Pt-Rh/CeO₂-Al₂O₃ for Controlling Emissions from Natural Gas Engines: Three-Way Catalytic Activity at Low Temperatures and Effects of SO₂ Aging

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Abstract The three-way catalytic activity of Pt-Rh/CeO₂-Al₂O₃ was examined at temperatures below 500 °C under conditions simulating gas engine exhaust, and the results were compared with those of O₂-CH₄, NO-O₂-CH₄, and NO-CH₄ model reactions. The catalyst exhibited sufficient three-way catalytic activity, even at 400 °C, in the absence of SO₂. After SO₂ aging, the activity under stoichiometric conditions remarkably decreased. In addition, methane conversion under rich (reducing) conditions severely decreased after SO₂ aging due to the suppression of steam methane reforming by sulfur poisoning.

Keywords Three-way catalyst (TWC) · Natural gas vehicle (NGV) · Platinum · Rhodium · Methane

1 Introduction

Among fossil fuels, natural gas produces the least carbon dioxide per unit of energy and is thus the most favorable in terms of environmental impact [1]. Recent advances in shale gas exploitation have significantly increased the supply of natural gas and stabilized the price of natural gas, increasing its attractiveness as a fuel [2]. Internal combustion engines fuelled by natural gas are widely used in natural gas vehicles (NGV), combined heat and power (CHP) plants, and gas engine-driven heat pump units (GHP). To control emissions from these engines, three-way catalyst systems similar to those used in gasoline-fuelled vehicles are widely applied. However, in contrast to gasoline engine exhaust, which contains a large amount of reactive hydrocarbons such as C₂H₄

and C₃H₆, the main hydrocarbon component in gas engine exhaust is methane [3]. Because methane is the least reactive hydrocarbon, obtaining a high methane conversion at low temperatures is the principal issue in controlling emissions from natural gas engines by three-way catalysts [4–6].

A Pt-Rh/CeO₂-Al₂O₃ catalyst with high Pt loading has been developed as a catalyst that exhibits high durability under the conditions of emission control from gas engines, with a reported long-term durability of more than 30,000 h [7–9]. However, with growing concerns about global warming and concomitant tightening of fuel efficiency regulations, further increases in the efficiencies of gas engines are sought, and efficiency improvement measures such as exhaust gas recirculation (EGR) are being intensively studied. Improvements in fuel efficiency inevitably cause a decrease in the exhaust temperature. This imposes a further challenge for controlling emissions from natural gas engines. The selective catalytic reduction of NO_x with methane (CH₄-SCR) coupled with lean combustion can be an alternative solution and has been studied extensively [10–15]. However, activities of the reported catalysts are not sufficient to obtain NO_x and CH₄ conversions required in practical applications.

A number of studies have examined three-way catalysts for natural gas engines and related reactions. Subramanian and coworkers extensively investigated model reactions (CH₄-NO-CO-H₂-O₂, CH₄-NO-CO-O₂, CH₄-O₂, CH₄-NO, etc.) over 1 % Pd/Al₂O₃ with different feedstream compositions, from reducing to stoichiometric to oxidizing atmospheres [16]. However, the temperature examined in their study was limited to 550 °C, and activity at lower temperatures was not examined. Oh and coworkers investigated methane oxidation over noble metal (Pt, Pd, Rh) catalysts supported on Al₂O₃ and CeO₂/Al₂O₃ with varying oxygen concentrations between 0.2 and 1 % [17, 18]. They observed that methane conversion was maximal at approximately stoichiometric oxygen concentrations and decreased under oxidizing conditions, concluding

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that the decrease in methane conversion under oxidizing conditions was due to strong adsorption of oxygen on the surface of the noble metals comprising the active sites. Burch and Ramli investigated NO reduction by CH₄ over Pt, Pd, and Rh catalysts supported on SiO₂ and Al₂O₃ [19, 20]. They determined that Pt had the highest activity, which was an order of magnitude higher than those of Pd and Rh. It was suggested that the relative activities of the catalysts reflected the ease of reduction of the catalysts. González-Velasco and coworkers investigated three-way catalytic reactions over Pt/Al₂O₃ in the presence of H₂O (10 %) and CO₂ (10 %), which are present in actual engine exhaust [21]. In a comparison of CH₄, C₂H₄, C₃H₆, and C₄H₈ as the hydrocarbon components, they demonstrated that a high hydrocarbon conversion of ca. 100 % was obtained under net oxidizing conditions when hydrocarbons other than CH₄ were used, while CH₄ conversion was very low except under slightly reducing conditions.

