A highly selective oxidation performance, which has a higher oxidation activity for hydrocarbons than that for SO$_2$, is required for diesel oxidation catalysts. We examined the oxidation reaction of $n$-C$_6$H$_{14}$ and SO$_2$ over two types of Pt/ZrO$_2$ catalysts with low (8 m$^2$/g) and high (75 m$^2$/g) surface areas of the ZrO$_2$ supports (referred to as ZrO$_2$-8 and ZrO$_2$-75, respectively). The Pt/ZrO$_2$-75 exhibited a desirable higher selectivity for the complete oxidation of $n$-C$_6$H$_{14}$ than that of SO$_2$, as compared with the Pt/ZrO$_2$-8. In order to clarify the cause of this selective oxidation, we investigated the Arrhenius parameter for these oxidation reactions and characterized these catalysts using XPS, XRD, TEM, IR and CO$_2$-TPD methods. The amount of Pt$^0$ (metal) in the Pt/ZrO$_2$-75 was significantly lower than that in Pt/ZrO$_2$-8, because the high basicity of the ZrO$_2$-75 support stabilized the high oxidation state of Pt such as Pt$^{2+}$ and Pt$^{4+}$. It was concluded that the difference in the number of Pt$^0$ sites as catalytic active sites causes the apparent selectivity to change due to the much slower reaction rate for the SO$_2$ oxidation than that for the $n$-C$_6$H$_{14}$ oxidation.

**Keywords**

Diesel engine, Sulfur dioxide oxidation, Hydrocarbon oxidation, Oxidation selectivity, Platinum/zirconia
1. Introduction

Diesel emissions are composed of three phases; (1) solids (carbon or soot); (2) liquids (soluble organic fraction and liquid sulfate); and (3) gases (CO, hydrocarbon compounds, NOx and SO2). The complete oxidation of carbon, CO and hydrocarbon (HC) compounds is required for the diesel oxidation catalyst\(^1, 2\). However, any sulfur compound contained in the diesel fuel is oxidized to SO\(_2\) during the engine combustion cycle. In the presence of an oxidation catalyst, SO\(_2\) is further oxidized to SO\(_3\), which quickly reacts with the moisture in the exhaust to form sulfate. The sulfate leads to an increase in the weight of the total particulates emitted from the diesel engine and also causes acid rain. Therefore, a highly selective oxidation catalyst, which has a higher oxidation activity for carbon, CO and HC compounds than that for SO\(_2\), is required.

Although it is important to investigate the key factor in developing a highly selective oxidation catalyst, surprisingly, few studies have been conducted\(^3\). In this study, we examined the oxidation of \(n\)-hexane (gaseous HC) and SO\(_2\) over two types of Pt/ZrO\(_2\) catalysts with low and high ZrO\(_2\) support surface areas. These Pt/ZrO\(_2\) catalysts exhibited different selectivities for the oxidation of \(n\)-hexane and SO\(_2\)\(^4\). The purpose of this study is to clarify the cause of this oxidation selectivity. For this purpose, we investigated the Arrhenius parameter for this oxidation reaction and characterized the catalysts using XPS, XRD, TEM, IR and CO\(_2\)-TPD methods\(^5\).

We employed \(n\)-hexane as a gaseous HC, because many \(n\)-alkane species are contained in the exhaust gas phase\(^6\). A number of studies have been conducted on the complete catalytic oxidation of the C\(_1\)–C\(_3\) hydrocarbons such as methane, ethane, propane, etc.\(^7\)\(^\text{–}\)\(^\text{11}\). Actual exhaust gases include alkanes with a carbon number higher than C\(_3\). Therefore, we chose \(n\)-hexane as the HC species. Besides, few studies on the complete catalytic oxidation of hexane (C\(_6\)) have been reported. In addition to the foregoing main purpose of clarifying the cause of the reaction selectivity, another purpose of this study is to estimate the complete oxidation of \(n\)-hexane over platinum catalysts.

