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Carbon Formation and Active Site of Alumina Supported Platinum Catalyst in Steam Methane Reforming Containing Sulfur

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Effect of sulfur poisoning on Pt/α-Al_2O_3 catalysts in steam methane reforming (SMR) was investigated using dimethyl sulfide (DMS). SMR with and without 10 ppm DMS addition was performed over 0.1-2.0 wt% Pt/α-Al_2O_3 catalysts. Catalyst deterioration occurred at an early stage, but not inactivation in the presence of DMS. Moreover, after the supply of DMS was stopped, the activity was completely restored. DMS in the reaction gas also caused severe sintering of the Pt particles and promoted carbon formation on the 1.0-2.0 wt% Pt catalysts. On the other hand, carbon formation did not occur on the 0.1 wt% Pt catalysts. The Pt sintering and carbon formation behaviors were independent of the SMR activity. These results suggest that three different active sites are formed on the Pt/α-Al_2O_3. The first is a SMR active site not affected by DMS. The second is an active site that loses activity due to DMS, but completely regenerates after the supply of DMS is stopped. The third is not an active site of SMR but where sintered Pt accelerates methane decomposition to produce carbon.

Keywords
Steam methane reforming, Platinum catalyst, Sulfur poisoning, Sintering, Carbon formation, Active site

1. Introduction

Production of synthesis gas ($CO + H_2$) is one of the most important processes in the chemical industry. Synthesis gas is required to produce important chemical products such as ammonia, methanol, aldehyde, and pure hydrogen[1)~5)]. Recently, fuel cell systems have been proposed as an effective method for the utilization of hydrogen. Steam methane reforming (SMR, Eq. (1)) is the most common industrial process for the production of hydrogen and synthesis gas.

$$CH_4 + H_2O \rightarrow CO + 3H_2 \qquad (1)$$

In general, natural gas is used as the methane (CH_4) source. Research on steam reforming technology commonly uses CH_4 as a model substance for natural gas. Ni-based catalyst is widely used in industrial scale hydrogen production because of the cost effectiveness in operations at 1073 K or higher[6)~9)]. However, Ni-based catalyst tends to accumulate considerable carbon deposits during SMR under a low steam carbon ratio (S/C). In contrast, Ru-based catalyst is tolerant to carbon formation and can function under relatively lower S/C. However, few studies have considered the impurities contained in natural gas. Indeed, Ni and Ru catalysts are sensitive to sulfur poisoning[10)~12)]. Natural gas deposits are widely distributed throughout the world, and supplies are transported by tanker after liquefaction to liquefied natural gas (LNG) or by pipeline after compression. Such impurities are completely removed during the liquefaction process of LNG, but are often incompletely removed during compression. Natural gas contains impurities such as sulfur compounds, carbon dioxide, and nitrogen in addition to the main light hydrocarbon components. We previously reported on the effects of nitrogen contained in natural gas on SMR[13)].

Natural gas typically contains 5-500 ppm of sulfur compounds, and these compounds are well-known poisons for catalysts[10),14),15)]. Therefore, desulfurization is generally involved in the utilization of natural gas[16),17)]. Hydrodesulfurization process is often used in petroleum refining process, and requires high-pressure hydrogen and high reaction temperatures. In contrast, the sulfur compounds in natural gas are removed by adsorption under ambient temperature and pressure[16)]. Simplified desulfurization processing is a cost-effective method for

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residential fuel cell systems. However, sulfur leaks may occur during load changes such as at start-up and shut-down. Therefore, catalysts with high sulfur tolerance are key technology for developing new cost-effective processes.

Dimethyl sulfide (DMS) is one of the most difficult sulfur components to remove from natural gas by the adsorption process[18]. Previously, we examined the sulfur tolerance of alumina-supported Rh, Pt, Ir, and Ru catalysts for SMR in the presence of DMS[12]. Rh and Ru catalysts were completely deactivated by DMS, whereas the Pt and Ir catalysts maintained *ca.* 50 % and 20 % of initial activity, respectively. Pt and Ir catalysts also showed good regeneration behavior after stopping the DMS feed. Pt catalyst may show sulfur tolerance in the presence of other sulfur compounds[19]~[23].

The present study investigated the mechanisms of deactivation and regeneration behavior of alumina-supported Pt catalyst (Pt/α-Al_2O_3) during SMR with and without DMS addition.