In this work, the three-way catalytic activity of a Pt-Rh/CeO₂-Al₂O₃ catalyst that is widely used in natural gas engines was investigated at relatively low temperatures (400–500 °C) under conditions simulating natural gas engine exhaust. The effects of S poisoning, which are expected to be severe at lower temperatures, were also examined.

2 Experimental

2.1 Catalyst Preparation

Commercial γ -Al₂O₃ (4- to 6-mm spheres, Kishida Chemical, Osaka) was crushed and sieved to 1- to 2-mm grains, which were impregnated with Ce (10 wt%) using an aqueous solution of cerium nitrate (Ce(NO₃)₃·6H₂O, Mitsuwa Chemicals, Osaka), followed by drying at 120 °C and calcining in air at 700 °C for 6 h to obtain a CeO₂-Al₂O₃ support.

The support was loaded with Pt (2.0 wt%) and Rh (0.2 wt%) by impregnation using Pt(NO₂)₂(NH₃)₂ (Kojima Chemicals, Tokyo) and Rh(NO₃)₃ (N.E. Chemcat, Tokyo) as precursors. The impregnated solid was dried at 120 °C and calcined in air at 550 °C for 6 h to obtain the Pt-Rh/CeO₂-Al₂O₃ catalyst.

2.2 Catalytic Activity Measurements

Catalytic activity was measured using a fixed-bed flow reactor. The catalyst grains (1.45 g, ca. 1.9 mL) were placed in a quartz tube (inside diameter 14 mm, length 740 mm) and heated with an electric furnace (ARF3-500, Asahi Rika, Chiba, Japan). The temperature of the catalyst bed was measured with a thermocouple inserted into the quartz tube. The reaction gas was prepared by mixing 5000 ppm NO/He, 3 % CH₄/He, 2 % CO, 1.2 % H₂/He, 30 ppm SO₂/He, O₂ (99.97 %, Takachiho Chemical, Tokyo), CO₂ (99.999 %, Takachiho

Chemical), and He (99.999 %, Iwatani Industrial Gases, Osaka) gases using mass flow controllers (HM5141B, Hemmi Slide Rule, Tokyo). Water vapor was introduced by passing a portion of the helium through a water saturator. The gas flow rate was 1.675 L/min, which corresponded to a gas hourly space volume (GHSV) of 53,000/h.

The feedstream compositions shown in Table 1 were used in the experiments under simulated gas engine exhaust conditions. The compositions were similar to those of actual gas engine exhaust, except the concentrations of CO₂ and H₂O, which were reduced for experimental accuracy. The O₂-CH₄, NO-O₂-CH₄, and NO-CH₄ reactions were also examined as model reactions for three-way catalytic reactions. All activity measurements were performed under a range of conditions from rich (reducing) conditions to lean (oxidizing). For activity measurements of model reactions, pretreatment with a gas containing 3000 ppm CO, 1800 ppm H₂, and 5 % H₂O in He for 10 min was conducted before measurements at each temperature.

The feedstream composition was maintained constant for 25 min before the effluent gas was analyzed. A pair of chemiluminescence NO_x analyzers (ECL-88A Lite, Anatec Yanaco, Kyoto) was used to measure NO_x concentrations. The NO_x concentration is the sum of the NO and NO₂ concentrations, and the NO_x conversion (X_{NO}) is calculated by the following equation, where the suffixes “in” and “out” indicate the concentrations at the inlet and outlet of the reactor, respectively.

$$X_{\text{NO}}(\%) = 100 \times \left\{ 1 - \frac{([\text{NO}]_{\text{out}} + [\text{NO}_2]_{\text{out}})}{([\text{NO}]_{\text{in}} + [\text{NO}_2]_{\text{in}})} \right\}$$