2. Experimental

2.1 Catalyst preparation

The two types of Pt/ZrO\(_2\) catalysts examined for this study are summarized in Table 1 with the corresponding BET surface areas and ZrO\(_2\) phase. The low surface area zirconia (referred as to ZrO\(_2\)-8) was supplied by Mitsuwa Chemicals, Japan. On the other hand, the high surface area zirconia (referred as to ZrO\(_2\)-75) was prepared by calcining Zr(OH)\(_4\) (Hayashi Pure Chemical Industries, Japan) in air at 500°C for 3 h. The Pt/ZrO\(_2\) catalysts were prepared by the wet impregnation of ZrO\(_2\) powders with a Pt(NH\(_3\))\(_2\)(NO\(_2\))\(_2\) (Tanaka Precious Metals, Japan) aqueous solution. The impregnated powders were dried overnight at 110°C and calcined at 500°C for 3 h in air. The amount of Pt loading of these catalysts was 0.64 wt.%. Also, Pt/SiO\(_2\) (SiO\(_2\) Nippon Aerosil Co., Ltd., specific surface area: 50 m\(^2\)/g) catalysts with several Pt loading amounts were prepared as references. The catalysts for the activity measurements were pressed into disks and pulverized to 1.0-2.0 mm size.

2.2 Activity measurement

The catalytic activity was determined by using a conventional fixed-bed flow reactor at atmospheric pressure. The reaction temperature was detected by a thermocouple inserted into the catalyst bed, and controlled from 500°C to 150°C at a rate of -6°C min\(^{-1}\). The simulated exhaust gas was composed of 100 ppm \(n\)-hexane, 50 ppm SO\(_2\), 10 % O\(_2\), 5 % CO\(_2\),...
10 % H₂O and the balance N₂. The total flow rate was 8.36 l/min and 3.6 g of catalyst was used. The concentration of the HC and SO₂ were continuously analyzed by a flame ionization detector and a flame photometric detector, respectively. The pre-treatment was carried out at 500°C in the same flowing gas until the conversions of HC and SO₂ became constant. The conversions of HC and SO₂ were calculated based on the following equation:

\[
\text{Conversion(\%)} = \left( \frac{X_{\text{in}} - X_{\text{out}}}{X_{\text{in}}} \right) \times 100 \cdots \cdots (1)
\]

where \(X_{\text{in}}\) and \(X_{\text{out}}\) are the concentrations of HC or SO₂ entering and leaving the catalyst bed, respectively.

The Arrhenius parameter measurements were made using the same above-mentioned conditions, except using the feed gas without CO₂ and H₂O. The Arrhenius parameters were calculated from the conversions of HC and SO₂ at less than about 15%.

2. 3 Catalyst characterization

2. 3. 1 Surface area measurements

The specific surface areas of the samples were estimated using the N₂ adsorption isotherm at 77 K by the one-point Brunauer-Emmett-Teller (BET) method with an automatic surface analyzer (Micro Sorp 4232II from Micro Data Co., Ltd.). The samples were degassed in flowing N₂ at 200°C for 20 min.

2. 3. 2 X-Ray diffraction (XRD)

The powder XRD experiments were carried out using a RINT2000 (Rigaku Co., Ltd.) diffractometer with Cu-Kα radiation (1.5406 Å). The catalyst powder samples were pressed into wafers and affixed to standard-sized microscope slides. The identification of the phase was made by comparison to the JCPDS cards (Joint Committee on Powder Diffraction Standards). The average particle size of Pt was estimated from the Pt(1 1 1) line width using Scherrer’s equation with the Gaussian line shape approximation.

2. 3. 3 Transmission electron micrograph (TEM)

TEM images were obtained using a JEOL JEM-2000EX. The accelerating voltage was 200 keV. The samples used for the measurements were pretreated at 400°C in air for 30 min.

