions of 0.01–0.5 M were prepared. Each prepared solution and AC were mixed and dispersed solutions of solid/liquid ratio = 10 g/L were prepared. These dispersed solutions were treated at an ultra-sonicator (W-200, Honda electronics CO., LTD.) under frequency of 200 kHz of the output of 200 W. After ultrasonication, the solids were separated by suction filtration, washed with deionized water and were dried at 80°C for overnight. Then, Zr–O material/activated carbon composites, denoted as ZrO(Cl)/AC and ZrO(NO₃)/AC, were obtained.

Reference samples of ZrO₂ based composites were prepared by mixing the catalyst support with zirconia dispersed solution (Nanoco Inc.) and palladium nitrate solution to the catalyst support, followed by heating at 500°C under 3%H₂–Ar condition (Pd/AC and Pd/AA). Theses samples were subjected to XRD analysis, and reference samples were obtained.

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reference samples were used for comparison. The obtained various composites were characterized by XRD, SEM-EDS, and \( \text{N}_2 \)-adsorption method. Additionally, the particle size distribution of Zr–O material included in the dispersed solution after ultrasonication was evaluated by dynamic light scattering (DLS) method (Zetasizer Nano ZS, Malvern).

2.2 Evaluation of catalytic properties
Catalytic performance of the composite using AC for catalyst support was evaluated for carbon combustion. The combustion performance of the composite was measured by a thermo gravity and differential thermal analysis (TG–DTA: TG8120, Rigaku). Endothermal and exothermal reactions with weight change were analyzed under dry air flow (50 mL/min) from room temperature to 800°C rising rate of 10°C/min. The catalytic performance of carbon combustion was estimated based on the combustion start temperature.

Catalytic performance of the composite using AA for catalyst support was evaluated for methane combustion. Combustion performance test of methane was carried out in 200–800°C rising rate of 2.5°C/min using a continuous fixed-bed reactor containing 0.1 g of samples except for Pd composite was heated at 500°C for 1 h under air flow. The mixed test gas (\( \text{CH}_4: \text{O}_2: \text{Ar} = 5:10:85 \) vol %) was controlled at a flow rate of 100 mL/min. The composition of the vent gas was analyzed using an online gas chromatography (GC-9, Shimazu) with a thermal conductivity detector. The catalytic performance was estimated based on the rate of methane conversion defined as:

\[
\text{Conversion of methane} = \frac{\text{Consumption methane (mol)}}{\text{Supplied methane (mol)}} \times 100.
\]

The rate of carbon dioxide selectivity is defined as:

\[
\text{Selectivity of CO}_2 = \frac{\text{Creation carbon dioxide (mol)}}{\text{Consumption methane (mol)}} \times 100.
\]

3. Results and discussion
3.1 Precursor particles of zirconia
The oxy-salts used as the Zr source is well known to be hydrolyzed in water and form a precursor particle of zirconia. Particle size distributions of zirconium oxychloride and zirconium oxynitrate solutions before and after ultrasonication were shown in Fig. 1. In \( \text{ZrOCl}_2 \) solution, the precursor particles of zirconia existed at a size of approximately 1 nm. These particles were kept the same size after ultrasonication. In \( \text{ZrO(NO}_3)_2 \) solution, the precursor particles of zirconia existed a bimodal state about 1 nm and around 800 nm. These particles changed only in a particle of the distribution mainly on about 800 nm after ultrasonication.

The \( \text{ZrOCl}_2 \) solution is known to create zirconium tetramer \( [\text{Zr}_4(\text{OH})_8(\text{H}_2\text{O})_{16}]^{8+}\) by hydrolysis. Singhel et al. reported that the size of this tetramer is 0.76 nm.15),16) Although this tetramer was known to be relatively stable, it was revealed that the tetramer maintained the structure after ultrasonication. On the other hand, the stable tetramer slightly created by the hydrolysis of \( \text{ZrO(NO}_3)_2 \) and the created particles aggregated easily, and then large particles about 800 nm occurred. Furthermore, only large particles existed after ultrasonication because the particles of around 1 nm that slightly occurred were not a stable one in this condition.