2. Experimental

2. 1. Catalyst Preparation

The Pt/α-Al_2O_3 catalysts were prepared by a conventional impregnation method. The α-Al_2O_3 support was prepared by calcination of boehmite (Sasol, Catapal B) in air at 1573 K for 2 h. The boehmite powder was pressed into pellets, crushed, and sieved to obtain the appropriate pellet size of 150-250 μm prior to the calcination treatment. The calcined α-Al_2O_3 pellets were put into a flask with 100 mL distilled water and the mixture was degassed for 1 h under 100 hPa at room temperature. Then diamminedinitroplatinum(II) nitrate solution (Kojima Chemicals Co., Ltd.) was put into the flask and the mixture was stirred for 2 h under atmospheric pressure at room temperature. The resultant slurry was heated at 353 K under reduced pressure (above 100 hPa) using a rotary evaporator to remove the solvent. The obtained solid product was dried in air at 383 K overnight. Subsequently, the dried sample was calcined in air at 773 K for 2 h. The Pt metal loading of the prepared catalysts was adjusted to 0.1, 1.0, and 2.0 wt% in the metal state.

2. 2. Catalytic Activity Test

The SMR reaction tests were carried out using a fixed-bed flow reactor equipped with a quartz tube (I.D. 6 mm) at atmospheric pressure. The prepared catalyst was placed in the quartz tube and reduced at 973 K for 30 min in 10 % H_2/90 % N_2 using a total flow rate of 100 mL min^{-1}. The SMR reaction tests in the presence of DMS (DMS SMR) were then carried out using a reaction gas mixture containing 3.1 % N_2/27.7 % CH_4/69.2 % H_2O/10 ppm DMS at a total flow rate of 325 mL min^{-1} with steam carbon ratio (S/C) of 2.5. The SMR reaction tests without DMS (DMS-free SMR) also used a gas mixture of 3.1 % N_2/27.7 % CH_4/69.2 % H_2O under the same reaction conditions. Catalyst weight was 0.20, 0.25, and 0.50 g and gas hourly space velocity (GHSV) was *ca.* 100,000, 86,000, and 43,000 h^{-1}, respectively. The durability tests were carried out at the reaction temperature of 973 K and GHSV of *ca.* 43,000 h^{-1} or 86,000 h^{-1} for 8 h.

Regeneration of the deactivated catalysts was also studied. Fresh catalyst after reduction was reacted under DMS SMR conditions for the first 2 h. Subsequently, the reaction condition was changed to DMS-free SMR conditions and was reacted for a further 24 h. In addition, a DMS-free SMR reaction was also carried out using the fresh catalyst for 26 h for comparison. These tests were conducted at the reaction temperature of 973 K and GHSV of *ca.* 86,000 h^{-1}.

Outlet gas was cooled in an ice-cold trap, and dry gas product was analysed using an on-line gas chromatograph equipped with a thermal conductivity detector (GC-14B, Shimadzu Corp.) and a Shincarbon ST column (Shinwa Chemical Industries Ltd.). CH_4 conversion (X_{CH_4}) was calculated from Eq. (2).

$$X_{CH_4}[\%] = \frac{F_{in,CH_4} - F_{out,CH_4}}{F_{in,CH_4}} \times 100 \qquad (2)$$

where F_{in,CH_4}, and F_{out,CH_4} are the flow rates of CH_4 at the inlet and outlet of the reactor, respectively.

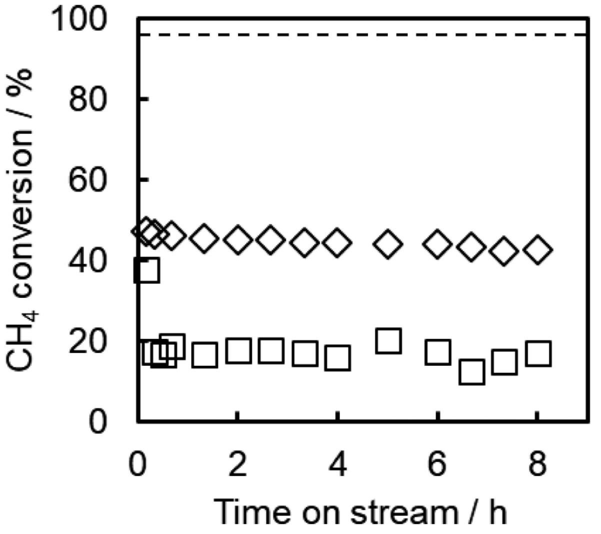
Arrhenius plots were graphed for DMS SMR and DMS-free SMR over the 0.1 wt% Pt/α-Al_2O_3 catalyst. These SMR reaction tests were conducted at the reaction temperature of 923-973 K and GHSV of *ca.* 100,000 h^{-1}. Under these reaction conditions, the catalyst is considered to be degraded by DMS immediately. First, CH_4 conversion was measured at 973 K, then the reaction temperature was lowered and the temperature dependence of CH_4 conversion for DMS SMR was evaluated. Assuming that the reaction is a primary consumption of CH_4, the apparent activation energy (E_a) and the frequency factor (A) were calculated from the obtained Arrhenius plots by Eq. (3).