2. 3. 4 X-ray photoelectron spectra (XPS)

The XPS measurements were carried out using a PHI model 5500MC with MgKα X-rays. The catalyst sample was placed on a grid, and pretreated under 0.1 atm O₂ pressure at 400°C for 15 min. The pretreated sample was cooled to room temperature, and then transferred to the XPS measurement stage.

2. 3. 5 Infrared (IR) spectra

The IR spectra were recorded using a JASCO FT/IR-8900 spectrometer equipped with a diffuse reflectance attachment (JASCO DR-800/H) and an MCT detector. The catalyst sample placed in an \textit{in situ} IR cell with a KBr window was pretreated at 400°C for 20 min in flowing 7% O₂/N₂ and then cooled to 200°C. The chemisorption of CO was then performed in flowing 0.28% CO/N₂ at 200°C. The IR spectra of CO adsorbed on the sample were obtained by subtracting the spectra before the CO adsorption from those after the adsorption.

2. 3. 6 CO₂ temperature-programmed desorption(TPD) experiments

The basicity of the zirconia was measured by CO₂-TPD. The TPD experiments were carried out using the same experimental set-up as that used for the activity measurements. An 18 g sample was pretreated at 500°C for 15 min in flowing N₂ (5 l/min), cooled to 100°C, then saturated with a 0.26% CO₂/N₂ flowing gas mixture. After purging the sample with the N₂ gas, the sample was heated to 400°C at the rate of 50°C/min in flowing N₂ (5 l/min). The concentration of the desorbed CO₂ was analyzed by a nondispersive infrared detector.

3. Results and discussion

3. 1 Catalytic activity

Figs. 1(a) and (b) show the conversion of \(n\)-C₆H₁₄ and SO₂ on the Pt/ZrO₂-8 and Pt/ZrO₂-75 catalysts, respectively, as a function of temperature. The conversion of both on Pt/ZrO₂-75 reached over 80% at 400°C. In contrast, it is noteworthy that the SO₂ conversion on Pt/ZrO₂-75 is much lower than that on Pt/ZrO₂-8. The Pt/ZrO₂-75 catalyst has only a 20% SO₂ conversion at 400°C. The temperature at 50% \(n\)-C₆H₁₄ conversion on Pt/ZrO₂-75 was 296°C, which was somewhat higher than that (273°C) on Pt/ZrO₂-8. The \(\Delta T\) shown in Fig. 1 denotes the temperature difference between the 50% conversion of \(n\)-C₆H₁₄ and SO₂. The \(\Delta T\) (203°C) of Pt/ZrO₂-75
was much wider than that (65°C) of Pt/ZrO₂-8. Therefore, the Pt/ZrO₂-75 catalyst has a desirably higher selectivity for the oxidation of \( n\)-C\(_6\)H\(_{14}\) than that of SO\(_2\).

3.2 Arrhenius parameters

The Arrhenius plots for the rates of the \( n\)-C\(_6\)H\(_{14}\) and SO\(_2\) conversions are shown in Figs. 2(a) and (b), respectively. All the data points obtained with the Pt/ZrO₂-8 and Pt/ZrO₂-75 catalysts provide a linear relationship. The apparent activation energy (\( E_a \)) and the pre-exponential factor (\( A \)) calculated from the Arrhenius plots are summarized in Table. 2. First, the Pt/ZrO₂-8 and Pt/ZrO₂-75 catalysts have almost same \( E_a \) value for the \( n\)-C\(_6\)H\(_{14}\) oxidation,
suggesting that these catalysts have identical active sites. On the other hand, the \( A \) value for the \( n-C_6H_{14} \) oxidation on Pt/ZrO\(_2\)-8 is one order of magnitude greater than that on Pt/ZrO\(_2\)-75. The term \( A \) is interpreted as being proportional to the number of catalytic active sites. Thus, an increase in \( A \) on Pt/ZrO\(_2\)-8 indicates an increase in the number of active sites. Secondly, the \( E_a \) for the SO\(_2\) oxidation on Pt/ZrO\(_2\)-8 is somewhat higher than that on Pt/ZrO\(_2\)-75, but its difference is not much greater, therefore, these catalysts would have identical active sites. As for the \( A \) value of the SO\(_2\) oxidation, the same trend as for the \( n-C_6H_{14} \) oxidation is observed. Based on the results mentioned above, it is suggested that for the oxidation of \( n-C_6H_{14} \) and SO\(_2\), these catalysts have identical active sites, and that the number of active sites on Pt/ZrO\(_2\)-8 is one order of magnitude greater than that on Pt/ZrO\(_2\)-75.

