Effects of surface fluorination on the dispersion stability of nano metal oxides using F\textsubscript{2} gas

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ABSTRACT

In this study, the surfaces of TiO\textsubscript{2} (rutile) and ZrO\textsubscript{2} nano-particles were modified by using F\textsubscript{2} gas (1-100 kPa). Also, the reaction temperature was 25-200 °C and the reaction time was 1-60 min. The obtained samples were analyzed by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and Field-Emission Scanning Electron Microscope (FE-SEM). Furthermore, to investigate the dispersion stability of obtained samples, sedimentation test, zeta potential and particle size were measured. The particle size of fluorinated samples had a smaller than that of untreated samples, and zeta potential of fluorinated samples increased. Also, the dispersion stability of fluorinated samples was improved.

1. INTRODUCTION

The use of nano-seized particles have been used and studied in various fields (e.g., electron materials, optical materials, and ceramics materials) because it has specific surface reactivity as well as product miniaturization and improve function. However, nanoparticles are influenced by intermolecular forces such as Van der walls force. Therefore, there are problems that the particles adhere and/or aggregate with each other to form secondary particle. In order to use nanoparticles as raw materials, dispersion stabilization of particle is required. To improve dispersion stability, it has been used beads mill or coupling agent. [1-3] However, these methods have problems that not only secondary particle but also primary particles are broken or addition-agent remains. [4] Surface modification of nanoparticles is an effective method to minimize the agglomeration of nanoparticles. Surface modification is done by UV irradiation and plasma treatment but these are limited by particles size and shape.

On the other hand, the surface modification of particles by using F\textsubscript{2} gas can process uniformly regardless of the size and shape of particle because it is gas. Also fluorination of particles surface changes surface charge. Therefore, particles repel each other by electrostatic repulsive forces. [5]
In this study, surface of TiO$_2$ (rutile) and ZrO$_2$ (monoclinic) which is nanoparticles of metal oxide were modified by F$_2$ gas and the effect of surface fluorination on the agglomeration of nanoparticles.

2. EXPERIMENTAL DETAILS

2.1 Preparation of fluorinated

For the fluorination, TiO$_2$ (201-13645, FUJIFILM Wako Pure Chemical Corporation, Ltd, Rutile; 99% purity, particle size 200-380nm) and ZrO$_2$ (A2716, DAIICHI KIGENSO KAGAKU CO., LTD., monoclinic, particle size 50-80nm) powder were placed in a reactor (volume of 150ml) and a reactor was evacuated to 1 Pa or less. And then F$_2$ gas was introduce inside a reactor. Reaction pressure, temperature, and reaction time were set at 1-100kPa, 20-200°C, and 1-60min. Sample names and reaction conditions of TiO$_2$ and ZrO$_2$ treated with F$_2$ gas show in table 1.

2.2 Characterizations of samples

The structural and electronic properties of samples were investigated using XRD (X-ray diffraction; XRD-6100, SHIMAZU, Ltd.) and XPS (X-ray photoelectron spectroscopy; JPS-9010MC, JEOL, Ltd.). The particle surface was observed using FE-SEM (Field Emission-scanning electron microscopy; ULTRA plus, ZEISS).

2.3 Dispersion stability measurements

Average particle size and Zeta potential profiles were measured using a zeta-potential/ particle-size measurement (ELSZ-2, Otsuka electronics Co., Ltd.). A sample was dispersed in pure water, and the pH was adjusted using a 0.1M NaOH or HCl solution. The dispersion stability of samples in some solvents was determined by sedimentation experiment. For preparing the suspension, 15mg of TiO$_2$ or ZrO$_2$ and 15mL of solvents were mixed and sonicated for 30min.

Table 1. Sample names and reaction conditions of TiO$_2$ and ZrO$_2$ treated with F$_2$ gas

<table>
<thead>
<tr>
<th>Sample name</th>
<th>F$_2$ pressure /kPa</th>
<th>Time /min</th>
<th>Temperature /°C</th>
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<td>25</td>
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<td>25</td>
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<td>60</td>
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<thead>
<tr>
<th>Sample name</th>
<th>F$_2$ pressure /kPa</th>
<th>Time /min</th>
<th>Temperature /°C</th>
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<tbody>
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<td>-</td>
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</tr>
<tr>
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<td>25</td>
</tr>
<tr>
<td>F4-ZrO$_2$</td>
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3. RESULTS and DISCUSSION

3.1 Characterization of samples

3.1.1 Structural analysis and Surface composition of TiO$_2$

The effects of different temperature and F$_2$ pressure on XRD patterns of TiO$_2$ powders are shown in Fig. 1. These fluorination conditions did not found new peaks and peak shifts. From XRD pattern, crystal structure of TiO$_2$ not changed by the fluorination using F$_2$ gas. This is understood because ionic radius of fluorine atom on particle surface (0.0133nm) is virtually the same as the replaced oxygen atom (0.0132nm).[6] FE-SEM images of untreated and fluorinated TiO$_2$ samples are shown in Fig. 2. As seen from Fig. 2, the fluorination effect on the surface state of TiO$_2$ particles could not be seen in the FE-SEM images. However, XPS spectra confirm the existence of fluorinated surface of TiO$_2$ particle as shown in Fig. 3.