The concentrations of H₂, CO, CO₂, CH₄, O₂, and N₂O were measured by gas chromatography (GC-2014ATF and GC-8AIT, Shimadzu, Kyoto). Hydrogen was separated using a MS-13X column (16 m); O₂, N₂, and CO were separated using a MS-5A column (2 m); and CO₂ and N₂O were separated using a Gaskuropack 54 (4 m, GL Sciences, Tokyo). The concentration of each component was measured using a

Table 1 Feedstream compositions for activity measurements under conditions simulating gas engine exhaust. Concentrations of other components were maintained constant: CH₄ 1500 ppm, CO₂ 6 %, H₂O 11 %

λ	NO (ppm)	O ₂ (ppm)	CO (ppm)	H ₂ (ppm)
0.985	1400	3440	5000	3000
0.990	1600	3650	4200	2520
0.995	1800	3870	3400	2040
0.998	1920	3990	2920	1750
0.999	1960	4040	2760	1660
1.000	2000	4080	2600	1560
1.002	2080	4170	2280	1370
1.005	2200	4300	1800	1080

thermal conductivity detector (TCD). Methane was separated using a Gaskuropack 54 (2 m) and measured with a flame ionization detector (FID). The minimum detectable concentrations for gas chromatography were approximately 40 ppm for O₂, CO, CO₂, and N₂O; 200 ppm for H₂; and 5 ppm for CH₄.

In experiments under simulated exhaust conditions, catalytic activity was measured from 550 to 400 °C in intervals of 25 °C. After measurements at 400 °C, the catalyst was subjected to SO₂ aging by introducing a gas with a composition of 100 ppm NO, 1000 ppm CO, 600 ppm H₂, 3 ppm SO₂, 1500 ppm CH₄, 5 % O₂, 6 % CO₂, and 11 % H₂O balanced with He for 18 h (flow rate 1.675 L/min) while the temperature of the catalyst bed was maintained at 400 °C. The activity of the aged catalyst was measured from 400 to 550 °C in intervals of 25 °C. The catalytic activity in the model reactions was measured at 500 °C followed by 450 and 400 °C for the fresh catalyst and at 400 °C followed by 450 and 500 °C for the SO₂-aged catalyst. During activity measurements after SO₂ aging, 1 ppm SO₂ was added to the feedstream to avoid de poisoning of the catalyst.

To compare conversions under simulated exhaust conditions with those of the model reactions, the conversions were plotted against the air to fuel equivalence ratio (λ), which is widely used as a parameter for controlling internal combustion engines. The air to fuel equivalence ratio (λ) is defined as the ratio of the actual amount of air introduced into the combustion chamber to the amount of air that is required to completely combust the fuel. When the only exhaust hydrocarbon is CH₄, λ is calculated according to the following equation [5], where the concentrations (ppm) of the species are in brackets.

$$\lambda = 1 + ([\text{O}_2] + 0.5[\text{NO}] - 0.5[\text{H}_2] - 0.5[\text{CO}] - 2[\text{CH}_4]) / (1.91 \times 10^5)$$

2.3 Characterization

Specific surface area measurements were obtained with an automatic surface area analyzer (AMS-8000, Ohkura Riken, Tokyo). The adsorption of N₂ was measured at 77 K and $P/P_0=0.3$, and the Brunauer-Emmett-Teller (BET) surface area was calculated according to the one-point method. Measurements of CO adsorption were conducted using a pulsed-flow adsorption analyzer (R-6015, Ohkura Riken). Samples were pretreated under a H₂ flow at 200 °C for 30 min, and the adsorption of CO was measured at 50 °C.

Powder X-ray diffraction patterns were measured using Cu K α radiation on an X-ray diffractometer equipped with a graphite monochromator (XRD-6100, Shimadzu). The X-ray tube (PW2233/20, PANalytical) was operated at 40 kV and a current of 40 mA. The patterns were recorded over a 2θ range of 20° to 74° with a step size of 0.02°, a dwell time of 1.2 s, and a rotation speed of 50 rpm.