$$\ln r = -\frac{E_a}{RT} + \ln A \qquad (3)$$

where r is the consumption rate of CH_4 corresponding to the reaction rate, R is the gas constant (8.314 J K^{-1} mol^{-1}), T is the reaction temperature, and A is the frequency factor.

2. 3. Characterization

The morphology of the Pt/α-Al_2O_3 catalysts was observed using a transmission electron microscope (TEM, JEM-2100 and JEM-2100F, JEOL Ltd.). The samples were crushed into powder, dispersed in ethanol with ultrasonic agitation, and transferred onto a copper grid. The operating voltage, emission current, and dark current were 200 kV, 230 μA, and 93-97 μA, respectively. Mean Pt particle diameter was estimated



SMR reaction conditions: 3.1 % N_2/27.7 % CH_4/69.2 % H_2O or 3.1 % N_2/27.7 % CH_4/69.2 % H_2O/10 ppm DMS, $T = 973$ K, total flow rate $= 325$ mL min^{-1}, and GHSV $= 86{,}000$ h^{-1}. Dotted line shows the chemical equilibrium conversion at the reaction conditions.

Fig. 1 CH_4 Conversion over 1.0 wt% Pt/α-Al_2O_3 for DMS-free SMR (diamonds) and DMS SMR (squares)

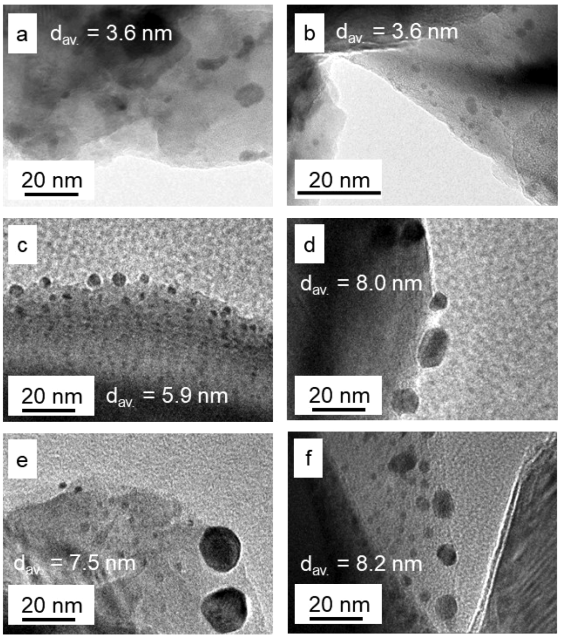


Fig. 2 TEM Images of the Fresh (a) and Spent 1.0 wt% Pt/α-Al_2O_3 Catalysts after DMS SMR for 0.5 h (b), 2 h (c), 4 h (d), 6 h (e), and 8 h (f)

from the TEM observations of *ca.* 100 Pt particles. Mean particle size of Pt was defined as follows in Eq. (4).

$$d_{\mathrm{mean}} = \frac{\Sigma d}{n} \quad (n = 100) \qquad (4)$$

where d_{mean} is the mean diameter of the Pt particles, and n represents the number of Pt particles.

The amount and types of the deposited carbon on the spent catalyst were studied with temperature programmed oxidation (TPO) using a BEL-CAT-ADVANCE (MicrotracBEL Corp.). The spent sample (0.05 g) was heated at 5 K min^{-1} from ambient temperature up to 1173 K under 20 % O_2 and 80 % N_2 with total gas flow rate of 30 mL min^{-1}. The TPO profiles were recorded by a quadrupole mass spectrometer (OmniStar, Pfeiffer) to measure the production of CO_2 ($m/z = 44$).