Fig. 3 show F 1s (A), Ti 2p (B) and O 1s (C) spectra of untreated and fluorinated TiO$_2$. In F 1s spectra (A), an unsymmetrical peak was observed TiO$_2$. It means that some chemical bonding of fluorine atom might exist. In F 1s (A) of Fig. 3, the peak 1 located at the binding energy (BE) of 684.9eV might be attributed to the fluorine atoms chemically adsorbed on TiO$_2$ surface. The peak 2 located at 687.9eV might be attributed substituted fluorine atoms in TiO$_2$. This peak originated from the fluorine atoms doped into TiO$_2$ crystal lattice. [7] In the case of Ti 2p (B), the Ti (IV) 2p1/2 and Ti (IV) 2p3/2 were located at BE of 465.0eV and 459.2eV. These peaks were not observed changing peak shift by fluorination. Therefore the valence state of Ti$^{4+}$ (459.0eV) doesn't change to Ti$^{3+}$ (458.9eV) or Ti$^{2+}$ (457.0eV) by fluorination. In case of O 1s (C), the peak was observed to shift to higher energy. This result seems to be related to dope into TiO$_2$ crystal lattice.

![Fig. 1 XRD patterns of untreated and fluorinated TiO$_2$ particles.](image1)

![Fig. 2 FE-SEM images of untreated TiO$_2$ [(A) and (B)] and fluorinated TiO$_2$ (F4-TiO$_2$) [(C) and (D)] particles.](image2)
3.1.2 Structural analysis and Surface composition of ZrO$\textsubscript{2}$

The effects of different F$\textsubscript{2}$ pressure on XRD patterns of ZrO$\textsubscript{2}$ powders are shown in Fig. 4. As with TiO$\textsubscript{2}$, from XRD pattern, crystal structure of ZrO$\textsubscript{2}$ was not changed by the fluorination. FE-SEM images of untreated and fluorinated ZrO$\textsubscript{2}$ samples are shown in Fig. 5. XRD pattern and FE-SEM images can not be seen fluorination effect on crystal structure and surface state. However XPS spectra confirm the existence of fluorinated surface of ZrO$\textsubscript{2}$ particles as shown in Fig. 6. Fig.6 shows F 1s (A), Zr 3d (B), and O 1s (C) spectra of untreated and fluorinated ZrO$\textsubscript{2}$.

In case of F 1s (A) in ZrO$\textsubscript{2}$, the peak 1 located at 683.5eV might be attributed to the fluorine atoms in ZrOF (III). The peak 2 located at 684.5eV is assigned by to fluorine atoms chemically adsorbed on ZrO$\textsubscript{2}$ surface. The peak 3 located at 685.5eV seen in F4-ZrO$\textsubscript{2}$ is seemed to substituted fluorine atoms in ZrO$\textsubscript{2}$. As with TiO$\textsubscript{2}$, this peak originates from formation of ZrOF$\textsubscript{2}$, because the fluorine atoms dope into ZrO$\textsubscript{2}$ crystal lattice. It seems to be related F$\textsubscript{2}$ pressure because this peak is not seen other than F4-ZrO$\textsubscript{2}$. ZrOF$\textsubscript{2}$ phase cannot easily observed in XRD pattern because it is not crystalline. In case of Zr 3d (B) and O 1s (C) of Fig. 6, the peaks especially were observed to shift to higher energy in F4-ZrO$\textsubscript{2}$. This result is seemed to due to be formation of ZrOF$\textsubscript{2}$.