3 Results

Figure 1 shows the X-ray diffractograms of the support and the catalyst. In the X-ray diffractogram of the support, diffraction lines for CeO₂ at 28.6°, 33.1°, 47.5°, and 56.3° and for Al₂O₃ at ca. 67° were observed. No appreciable changes in these diffraction lines were observed after loading Pt-Rh or after activity measurements. Table 2 shows the BET specific surface areas and CO adsorption results. The changes in the BET surface areas were also small. These results suggest that the support itself was not essentially affected by the loading of Pt-Rh or the activity measurements. In the X-ray diffractogram of the catalyst, a broad diffraction line for metallic Pt was observed at ca. 40°. The intensity of this line increased after activity measurements, suggesting that the supported Pt agglomerated to form metallic Pt particles under the reaction conditions. A significant decrease in the amount of CO adsorbed was observed after activity measurements. The catalysts exhibited a larger decrease in the amount of CO adsorbed after SO₂ aging, which may indicate that sulfur promoted Pt agglomeration, but the adsorbed sulfur species that remained after pretreatment may have inhibited the adsorption of CO, reducing the amount of CO adsorption on the SO₂-aged catalysts.

Figure 2 shows the NO_x, CO, and CH₄ conversions under conditions simulating gas engine exhaust. Over the fresh (before SO₂ aging) catalyst at 550 °C, all of the NO_x, CO, and CH₄ conversions exceeded 99 % under stoichiometric conditions ($\lambda=1.000$). Under rich conditions ($\lambda<1.000$), CO conversion decreased, but high CH₄ conversion was maintained. By contrast, under lean conditions ($\lambda>1.000$), NO_x conversion sharply decreased, with an increase in λ accompanied by a slight decrease in CH₄ conversion. As the reaction temperature decreased, the NO_x and CH₄ conversions

Fig. 1 X-ray diffractogram of the support and catalyst. a) CeO₂-Al₂O₃, b) Pt-Rh/CeO₂-Al₂O₃, c) Pt-Rh/CeO₂-Al₂O₃ after reaction under simulated gas engine exhaust conditions, d) Pt-Rh/CeO₂-Al₂O₃ after reaction under model gas conditions without S aging, and e) Pt-Rh/CeO₂-Al₂O₃ after reaction under model gas conditions with S aging

Table 2 BET surface areas and amounts of CO adsorption on the support and catalysts

	BET surface area (m ² /g)	CO adsorption (mL/g)
CeO ₂ -Al ₂ O ₃	109	— ^a
Pt-Rh/CeO ₂ -Al ₂ O ₃		
As prepared	106	1.09
After activity measurements		
Under simulated exhaust	102	0.242
Under model reactions without S aging	105	0.466
Under model reactions with S aging	105	0.281

^a Not measured

decreased under stoichiometric conditions ($\lambda=1.000$), with NO_x and CH₄ conversions at 400 °C of 91 and 89 %, respectively. CH₄ conversion under lean conditions decreased remarkably at lower temperatures, and CH₄ conversion also decreased under rich conditions. Concomitant with the decrease in CH₄ conversion under rich conditions, the CO conversion under rich conditions increased. That is, when components in the effluent gas were compared at the same λ , the concentration of CH₄ increased and the concentrations of CO and H₂ decreased. At all temperatures between 400 and 550 °C, the reaction effluent contained H₂ at a concentration of 4000–6000 ppm at $\lambda=0.985$, higher than the H₂ concentration in the feedstream. These results suggest that H₂ was formed by steam reforming of CH₄. The concentration ratio of H₂/CO was 5.9 (550 °C)–17 (400 °C), which is nearly identical to the ratio in the chemical equilibrium of the water-gas shift reaction (6.1 [550 °C]–21 [400 °C]). The effect of SO₂ aging on NO_x and CH₄ conversion was remarkable at 500 °C and lower temperatures under stoichiometric conditions ($\lambda=1.000$). After SO₂ aging, NO_x and CH₄ conversions decreased to 72 and 70 %, respectively, at 400 °C. While the CH₄ conversion under rich conditions remarkably decreased after SO₂ aging, the CH₄ conversion under lean conditions was affected very little or slightly increased. The effluent from the

aged catalyst under rich conditions contained almost solely CH₄ as the reducing component, while the concentrations of H₂ and CO were very low or below the detection limits. The conversion of CH₄ at $\lambda=0.985$ –0.995 did not change appreciably with the reaction temperature, most likely because CH₄ conversion was determined by the feedstream composition and not the reaction rate. In fact, under conditions of $\lambda=0.985$ –0.995, the NO_x and O₂ conversions were ca. 100 % between 400 and 550 °C, and the observed CH₄ conversion corresponded to the calculated CH₄ conversion under the assumption that excess reducing components exit the reactor as methane (5, 36, and 68 % for $\lambda=0.985$, 0.990, and 0.995, respectively).