3. Results and Discussion

3. 1. Comparison of SMR Activity Tests

SMR over 1.0 wt% Pt/α-Al_2O_3 catalyst was carried out at 973 K for 8 h with and without DMS. The change in CH_4 conversion is shown in **Fig. 1**. DMS-free SMR achieved CH_4 conversion of 47 % at 10 min, and slowly decreased to 43 % at 8 h. DMS SMR achieved CH_4 conversion of 38 % at 10 min, and sharply decreased to 18 % at 20 min. Subsequently, conversion remained stable at 18 %, even at 8 h. These results are consistent with our previous findings[12)].

3. 2. Sintering of Pt Particles and Carbon Formation

TEM images of the fresh catalyst after reduction treatment and spent catalysts after DMS SMR tests for 0.5-8 h are shown in **Fig. 2**. Mean Pt particle diameter at 0.5 h was 3.6 nm after DMS SMR reaction, similar to the value of fresh catalyst. With longer reaction time, d_{mean} increased to *ca.* 8.0 nm at 4 h, and then remained at *ca.* 8.0 nm. After DMS-free SMR, d_{mean} was 3.5 nm at 8 h, the same as the fresh catalyst. These results revealed that DMS in the reaction gas promoted the sintering of Pt particles.

Conversely, no sintering of Pt particles was observed at 0-0.5 h during the period of rapid decline in CH_4 conversion. CH_4 conversion was stable after 0.5 h subsequent to sintering of the Pt particles. Therefore, the reason for the catalyst deterioration up to 0.5 h was sulfur poisoning of the catalyst[10),14),15),24)~28)] and not sintering of the Pt particles.

The effect of carbon formation on the catalytic activity was investigated. **Figure 3** shows the TPO profiles of the spent 1.0 wt% Pt/α-Al_2O_3 after DMS SMR for 0.5-8 h. The presence of carbon species oxidized at 673 K or lower (low temperature TPO peak) was confirmed in all spent catalysts. The amount of carbon species oxidized above 673 K (high temperature TPO peak) increased with longer reaction time.

Figure 4 shows the relationship between reaction time, d_{mean} values estimated by the TEM observations, and the amount of carbon estimated by the TPO profiles. Mean diameter of the Pt particles was propor-

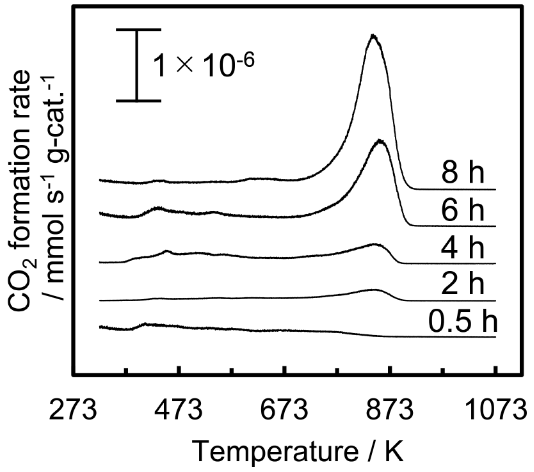


Fig. 3 TPO Profiles of the Spent 1.0 wt% Pt/α-Al_2O_3 Catalysts after DMS SMR

tional to the reaction time up to 4 h. No distinct sintering of the Pt particles was observed after 4 h reaction. The d_{mean} value stabilized at approximately 8.0 nm.

The amount of carbon formation (regardless of high/low temperature peaks) also increased with the reaction time. Formation of carbon that oxidized at low temperatures (circle in **Fig. 4(b)**) reached saturation in 4 h. On the other hand, formation of carbon oxidized at high temperature (square in **Fig. 4(b)**) accelerated after 4 h. Significant growth of carbon species oxidized above 673 K was observed in the spent catalysts after 6 h in the TPO profiles as shown in **Fig. 4**. Therefore, TEM observation of the spent catalyst after DMS SMR for 8 h was again investigated.

Figures 5(a) and **5(b)** show the TEM observations of the spent catalyst after DMS SMR at different locations in **Fig. 2(f)**. Whisker-like carbon species was observed on the Pt particles as shown in **Fig. 5(a)**. In contrast, almost no whisker-like carbon was observed in the spent catalysts in DMS SMR before 4 h. Therefore, the carbon species oxidized at high temperatures was identified as the whisker-like carbon species. The Pt particles covered by carbon deposits were remarkably sintered to 8.0 nm compared with those of the fresh catalyst (3.6 nm) as shown in **Fig. 5(b)**. Therefore, the formation of whisker-like carbon on the 1.0 wt% Pt/α-Al_2O_3 catalyst was closely related to the sulfur-poisoned alumina surface and the sintered Pt particles. However, further research is needed to elucidate why whisker-like carbon is produced on Pt under these conditions.