### 3.3 Characterization of catalysts

#### 3.3.1 Average platinum particle size of the Pt/ZrO\(_2\) catalysts

Table 3 shows the average platinum particle size of the catalysts estimated by XRD and TEM. The diffraction peaks from the Pt particles in both Pt/ZrO\(_2\)-8 and Pt/ZrO\(_2\)-75 could not be detected due to their small particle size. The average particle size in Pt/ZrO\(_2\)-8 estimated by TEM was 1-4 nm. On the other hand, the Pt particles in Pt/ZrO\(_2\)-75 could not be observed even by TEM, suggesting that the Pt particle size in Pt/ZrO\(_2\)-75 was less than 1 nm. It is found that the Pt/ZrO\(_2\)-75 catalyst has a higher Pt dispersion when compared to Pt/ZrO\(_2\)-8.

#### 3.3.2 Oxidation state of Pt in the Pt/ZrO\(_2\) catalysts

Fig. 3 shows the XPS spectra of the catalysts at the Pt 4f band. Metallic Pt (Pt\(^0\)) has Pt 4f\(_{7/2}\) and Pt 4f\(_{5/2}\) bands at 70.7 and 74.0 eV, respectively \(^{12}\). In addition, the binding energy of Pt\(^{2+}\) and Pt\(^{4+}\) is ca. 73.0 and 74.7 eV for 4f\(_{7/2}\) and 76.4 and 78.1 eV for 4f\(_{5/2}\), respectively \(^{13}\). The peak assigned to Pt\(^0\) 4f\(_{7/2}\) (70.7 eV) was observed for Pt/ZrO\(_2\)-8, while that peak for Pt/ZrO\(_2\)-75 almost disappeared. In contrast, the peak assigned to Pt\(^{4+}\) 4f\(_{5/2}\) (78.1 eV) was observed for Pt/ZrO\(_2\)-75, but not for Pt/ZrO\(_2\)-8. The proportion of Pt\(^0\), Pt\(^{2+}\) and Pt\(^{4+}\) in the catalysts was quantitatively calculated from the peak fitting of the XPS spectrum (Fig. 4). As shown in Fig. 4, the main Pt constituent in Pt/ZrO\(_2\)-8 was the Pt\(^0\) species.

### Table 2

Apparent activation energies (\( E_a \)) and pre-exponential terms (\( A \)) for the oxidation of \( n-C_6H_{14} \) and SO\(_2\) over Pt/ZrO\(_2\) catalysts.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>( E_a ) (kcal / mol) \n( n-C_6H_{14} )</th>
<th>( E_a ) (kcal / mol) \n( SO_2 )</th>
<th>( A ) (1/sec) \n( n-C_6H_{14} )</th>
<th>( A ) (1/sec) \n( SO_2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt/ZrO(_2)-8</td>
<td>21</td>
<td>19</td>
<td>3.2 ( \times ) 10(^{10})</td>
<td>5.6 ( \times ) 10(^{7})</td>
</tr>
<tr>
<td>Pt/ZrO(_2)-75</td>
<td>20</td>
<td>17</td>
<td>1.4 ( \times ) 10(^{9})</td>
<td>1.1 ( \times ) 10(^{8})</td>
</tr>
</tbody>
</table>

### Table 3

Average platinum particle size of the catalysts estimated by XRD and TEM.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>XRD (^a) (nm)</th>
<th>TEM (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt/ZrO(_2)-8</td>
<td>N.D. (^b)</td>
<td>1 - 4</td>
</tr>
<tr>
<td>Pt/ZrO(_2)-75</td>
<td>N.D. (^b)</td>
<td>N.D. (^c)</td>
</tr>
</tbody>
</table>

\(^a\) Average particle size was estimated from Pt(1 1 1) line width.