Figure 3 shows the N₂ yield from the activity measurements shown in Fig. 2. Over the fresh catalyst, the N₂ yield was in good agreement with the NO conversion under stoichiometric to lean conditions, which indicates that NO was converted to N₂ with high selectivity. By contrast, under rich conditions, the N₂ yield decreased significantly with decreasing λ . Under the experimental conditions, the large amount of CO₂ contained in the feedstream prevented precise determination of the effluent N₂O concentration, but formation of a large amount of N₂O can be ruled out. Therefore, NO that was not converted to N₂ most likely formed NH₃. After SO₂ aging, a decrease in the N₂ yield under rich conditions was not observed, and at 450 °C or higher, the N₂ yield was in good agreement with the NO conversion throughout the entire λ range examined. As mentioned above, the reaction effluent contained large amounts of H₂ before SO₂ aging but only small amounts of H₂ after SO₂ aging. Large amounts of NH₃ are formed in the NO-H₂ reaction over Pt catalysts under H₂-rich conditions [22]; the suppression of the formation of H₂, which is required to form NH₃, is likely responsible for the suppression of NH₃ formation after SO₂ aging.

Figure 4 shows the CH₄ conversion in the activity measurements under the simulated exhaust conditions as a function of temperature. Over the fresh catalyst, the CH₄ conversion at $\lambda=0.985$ was 82 % at 400 °C and increased with increasing reaction temperature, reaching 98 % at 500 °C.

Fig. 2 NO_x, CO, and CH₄ conversions over Pt-Rh/CeO₂-Al₂O₃ under gas engine exhaust conditions before (*upper column*) and after (*lower column*) S aging

Fig. 3 NO_x conversions and N_2 yields over Pt-Rh/CeO₂-Al₂O₃ under gas engine exhaust conditions before (*upper column*) and after (*lower column*) S aging

Under lean conditions ($\lambda=1.005$), the CH_4 conversion was 17 % at 400 °C, considerably lower than that under rich conditions. CH_4 conversion under lean conditions also increased with increasing reaction temperature but reached only 73 % at 500 °C and 92 % at 550 °C. The effects of SO_2 aging on CH_4 conversion were remarkably different under rich or lean conditions. Under lean conditions, SO_2 aging did not affect or slightly promoted CH_4 conversion. By contrast, SO_2 aging drastically suppressed CH_4 conversion under rich conditions. CH_4 conversion after SO_2 aging exhibited a maximum at 425 °C and decreased with increasing temperature up to 500 °C.

Figure 5 shows the CH_4 conversion in the O_2 - CH_4 reaction. Before SO_2 aging, a high CH_4 conversion was observed under stoichiometric and rich conditions. At $\lambda=1.000$, the CH_4 conversion was 91 % at 400 °C and ca. 100 % at 500 °C. At $\lambda=0.984$, the CH_4 conversion was 84 % at 400 °C and ca. 100 % at 500 °C. By contrast, under lean conditions, the CH_4 conversion decreased with increasing λ . At 400 °C, the CH_4 conversion fell to 16 % at $\lambda=1.010$. The feedstream composition at $\lambda=0.984$ was 1500 ppm CH_4 and 11 % H_2O balanced with He. Obviously, the CH_4 was converted solely by steam reforming under this condition, as demonstrated by H_2 formation. The reaction

effluent contained ca. 6000 ppm H_2 at 500 °C and ca. 5000 ppm H_2 at 400 °C, in agreement with the calculated H_2 concentrations assuming steam reforming and water-gas shift reactions (H_2 4 mol/mol- CH_4). In the presence of O_2 , the concentration of H_2 decreased, but H_2 formation was still observed (ca. 2000 ppm H_2 at 500 °C and $\lambda=0.995$, i.e., CH_4 1500 ppm, O_2 2000 ppm, 11 % H_2O).