3. 3. Effect of Pt Loading Amount

Carbon formation during DMS SMR was strongly influenced by Pt particle size. Therefore, the effect of Pt loading was investigated. CH_4 conversions for DMS SMR and DMS-free SMR for 8 h over 0.1, 1.0, and 2.0 wt% Pt/α-Al_2O_3 catalysts are shown in **Fig. 6**. The open bar shows CH_4 conversion for DMS-free SMR, and the closed bar for DMS SMR. Catalyst deterioration for the 2.0 wt% Pt/α-Al_2O_3 catalyst was remarkable. Mean Pt particle diameter of the spent catalysts after DMS-free SMR with Pt loadings of 0.1, 1.0, and 2.0 wt% were 2.4, 3.5, and 4.2 nm, respectively. Mean Pt particle diameter of the spent catalysts after DMS SMR with Pt loadings of 0.1, 1.0, and 2.0 wt% were 2.2, 8.3, and 8.9 nm, respectively. This result suggested that the 0.1 wt% Pt/α-Al_2O_3 catalyst was resistant to sintering. In addition, Pt loading of 1 wt% and 2 wt% led to an increase in Pt particle size.

Figure 7 shows the TPO profiles of the 0.1, 1.0, and 2.0 wt% Pt/α-Al_2O_3 catalysts after DMS SMR for 8 h. The high-temperature TPO peaks increased with higher Pt loading. The TPO profile of the spent 0.1 wt% Pt/α-Al_2O_3 catalyst contained no peak after DMS SMR

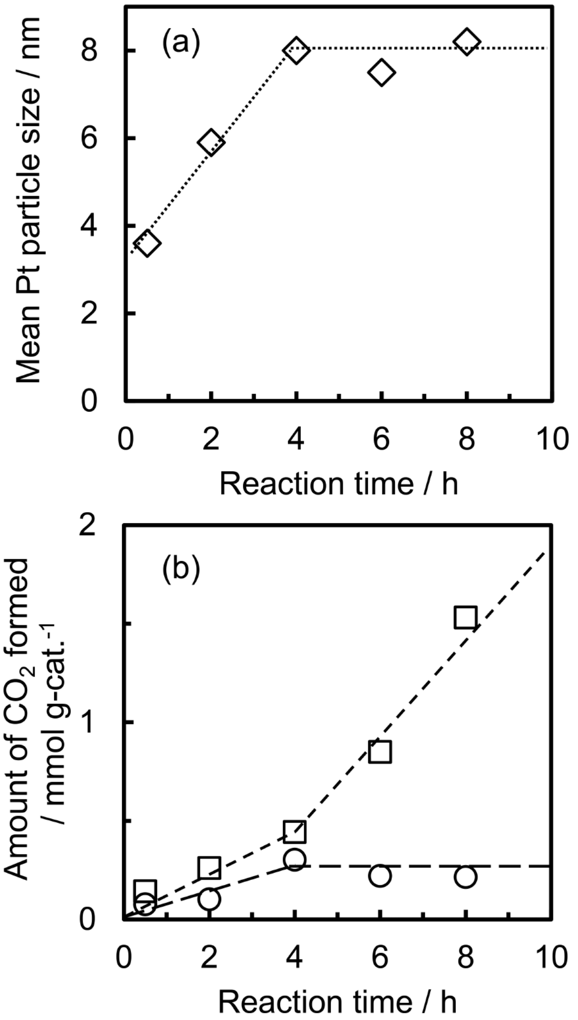


Fig. 4 Relationships between Mean Size of Pt Particles (a) and Amount of Carbon Formation (b) Calculated from Low-temperature TPO Peaks (circle) and High-temperature TPO Peaks (square) over the Spent 1.0 wt% Pt/α-Al_2O_3 Catalysts after DMS SMR