3.2 Characterization of obtained composites
XRD patterns of the obtained composites and the supports for catalyst were shown in Fig. 2. Composites of \( \text{ZrO(Cl)} \) and \( \text{ZrO(N)} \) were not observed a diffraction peak from Zr–O materials and were only observed the support pattern, i.e. halo pattern for AC and \( \text{Al}_2\text{O}_3 \) and \( \text{AlOOH} \) for AA. Composites of \( \text{ZrO}_2 \) sol and Pd were observed peaks of tetragonal zirconia and metal palladium, respectively, together with the pattern of catalyst support. Enomoto et al. have already reported that zirconia fine particle from zirconium oxychloride showed the amorphous phase.17) Therefore, the Zr–O material in this work is considered to have an amorphous phase of zirconia. In addition, the Zr–O material is regarded as an oxygen deficient type zirconia by considering of...
a chemical composition of zirconium tetramer that is mentioned above.

Microtextures of obtained composites were shown in Fig. 3. In all samples, the shape that is an indeterminate form of carbon was observed in a secondary electron image. However, a clear difference was observed in each backscattering electron image. ZrO(Cl)/AC showed no clear image of segregated Zr. It is thought that fine ZrO particles of about 1 nm that was mentioned above was hybridized with carbon. ZrO(Cl)/AC showed an image of segregated Zr from several ten nm to 100 nm. ZrO2/AC showed an image of segregated Zr of several hundred nm. And, Pd/AC showed an image of the segregated Pd from 200 to 300 nm.

Catalyst amount of ZrO(Cl)/AC and ZrO(N)/AC with reference composites were listed in Table 1 and Table 2, respectively. The amounts of the Zr-O material in obtained composite increased both of ZrO(Cl)/AC and ZrO(N)/AC with increase in concentration of the zirconium reaction solution. When the starting solution of the same density was used, the Zr-O amount of ZrO(N)/AC was higher than that of ZrO(Cl)/AC.

In addition, the saturated Zr-O amount of these composites was about 10 mass% when the concentration of starting solution was raised. Although the details are omitted, if the Zr-O amount of obtained composite is on the same level, the segregation of Zr was restricted in the composite prepared using ultrasonication and the Zr-O material was dispersed homogeneously in the composite prepared using ultrasonication.

3.3 Evaluation of catalytic properties

Combustion performances for carbon and methane were used for the index of catalytic properties. Figure 4 shows DTA curves of various composites. In all curves, exothermic peak was observed and this peak was assigned as combustion of carbon. The combustion start temperature is different with a catalyst amount. The peak profile of ZrO(N)/AC is different from ZrO(Cl)/AC and ZrO2/AC. This is due to the difference in combustion of carbon. The combustion start temperature decreased in any composite with increasing in catalyst amount.

The relationships of the combustion start temperature and the amount of catalyst were indicated in Fig. 5. Decreasing of the combustion start temperature saturated at 3–5 mass% of catalyst and it did not depend on the kind of catalyst. Falling temperatures of the combustion start of ZrO2/AC and Pd/AC were about 50°C and about 80°C, respectively. For SiO2/AC and Al2O3/AC that have same content SiO2 and Al2O3 with ZrO2 in ZrO2/AC, the combustion start temperature was almost same with AC or

Fig. 3. SEM images of secondary electron image (SEI) and backscattered electron image (BEI) of (a) ZrO(Cl)/AC, (b) ZrO(N)/AC, (c) ZrO2/AC, and (d) Pd/AC.

Fig. 4. DTA curve of various composites supported on carbon: (a) ZrO(Cl)/AC and reference composites (listed in Table 1) and (b) ZrO(N)/AC and reference composites (listed in Table 2).

| Table 1. Catalyst amount of ZrO(Cl)/AC with initial concentration and reference composites (Tr denotes a trace detection) |
|---|
| Samples | ZrO(Cl)/AC | ZrO2/AC | Pd/AC |
|---|---|---|---|
| Catalyst amount (mass %) | Tr | Tr | 0.5 | 1.0 | 1.6 | 5.4 | 7.8 | 1.7 | 1.2 |
| Samples | 0.01 M | 0.05 M | 0.10 M | 0.25 M | 0.50 M | 1.00 M | 2.00 M |
|---|---|---|---|---|---|---|---|