The effects of SO_2 aging on CH_4 conversion in the O_2 - CH_4 reaction differed substantially under rich or lean conditions. Under rich conditions, CH_4 conversion was drastically suppressed, and H_2 formation became insignificant after SO_2 aging, indicating nearly complete suppression of steam reforming of CH_4 . By contrast, SO_2 aging did not significantly affect CH_4 conversion under lean conditions. The CH_4 conversion characteristics and the effects of SO_2 aging in the O_2 - CH_4 reaction resembled those under simulated exhaust conditions.

Figure 6 shows the NO_x and CH_4 conversions in the NO - O_2 - CH_4 reaction. Over the fresh catalyst, a NO_x conversion of 93 % and a CH_4 conversion of 93 % were obtained under stoichiometric conditions (2000 ppm NO , 2000 ppm O_2 , 1500 ppm CH_4) at 400 °C, in good agreement with the NO_x and CH_4 conversions under simulated exhaust conditions (91 and 89 %, respectively). After SO_2 aging, the NO_x and CH_4 conversions in the NO - O_2 - CH_4 reaction were also similar to those under simulated exhaust conditions.

Figure 7 shows the N_2 and N_2O yields in the NO - O_2 - CH_4 reaction. Over the fresh catalyst, the N_2 yield was in good agreement with the NO_x conversion under stoichiometric to lean conditions but decreased with decreasing λ under rich conditions. Because N_2O was not observed in the effluent under rich conditions, the NO_x that did not form N_2 was likely converted to NH_3 . After SO_2 aging, N_2O formation was observed at 400 °C, $\lambda=0.995$ (N_2O yield 7 %), but the N_2

Fig. 4 CH_4 conversions over Pt-Rh/CeO₂-Al₂O₃ as a function of temperature under gas engine exhaust conditions

Fig. 5 CH₄ conversions over Pt-Rh/CeO₂-Al₂O₃ in the O₂-CH₄ reaction. Reaction conditions: 1500 ppm CH₄, 0–5000 ppm O₂, 11 % H₂O

yield was otherwise nearly in agreement with the NO_x conversion. Similar to the results obtained under simulated exhaust conditions, the effluent from the fresh catalyst contained H₂ under rich conditions, with a H₂ concentration of ca. 2000 ppm at λ=0.995. These results indicate that the NO_x and CH₄ conversions and the N₂ yield in the NO-O₂-CH₄ reaction are in good agreement with those obtained under simulated exhaust conditions.

Figure 8 shows the NO_x and CH₄ conversions in the NO-CH₄ reaction. At 400 °C, λ=1.000, the NO_x conversion was 99.7 % over the fresh catalyst and 96 % over the SO₂-aged catalyst. At 450 and 500 °C, the NO_x conversion at λ=1.000 was ca. 100 % over both of the fresh catalyst and the SO₂-aged catalyst. These conversions are remarkably higher than those observed under simulated exhaust conditions or in the NO-O₂-CH₄ reaction. However, the NO_x and CH₄ conversions decreased under lean conditions. Under rich conditions, H₂ formation was observed over the fresh catalyst but not the SO₂-aged catalyst, which indicates that the fresh catalyst efficiently catalyzed steam reforming of CH₄ but was suppressed by sulfur poisoning. In these respects, the results of the NO-CH₄ reaction resemble those obtained under simulated exhaust conditions or in the NO-O₂-CH₄ reaction.

Figure 9 shows the N₂ yield from the NO-CH₄ reaction. Regardless of the reaction temperature and SO₂ aging, a high N₂ yield was obtained under stoichiometric conditions, but significant N₂O formation was observed under lean conditions. N₂O formation was observed at 400 and 450 °C after SO₂ aging. In particular, at 400 °C and λ=0.990, a large discrepancy was observed between the NO_x conversion and the N₂+N₂O yield, suggesting that a significant amount of NH₃ was formed.