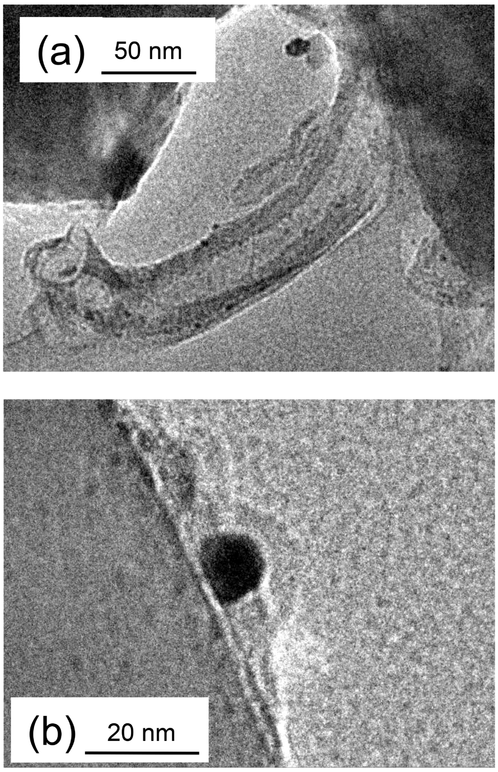
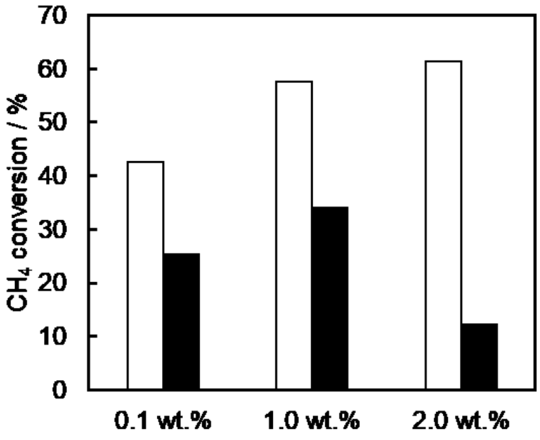


Fig. 5 TEM Images of the Spent 1.0 wt% Pt/α-Al_2O_3 Catalysts after DMS SMR for 8 h ((a) and (b))



SMR reaction conditions: 3.1 % N_2/27.7 % CH_4/69.2 % H_2O or 3.1 % N_2/27.7 % CH_4/69.2 % H_2O/10 ppm DMS, $T = 973$ K, time on stream = 8 h, total flow rate = 325 mL min^{-1}, and GHSV = 43,000 h^{-1}.

Fig. 6 CH_4 Conversion over Pt/α-Al_2O_3 Catalysts with Pt Loadings of 0.1, 1.0, and 2.0 wt% for DMS-free SMR (open) and DMS SMR (closed)

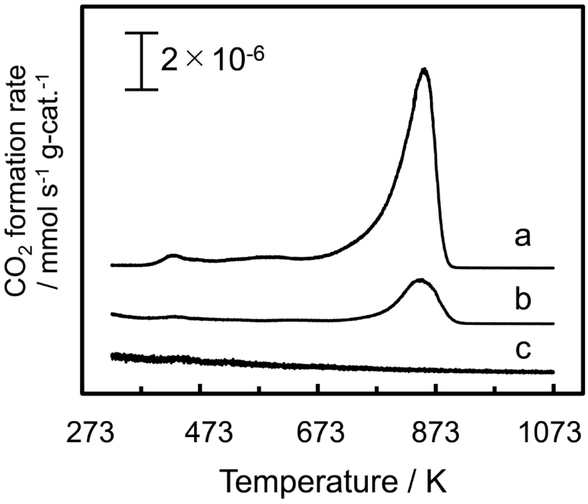


Fig. 7 TPO Profiles of the Spent 2.0 wt% Pt/α-Al_2O_3 (a), 1.0 wt% Pt/α-Al_2O_3 (b), and 0.1 wt% Pt/α-Al_2O_3 (c) Catalysts after DMS SMR for 8 h

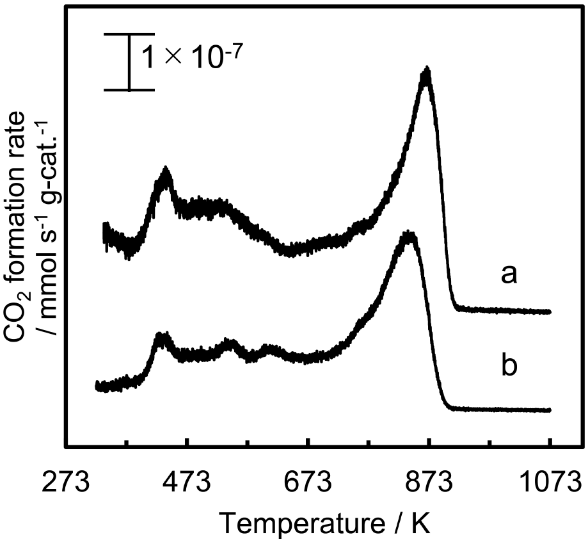


Fig. 8 TPO Profiles of the Spent 1.0 wt% Pt/α-Al_2O_3 Catalysts after DMS SMR for 2 h and DMS-free SMR for 24 h (a), and after DMS SMR for 2 h (b)