3.2 Dispersion stability of samples.

3.2.1 Sedimentation test and Measurement of the zeta potential and average particle size of TiO$\textsubscript{2}$

Fig. 7 shows the suspension of untreated and fluorinated TiO$\textsubscript{2}$ powder dispersed in water (A), ethanol (B), and acetone (C). In the untreated TiO$\textsubscript{2}$ (a) suspension, TiO$\textsubscript{2}$ particles was observed to form into agglomerates within 4h in water (A) and in ethanol (B) within 6h. However, samples of fluorinated TiO$\textsubscript{2}$ were observed to increase dispersion stability in water (A) and ethanol (B). In case of acetone (C),
samples of fluorinated TiO$_2$ were not observed to increase dispersion stability because acetone is polar aprotic solvent. From Fig.3, this result are seemed that the dispersion stability improves by fluorine atoms chemically adsorbed on the particle surface. Because the dispersion stability of colloidal suspensions is primarily depend on interparticle force and on the repulsive electrostatic interaction of these charges and fluorine at particle surface has high electronegativity and high acidity, it changes the OH
at particle surface to O\(^-\) by releasing H\(^+\) and/or the fluorine(F) changes into the fluoride ion (F\(^-\)) by taking the electron (e\(^-\)) from the O\(^-\). that is, the surface of F-TiO\(_2\) and particles become negatively charged and enhances the repulsive interaction between particles.

[8]

Fig. 8 shows the effects of surface fluorination on the particle size of TiO\(_2\) in water (at pH7), ethanol, and acetone (A) and zeta potential of TiO\(_2\) in water (at pH 7) (B). The average size of fluorinated particles in all solvents were smaller than untreated particles and the absolute value of zeta potential on fluorinated particles were larger than untreated particle. Therefore, it can be said that the fluorinated particles can be stabilized agglomerarion by electrostatic forces because the charges increased by surface fluorination can create electrostatic repulsion between the particles. To improve the dispersion stability of TiO\(_2\) particles, it is important to control the surface fluorination to on the state of fluorine adsorbed on the TiO\(_2\) surface without TiOF\(_2\) formation.

Fig. 7 The suspension of untreated and fluorinated TiO\(_2\) powder dispersed in water (A), ethanol (B), and acetone (C) with retention times [(a)TiO\(_2\), (b)F1- TiO\(_2\), (c)F2- TiO\(_2\) (c)F3- TiO\(_2\), and (e)F4- TiO\(_2\)].
3.2.2 Sedimentation test and Measurement of the zeta potential and average particle size of ZrO$_2$

Fig. 9 shows the suspension of untreated and fluorinated ZrO$_2$ powder dispersed in water. As seen from Fig. 9, samples of fluorinated ZrO$_2$ were observed to increase dispersion stability. However, F4-ZrO$_2$ was formed agglomerates and precipitated. As mentioned in 3.2.1, the surface of F-TiO$_2$ and particles become negatively charged and enhances the repulsive interaction between particles.

Fig. 10 shows the effects of surface fluorination on the particle size and zeta potential of ZrO$_2$ in water. The average size of fluorinated particles in all solvents were smaller than untreated particles and the absolute value of zeta potential on fluorinated particles were larger than untreated particle. However, F4-ZrO$_2$ cannot be measured particle size and zeta potential.
Fig. 9 The suspension of untreated and fluorinated ZrO₂ powder dispersed in water with retention times [(a)ZrO₂, (b)F1- ZrO₂, (c)F2- ZrO₂, (d)F3- ZrO₂, and (e)F4- ZrO₂].

Because, it quickly agglomerates and precipitates. The dispersion stability of F4-ZrO₂ decreased due to the formation of ZrOF₂ film at the particle surface. As with as TiO₂, To improve the dispersion stability of and ZrO₂ particles, it is important to control the surface fluorination to on the state of fluorine adsorbed on the ZrO₂ surface without ZrOF₂ formation.

Fig. 10 shows the effects of surface fluorination on the particle size and zeta potential of ZrO₂ in water. The average size of fluorinated particles in all solvents were smaller than untreated particles and the absolute value of zeta potential on fluorinated particles were larger than untreated particle. However, F4-ZrO₂ cannot be measured particle size and zeta potential. Because, it quickly agglomerates and precipitates. The dispersion stability of F4-ZrO₂ decreased due to the formation of ZrOF₂ film at the particle surface. As with as TiO₂, To improve the dispersion stability of and ZrO₂ particles, it is important to control the surface fluorination to on the state of fluorine adsorbed on the ZrO₂ surface without ZrOF₂ formation.

4. CONCLUSIONS
The surface fluorination of TiO₂ and ZrO₂ particles using F₂ gas improved the dispersion stability under fluorine pressure of 50kPa at 200°C for 1h and fluorine pressure of 1kPa at room temperature (25°C) for 10min. However, F4-ZrO₂ was created ZrOF₂ film on particle surface and decreased the dispersion stability. Also, the average particle size of fluorinated particle was smaller and the absolute value of zeta potential of fluorinated particle was larger than untreated particle. From XPS and XRD patterns, the surface of TiO₂ and ZrO₂ particles was fluorinated but crystal structure was not changed. From these results, the particles of TiO₂ and ZrO₂ modified by using F₂ gas can be increased dispersion stability in various solvent.
REFERENCES