Fig. 6 NO_x and CH₄ conversions over Pt-Rh/CeO₂-Al₂O₃ in the NO-O₂-CH₄ reaction. Reaction conditions: 2000 ppm NO, 1500 ppm CH₄, 1000–4000 ppm O₂, 11 % H₂O

4 Discussion

Many reactions proceed simultaneously over three-way catalysts under conditions of actual emission control, and the chemistry of three-way catalysis is complicated [23]. When methane is the only the hydrocarbon species in the feedstream, as was investigated in this study, and only N₂ is considered as a product of NO_x reduction, the following reactions contribute to exhaust purification:

Among these reactions, the reaction of NO (or O₂) and CO (or H₂) proceeds rapidly at temperatures of 300 °C or higher over noble metal catalysts. For example, Kobayashi and Taylor reported that NO reduction by H₂ over 0.5 wt% Pt/Al₂O₃ gave 50 % conversion of NO at 121 °C and that NO

Fig. 7 NO_x conversions and N_2 and N_2O yields over Pt-Rh/CeO₂-Al₂O₃ in the $\text{NO-O}_2\text{-CH}_4$ reaction before (upper column) and after (lower column) S aging. The reaction conditions were the same as in Fig. 6

reduction by CO over 0.5 wt% Rh/Al₂O₃ gave 50 % conversion of NO at 296 °C [24]. Oh and coworkers investigated the $\text{CO-CH}_4\text{-O}_2$ reaction over 0.2 wt% Pt/Al₂O₃ and 0.14 wt% Rh/Al₂O₃ catalysts. They observed complete conversion of CO at 200 °C over Pt/Al₂O₃ and at 400 °C over Rh/Al₂O₃ in an oxidizing feedstream and at 200 °C over both of Pt/Al₂O₃ and Rh/Al₂O₃ in a reducing feedstream [17]. By contrast, reactions involving CH_4 (reactions 6–8) proceed relatively slowly under the conditions used in this study (400–550 °C).

Steam reforming of CH_4 (8) is a highly endothermic reaction ($\Delta H^\circ = 206$ kJ/mol) and is controlled by a thermodynamic equilibrium under typical conditions for H_2 production from CH_4 . However, under the conditions examined in this study (1500 ppm CH_4 , 11 % H_2O , 6 % CO_2 , 400–550 °C), the equilibrium conversions of CH_4 are 99 % or higher, that is, the reaction is controlled by the reaction rate rather than the chemical equilibrium. The water-gas shift reaction (5) is a slightly exothermic reaction ($\Delta H^\circ = -41$ kJ/mol) and is controlled by a chemical equilibrium with H_2/CO ratios of ca. 6–20 under the conditions in this study (11 % H_2O , 6 % CO_2 , 400–550 °C).

Therefore, in the three-way catalytic reaction under the conditions of gas engine exhaust at low temperatures, reactions of NO (or O_2) and CO (or H_2) are completed in an upstream part of the catalyst bed, and the overall conversion

is determined by reactions involving CH_4 (i.e., reactions 6–8) and the equilibrium-controlled water-gas shift reaction (5). Accordingly, the NO_x and CH_4 conversions under simulated exhaust conditions were in good agreement with those in the $\text{NO-O}_2\text{-CH}_4$ reaction.

The methane conversion characteristics under the simulated exhaust conditions and in the $\text{NO-O}_2\text{-CH}_4$ reaction were in good agreement with those in the $\text{O}_2\text{-CH}_4$ reaction, and a large decrease with increasing λ under lean ($\lambda > 1$) conditions was observed for all reactions. It is widely accepted that the CH_4 oxidation activities of Pt and Rh catalysts are maximal at approximately stoichiometric conditions and decrease under lean conditions due to strong adsorption of oxygen onto the active sites [17, 18].