for 8 h, indicating that whisker-like carbon species was little formed on the Pt particles on this catalyst. Mean Pt particle diameter of the spent 0.1 wt% Pt/α-Al_2O_3 catalysts after DMS-free SMR and DMS SMR were almost the same. Therefore, no active sites for carbon formation were present on the 0.1 wt% Pt/α-Al_2O_3 catalyst.

3. 4. Formation of Whisker-like Carbon

We previously found that the decrease in SMR activity due to sulfur poisoning was temporary, and CH_4 conversion recovered completely after the supply of DMS was stopped in SMR[12]. DMS SMR was carried out for 2 h, and then was changed to DMS-free SMR. The degraded catalyst recovered similarly to spent catalyst after DMS-free SMR from the beginning at around 24 h after stopping the supply of DMS. **Figure 8** shows the TPO profiles of the spent catalysts in the degraded state after DMS SMR for 2 h and in the regenerated state after DMS-free SMR for up to 24 h. These

TPO profiles were almost the same, indicating no differences in the state of carbon species formed on the catalyst. Therefore, carbon formation is independent of the recovery of SMR activity.

3. 5. Active Sites for Carbon Formation

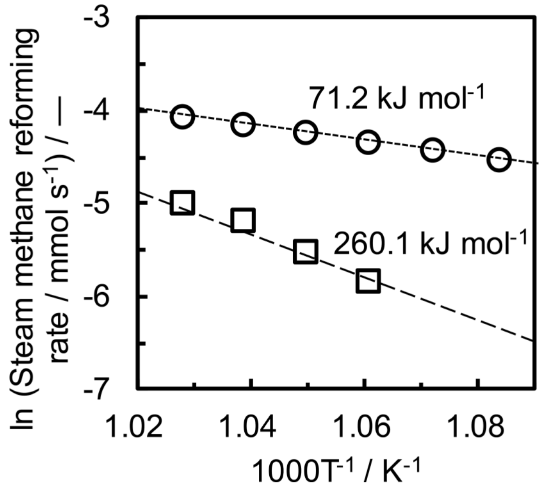
Sintering of Pt particles was observed only in the spent 1.0-2.0 wt% Pt/α-Al_2O_3 catalysts after DMS SMR. Pt particle size increased with longer reaction time. Therefore, sintering of Pt is irrelevant to SMR activity. Furthermore, formation of whisker-like carbon was observed as sintering proceeded, indicating that carbon formation is also independent of the SMR reaction. Therefore, the active sites that form the whisker-like carbon are located on the sintered Pt particles and only CH_4 decomposition occurs. Generally, the SMR mechanism is considered to involve first methane decomposition to form carbonaceous species, which are removed by oxygen-containing species activated on the support surfaces. Based on this mechanism, the carbon formation sites are located on the sintered Pt surfaces are far away from the support, so the supply of oxygen-containing species for deposited carbon removal is severely limited.

3. 6. Active Sites for SMR

DMS has the effect of primary poisoning but the adsorbed sulfur species can be desorbed easily in the absence of DMS[12)]. Indeed, adsorption of sulfur species was difficult to detect by analysis techniques such as CO chemisorption, XRD, XRF, and SEM-EDS of the spent catalysts. Therefore, the characteristics of the sulfur-poisoned catalyst were investigated by the apparent activation energy.

The Arrhenius plots of 0.1 wt% Pt/α-Al_2O_3 during DMS-free and DMS SMR are shown in **Fig. 9**. The activation energy was evaluated in the CH_4 conversion range of 17.6 to 28.4 % for DMS-free SMR, and in the CH_4 conversion range of 4.7 to 10.9 % for DMS SMR. The E_a in DMS-free SMR was 71.2 kJ mol^{-1}, close to the reported value[29)~31)]. In contrast, the E_a was 260.1 kJ mol^{-1} for DMS SMR, approximately 3.6 times as large.