\(^b\) The diffraction peak from the Pt particles could not be detected.

\(^c\) Pt particles could not be detected in the TEM images.

### Fig. 3

XPS spectra of the catalysts at the Pt 4f bands. (a) Pt/ZrO\(_2\)-8, (b) Pt/ZrO\(_2\)-75.
while the Pt$^{2+}$ and Pt$^{4+}$ species with a high oxidation state were mainly present in Pt/ZrO$_2$-75.

Furthermore, we examined the state of Pt by IR using CO as the probe molecule. **Fig. 5** shows the IR spectra of CO adsorbed at 200°C on Pt. The peaks at around 2070-2090 cm$^{-1}$ observed in both Pt/ZrO$_2$-8 and Pt/ZrO$_2$-75 are assigned to CO adsorbed on Pt$^0$. The peak intensity for Pt/ZrO$_2$-75 drastically decreased as compared with Pt/ZrO$_2$-8. This result is in accord with the XPS observation that the proportion of Pt$^0$ in Pt/ZrO$_2$-75 is much lower than that in Pt/ZrO$_2$-8. We have confirmed that the peak area of the IR is proportional to the amount of CO adsorbed on the catalysts. Therefore, the ratio of the peak area in the IR spectrum is equivalent to that of the number of Pt$^0$ sites. Consequently, it is found that the number of Pt$^0$ sites for Pt/ZrO$_2$-8 is about eighteen times greater than that for Pt/ZrO$_2$-75.

### 3.3.3 Relationship between the basicity of zirconia supports and the oxidation state of Pt

The basicity of the zirconia supports was measured by CO$_2$-TPD. The CO$_2$-TPD profiles of ZrO$_2$-8 and ZrO$_2$-75 are shown in **Fig. 6**. The basicity of the ZrO$_2$-75 with a high surface area was much higher than that of ZrO$_2$-8 having a low surface area, indicating that the basicity is related to the surface area.

Yoshida et al. investigated the support effect on the state of the Pt catalysts by XAFS analysis$^{15}$. The Pt on a basic support such as MgO and La$_2$O$_3$ is fully oxidized in an oxidative atmosphere, while the Pt on the acidic support contains more metallic Pt. Thus, it could be considered in our system that the high basicity of ZrO$_2$-75 stabilized the high oxidation state of Pt such as Pt$^{2+}$ and Pt$^{4+}$ compared to ZrO$_2$-8.

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**Fig. 4** The proportion of Pt$^0$ (metal), Pt$^{2+}$ and Pt$^{4+}$ in the catalysts determined by XPS measurements.

**Fig. 5** IR spectra of CO adsorbed at 200°C on the catalysts.

**Fig. 6** CO$_2$-TPD profiles of the ZrO$_2$ supports.
3. 4 The cause of the reaction selectivity for n-hexane and SO$_2$ oxidations