The effects of SO_2 aging were small under lean conditions, but the NO_x and CH_4 conversions under stoichiometric conditions decreased remarkably at 450 °C and lower temperatures, while CH_4 conversion decreased drastically under rich conditions. Ansell and coworkers investigated the effects of SO_2 aging on the three-way catalytic reactions over Pt-Rh/CeO₂-Al₂O₃ in simulated exhaust containing CH_4 and C_3H_8 [25]. They reported that CH_4 conversion under a lean condition of $\lambda = 1.02$ slightly increased after SO_2 aging, while CH_4 conversion under a rich condition of $\lambda = 0.98$ remarkably decreased after SO_2 aging. They concluded that the large

Fig. 8 NO_x and CH_4 conversions over Pt-Rh/CeO₂-Al₂O₃ in the NO-CH_4 reaction. Reaction conditions: 2000 ppm NO, 300–1500 ppm CH_4 , 11 % H_2O

Fig. 9 NO_x conversions and N_2 and N_2O yields over Pt-Rh/CeO₂-Al₂O₃ in the NO-CH₄ reaction before (upper column) and after (lower column) S aging. The reaction conditions were the same as in Fig. 8

decrease in CH₄ conversion was caused by suppression of steam reforming due to sulfur poisoning. They also reported that the CH₄ conversion of the SO₂-aged catalyst under rich conditions was maximal at 425 °C and decreased with increasing temperature up to 550 °C, in agreement with the results of the present study shown in Fig. 3. Taken together with the decrease in CH₄ conversion in the NO-O₂-CH₄ reaction and the reaction under simulated exhaust as well as in the O₂-CH₄ reaction, these results indicate that the decrease was caused by the suppression of steam reforming. The decrease in NO_x and CH₄ conversions under stoichiometric conditions after SO₂ aging may be explained as follows. Over the fresh catalyst, in addition to the reaction path in which CH₄ reacts directly with O₂ and NO, another path exists in which CH₄ is converted to H₂ and CO via steam reforming, and the subsequent H₂ and CO react with O₂ and NO. Because the latter path is inhibited by sulfur poisoning, the reaction of CH₄ is limited to direct reactions with O₂ and NO, which leads to decreased activity.

By contrast, the NO_x and CH₄ conversions under the simulated exhaust conditions and in the NO-O₂-CH₄ reaction were strongly affected by SO₂ aging and were not sufficient at 450 °C or lower temperatures, and NO_x and CH₄ conversions in the NO-CH₄ reaction at approximately stoichiometric conditions remained high even after SO₂ aging. The NO-CH₄ reaction over Pt/Al₂O₃ has been investigated by Burch and Ramli [19, 20] and by Balint and coworkers [26], but these reports mainly focused on experiments under rich conditions, and catalytic activity under stoichiometric conditions and the differences between the NO-CH₄ and the NO-O₂-CH₄ reactions remained unclear. The high NO_x and CH₄ conversion in the NO-CH₄ reaction under stoichiometric conditions observed in the present study may be explained as follows. Under stoichiometric conditions in the NO-O₂-CH₄ reaction,

O₂, which is present at high concentrations, strongly adsorbs onto active sites and prevents the reaction of CH₄ and NO. In the NO-CH₄ reaction, the absence of O₂ increases the number of active sites available for reaction. If it is possible to increase activity by removing O₂ in the reactant, a combination of oxygen storage materials (e.g., CeO₂) and suitable control of the air/fuel ratio may be effective for improving activity at lower temperatures. This effect may partly contribute to improved activity under periodic air/fuel control actually applied to automotive emission control systems [27–29]. However, an insignificant amount of N₂O, which has a high global warming potential, was formed in the NO-CH₄ reaction at low temperatures under both rich and lean conditions. Suppression of N₂O formation would be required to implement this strategy for improving low-temperature activity in practical applications.

5 Conclusions

This work demonstrates that Pt-Rh/CeO₂-Al₂O₃ exhibits sufficient three-way catalytic activity for controlling emissions from natural gas engines, even at 400 °C, in the absence of SO₂. However, the catalyst is sensitive to sulfur poisoning, and its activity is insufficient at temperatures of 450 °C or lower. The decrease in activity is mainly due to suppression of steam reforming of CH₄. Next-generation natural gas engines will have improved efficiencies, and the exhaust temperatures of these improved engines will be lower than those of current engines. Therefore, further catalyst improvements will be required to ensure low emissions from these improved engines, and the key issue will be to promote CH₄ conversion at low temperatures even in the presence of SO₂.

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