These results indicate the presence of two different SMR active sites on Pt/α-Al_2O_3, located at the metal-support interface, and on the surface of the Pt metal. Dissociation of water occurs on the support and the formed oxygen-containing species reacts with the carbonaceous species dissociated on the Pt metal at the interface, leading to the high catalytic performance. The obtained E_a (71.2 kJ mol^{-1}) was almost the same as the reported value[29)~31)], implying that this mechanism of the interfacial reaction is predominant in the absent of DMS. However, poisoning by sulfur might temporarily block this site because the whole alumina surface containing with the metal-support interface site is poisoned by sulfur species. Alumina severely affected by sulfur results in decreased SMR activity due to the insufficient supply of oxygen-containing species obtained by water activation. The poisoned catalyst would recover if the DMS supply is stopped in the reaction gas due to easy desorption of sulfur species. Therefore, no sulfur species were detected directly on the catalyst.



SMR reaction conditions: 3.1 % N_2/27.7 % CH_4/69.2 % H_2O or 3.1 % N_2/27.7 % CH_4/69.2 % H_2O/10 ppm DMS, T = 923-973 K, total flow rate = 325 mL min^{-1}, and GHSV = 100,000 h^{-1}.

Fig. 9 Arrhenius Plots of 0.1 wt% Pt/α-Al_2O_3 Catalyst for DMS-free SMR (71.2 kJ mol^{-1}) and DMS SMR (260.1 kJ mol^{-1}) after Degradation

On the other hand, all primary reactions occur only on the Pt metal surface, resulting in low catalytic performance. The obtained E_a (260.1 kJ mol^{-1}) was very large, but the sites on the Pt surface were not poisoned by DMS. These findings show that the DMS in the reaction gas affects the adsorption of sulfur species on the whole alumina support surface. Additionally, the catalytic performance of Pt/α-Al_2O_3 was maintained at *ca.* 40 % at 973 K even after deterioration due to sulfur poisoning, because the SMR reaction proceeded only at the reaction site on the Pt surface. It is unclear whether oxygen-containing species are supplied from the sulfur-contaminated alumina support or whether oxygen-containing species are supplied on the Pt surface.

4. Conclusions

The effect of DMS on SMR over the Pt/α-Al_2O_3 catalyst was studied. The presence of DMS caused catalytic deterioration, sintering of Pt, and formation of whisker-like carbon. The whisker-like carbon species selectively accumulated on the sintered Pt metal particles, which are considered to be irrelevant to SMR activity. Examination of the effect of Pt particle size by changing the metal loading found that sintering of Pt metal particles and formation of carbon species occurred significantly during DMS SMR over 1.0 wt%

and 2.0 wt% Pt/α-Al_2O_3. In contrast, no sintering and formation of carbon species were observed over 0.1 wt% Pt/α-Al_2O_3.

The apparent activation energy for DMS-free SMR over 0.1 wt% Pt/α-Al_2O_3 was 71.2 kJ mol^{-1} and that for DMS SMR was 260.1 kJ mol^{-1}. Furthermore, catalyst deterioration caused by DMS completely recovered after stopping the DMS feed. Therefore, two different active sites are present on Pt/α-Al_2O_3 for SMR, one not affected by DMS and the other is temporarily deactivated by DMS. The main factor for the temporary deterioration of Pt/α-Al_2O_3 catalyst caused by DMS addition is the adsorption of sulfur species on the alumina surface blocking the interface sites of Pt and α-Al_2O_3.

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要　旨

硫黄を含むメタン水蒸気改質反応でのアルミナ担持白金触媒の炭素析出と活性点

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メタン水蒸気改質 (SMR) 反応を0.1～2.0 wt% Pt/α-Al_2O_3触媒を用いて10 ppmのジメチルスルフィド（DMS）を含む条件と含まない条件で行った。DMSを含む場合は初期に劣化が生じるが失活には至らなかった。DMSの供給を停止すると活性は完全に元に戻った。DMSを含むガスの場合は1.0～2.0 wt% Pt/α-Al_2O_3触媒上のPtはシンタリングして炭素析出を促進した。このシンタリングと炭素生成挙動はSMR反応と無関係であった。一方，Pt担持量が0.1 wt%だと炭素析出は起こらなかった。これらの結果からPt/α-Al_2O_3触媒上には三つの活性サイトが形成されたと考えた。一つ目はDMSの影響を受けない活性点，二つ目はDMSにより活性を失うがDMSの供給を停止すると完全に再生する活性点，三つ目はSMRの活性点ではなくシンタリングしたPtがメタン分解を促進して炭素を生成する活性点である。