| Table 2. Catalyst amount of ZrO(N)/AC with initial concentration and reference composites |
|---|
| Samples | ZrO(N)/AC | ZrO2/AC | Pd/AC |
|---|---|---|---|
| Catalyst amount (mass %) | 2.5 | 7.0 | 10 | 9.8 | 9.8 | — | — | 11 | 9.6 |
| Samples | 0.01 M | 0.05 M | 0.10 M | 0.25 M | 0.50 M | 1.00 M | 2.00 M |
slightly increased. This is caused by the surface of carbon covered with a different material. In contrast, combustion start temperature of ZrO2/AC decreased because of oxygen supply through surface ZrO2 on carbon due to oxygen conductivity of zirconia. In the case of Pd/AC, mechanism is different. It is well known that dissociation of oxygen occurs easily on the surface of Pd. Therefore, combustion of carbon is promoted by high reactivity of this dissociated oxygen atoms.

On the other hand, the falling temperatures of the combustion start of ZrO(Cl)/AC and ZrO(N)/AC were 110 and 200°C, respectively. These degrees of the falling temperature were larger than that of Pd/AC and ZrO2/AC. The Zr-O fine particles in this paper [ZrO(Cl) and ZrO(N)] showed higher performance of falling temperature of carbon combustion start than ZrO2 particle. Therefore, it is considered that the origin of catalytic performance of the Zr-O fine particles depended not only on high oxygen conductivity of zirconia but also new activation by the fine particle state. This new activity by the fine particle state is considered to be depending on the promotion of the dissociation of oxygen on the catalytic surface.

About the combustion of methane, reaction temperature dependence of CH4 conversion and CO2 selectivity was shown in Fig. 6. The Pd/AA showed high catalytic activity in combustion of methane, and combustion of methane occurred at 400°C that is 100°C lower than an ignition point of methane. As a result, the Pd/AA showed high CH4 conversion of over 90% and high CO2 selectivity of about 90%. In contrast, ZrO(Cl)/AA, ZrO(N)/AA, and ZrO2/AA showed low catalytic activity in combustion of methane, and combustion of methane occurred at over 600°C that is higher than an ignition point of methane. And, they showed a low CH4 conversion of about 50% at 800°C and low CO2 selectivity of 50–60% at 800°C. In any sample, the generation of carbon monoxide was observed in addition to the generation of CO2 above the combustion temperature of methane. Besides, carbon deposition was not observed in any sample.

In the combustion of methane, a dissociation adsorption of methanol occurred on the surface of PGM catalyst including Pd at comparative low temperature (in this paper, around 400°C). The dissociation adsorption is described as CH4 → C + 4H and is well known as a dehydrogenation reaction. This dehydrogenation reaction promotes an oxygen addition reaction to occur next step. Therefore, Pd/AA catalyst showed high conversion and high selectivity. Although ZrO(Cl)/AA and ZrO(N)/AA catalysts have a higher catalytic performance for an oxygen addition reaction described as C + O2 → CO2, they showed low catalytic activity in combustion of methane because of less catalytic performance for a dehydrogenation reaction of methane. Castleman et al. suggested the substitution of Pd by two atomic cluster of ZrO because the ZrO cluster shows a similar electronic state with Pd. However, the real nano-sized ZrO particle that shows a catalytic activity of the oxygen additional reaction could not show a catalytic activity of the dehydrogenation reaction. In other word, it is necessary for substituting Pd catalyst by Zr-O particle to prepare a smaller particle of Zr-O material.

4. Conclusion

Zirconia based composites were prepared with Zr-O material derived from zirconium oxychloride or zirconium oxynitride using ultrasonication and catalytic properties of them were evaluated. And then, the following results were obtained.

• Ultrafine particles of Zr-O material of approximately 1 nm were formed by using zirconium oxychloride for zirconia source, and fine particles of Zr-O material of the sub-micrometer size were formed by using zirconium oxynitride for zirconia source.

• By evaluation of oxygen addition activity using a composite with activated carbon, the zirconia based composite showed higher activity than Pd.

• By evaluation of the combustion activity of methane using a composite with activated alumina, the zirconia based composite showed low activity. But, the selectivity of CO2 gas of the zirconia based composite was higher than that of the activated alumina that was used as a support of the composite.

• Because of higher combustion performance of carbon, the obtained zirconia based composite is expected to use for the elec...
trode material of the fuel cell that carbon deposition is significantly problem.

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