As mentioned above, the Arrhenius parameter measurements indicated that both catalysts have identical active sites for the complete oxidation of $n$-C$_6$H$_{14}$, and that the pre-exponential factor on Pt/ZrO$_2$-8 is one order of magnitude greater than that on Pt/ZrO$_2$-75. This same trend applies to the oxidation of SO$_2$. On the other hand, from the IR peak area of adsorbed CO, the number of Pt$^0$ sites on Pt/ZrO$_2$-8 is at least ten times greater than that for Pt/ZrO$_2$-75. The correlation between the pre-exponential factor and the Pt$^0$ sites indicates that the Pt$^0$ sites mainly act as active sites for the $n$-C$_6$H$_{14}$ and SO$_2$ oxidations. Additionally, it is postulated that the difference in the number of Pt$^0$ active sites causes the apparent selectivity for the $n$-C$_6$H$_{14}$ and SO$_2$ oxidations to change. Since the reaction rate for the SO$_2$ oxidation is much slower than that for the $n$-C$_6$H$_{14}$ oxidation, the decrease in the active Pt$^0$ sites apparently suppresses the SO$_2$ oxidation compared to the $n$-C$_6$H$_{14}$ oxidation. Therefore, the cause of the high selectivity for Pt/ZrO$_2$-75 is the extreme decrease in the active Pt$^0$ site. Furthermore, in order to verify this hypothesis, we estimated the catalytic activity on the Pt/SiO$_2$ catalysts with various numbers of Pt$^0$ sites (Fig. 7). These Pt/SiO$_2$ catalysts were prepared by modifications of the Pt loading amount and calcination temperatures. In addition, it has been reported that most of the Pt on the SiO$_2$ support exist in the metallic state in an oxidative atmosphere$^{15}$). As shown in Fig. 7, the SO$_2$ oxidation is more suppressed by decreasing the active Pt$^0$ sites than the $n$-C$_6$H$_{14}$ oxidation, causing $\Delta T$ to widen. From these results, it is clear that the apparent oxidation selectivity between $n$-C$_6$H$_{14}$ and SO$_2$ could be controlled by the number of active Pt$^0$ sites.

4. Conclusion

In this study, we estimated the reaction selectivity for the $n$-C$_6$H$_{14}$ and SO$_2$ oxidations over two types of Pt/ZrO$_2$ catalysts with low and high ZrO$_2$ support surface areas. The Pt/ZrO$_2$-75 catalyst with a high surface area has a desirably higher selectivity for the complete oxidation of $n$-C$_6$H$_{14}$ than that of SO$_2$, as compared with the Pt/ZrO$_2$-8 catalyst with a low surface area. Namely, the Pt/ZrO$_2$-75 remarkably suppresses the SO$_2$ oxidation as compared with the $n$-C$_6$H$_{14}$ oxidation. In order to clarify the cause of this reaction selectivity, we investigated the Arrhenius parameter for these oxidation reactions and characterized the catalysts using XPS, XRD, TEM, IR and CO$_2$-TPD methods. The number of Pt$^0$ (metal) sites in the Pt/ZrO$_2$-75 was significantly lower than that in the Pt/ZrO$_2$-8, because the high basicity of the ZrO$_2$-75 stabilized the high oxidation state of Pt such as Pt$^{2+}$ and Pt$^{4+}$. Since the reaction rate for the SO$_2$ oxidation is much slower than that for the $n$-C$_6$H$_{14}$ oxidation, the decrease in the active Pt$^0$ site apparently suppresses the SO$_2$ oxidation as compared with the $n$-C$_6$H$_{14}$ oxidation. Therefore, the cause of the high selectivity for the Pt/ZrO$_2$-75 was the extreme decrease in the active Pt$^0$ sites. It was clarified that the apparent oxidation selectivity between $n$-C$_6$H$_{14}$ and SO$_2$ could be controlled by the number of active Pt$^0$ sites.

Acknowledgements

This research was completed thanks to Messrs. K. Doumae (XPS), Y. Matsuoka (TEM), Y. Watanabe and K. Banno.

Fig. 7  The relation between the conversion of $n$-C$_6$H$_{14}$ and SO$_2$ oxidation and the amount of the Pt$^0$ (metal) site. Pt/SiO$_2$ catalysts with various amounts of Pt$^0$ sites were employed. The IR peak area of CO adsorbed on Pt$^0$ is proportional to the amount of the Pt$^0$ site. $\Delta T$ denotes the temperature difference between the 50% $n$-C$_6$H$_{14}$ and SO$_2$ conversion efficiencies.
References

    (Report received on Dec. 11, 2001)