Study with Micro-reactor on Deactivation of Pd Methane Oxidation Catalyst for Marine Lean Burn Gas Engines*

Yoshifuru Nitta**
Koichi Hirata**

Yasuhisa Ichikawa**
Yudai Yamasaki***

Marine lean burn gas engines use natural gas as a fuel and contribute to reducing both NO_x and CO₂ emissions. On the other hand, the slipped methane which is the unburned methane emitted from the marine lean burn gas engines may have an impact on global warming. Palladium (Pd) catalysts for CH₄ oxidation are considered to be one of the most effective means to suppress the slipped methane from lean burn gas engines because they are still active in the lower exhaust gas temperature. However, recent studies have shown that water vapor (H₂O) inhibits CH₄ oxidation on these catalysts and deactivates their oxidation capacity. When using Pd catalysts for an exhaust gas aftertreatment in order to reduce the volume of slipped methane from lean burn gas engines, we need to overcome the issue of these catalysts deactivation at the time of higher H₂O concentration. This paper explored conditions necessary for sound operations of marine lean burn gas engines by investigating possible impacts of the temperature and composition of simulated exhaust gas and characterization of Pd catalysts on their CH₄ oxidation performance. Our case study also produced an appropriate geometric size as a design parameter for a CH₄ converter to be installed on a marine lean burn gas engine to reduce the slipped methane.

1. Introduction

In view of protection of marine environment, nitrogen oxides (NO_x), sulphur oxides (SO_x) and carbon dioxide (CO₂) as emissions on ships have been gradually suppressed by some mandatory regulations. In order to meet these strengthened emissions regulations, lean burn gas engines have been thus recently focused in the maritime industry to be installed in the gas fueled ships. Because they can use natural gas as sources of power and suppress NO_x, SO_x and CO₂ emissions. However, since methane is the main component of natural gas, the slipped methane may have been anxious about global warming. From the results of onboard measurements of emissions from lean burn gas engines installed in a cruise ferry operating in the Baltic Sea, high total hydrocarbons (THC) emission including CH₄ was confirmed. It is thus recommended that the use of after-treatment systems like oxidation catalysts can be one of available strategies to reduce the slipped methane in exhaust gas ¹⁾.

The Palladium (Pd) catalysts for CH₄ oxidation can provide one of the most feasible methods to suppress the slipped methane because they can show the most remarkable activity for CH₄ oxidation in the various CH₄ oxidation catalysts and activate in the lower temperature (under 773 K) which is partially achieved by the exhaust gas from the lean burn gas engine ²⁾. However, some studies have featured on inhibit effects by H₂O on CH₄ oxidation over Pd catalysts ³⁾. In order to apply the Pd oxidation catalysts for lean burn gas engines, the mechanism of the effects thus should be made clear. The possibility mechanism for the effects was proposed that hydroxyl accumulation derived from H₂O prevents oxygen migration and exchange processes on the support of catalysts ⁴⁻⁵⁾. Based on these observations, the part of CH₄ oxidation process on Pd catalyst was proposed that, in order to reoxidize Pd active sites, O₂ molecules dissociate on Pd sites and exchange with oxygen on the support. It was therefore confirmed that CH₄ oxidation activity was limited ⁶⁾.

When the Pd catalyst is applied to the CH₄ oxidation catalyst as after-treatment systems for marine lean burn gas engines, the inhibition effects

*Received September 18, 2018

**National Institute of Maritime, Port and Aviation and Technology

***The University of Tokyo

of H₂O for CH₄ oxidation on Pd catalyst therefore can be one of the biggest issues to be faced. In addition, in harbor or coastal area, because the lean burn gas engine is operated at partial load, the exhaust gas temperature can decrease. It can therefore be hard to maintain the high CH₄ oxidation activity of Pd catalysts in the exhaust gas due to high H₂O concentration and lower temperature.

Based on these discussions, if Pd catalysts are applied for the slipped methane reactor of marine lean burn gas engine, this paper explored conditions necessary for sound operations of marine lean burn gas engines by investigating possible impacts of the temperature and composition of simulated exhaust gas. In addition, Pd surface area was measured by volumetric CO chemisorption measurements to investigate the relationships Pd loading and CH₄ oxidation activity of Pd catalysts. Consequently, an appropriate geometric size as a design parameter of a CH₄ converter to be installed on a for marine lean burn gas engine to reduce the slipped methane is also produced by the case study.

2. Instrument and Equipment

2.1 Catalyst performance evaluation system

Figure 1 shows the schematic diagram of catalyst performance evaluation system. The micro-reactor can evaluate catalytic performance in simulated exhaust gas compositions by mixing gas. Gas compositions are nitrogen (N₂) and CH₄ from the cylinder gases, H₂O is supplied from distilled

Figure 1 Schematic diagram of the catalyst performance evaluation system

water vaporized in an evaporator, and oxygen (O₂) from compressed air. The flow rate of each prepared gas or distilled water is adjusted by a mass flow controller or a feed pump. Preheated simulated exhaust gas, mixed with water is led to the sample of catalyst set in the electric furnace, where CH₄ is converted. Gas is analyzed by the exhaust gas analyzer (Horiba, MEXA-FTIR 6000) at the inlet and outlet of catalyst. The temperature of catalyst inlet in the electric furnace can be set arbitrary within the temperature range of 473 to 773 K.

2.2 Catalyst sample

All Pd catalysts used in this study are conventional and commercialized for general chemosynthesis such as olefin hydrogenation. Three kinds of Pd catalysts which are 0.5, 1.0, 2.0 mass% of Pd coated and supported on a porous γ -Al₂O₃ ball ($\phi = 2\text{--}4$ mm) are prepared.

3. Experimental setup

3.1 Catalyst performance test

Table 1 shows the conditions of CH₄ oxidation performance test on the Pd catalysts. The gas compositions and concentrations are determined from the results of analysis of exhaust gas of a lean burn gas engine. Comparing with a diesel engine, because the exhaust gas from lean burn gas engine contains higher H₂O concentration due to high H/C ratio of CH₄, it can be hard that Pd catalyst exhibits high CH₄ oxidation performance. This study therefore focused on CH₄ oxidation performance of Pd catalyst in 10% of H₂O concentration. In order to measure the difference of CH₄ concentration clearly, gas hourly space velocity (*SV*) is 50000 1/h. Total volume flow rate is set to approximately 13 L/min to exceed the required flow rate of the exhaust gas analyzer.

Table 1 Conditions of catalyst performance test

Gas composition	Dry	Wet
CH ₄ [ppm]	2500	
O ₂ [%]	10	
H ₂ O [%]	-	10
N ₂	balance	

CH₄ oxidation performance is estimated by using methane conversion (η) defined as a following equation:

$$\eta = 1 - \frac{C_{outlet}}{C_{inlet}}, \quad (1)$$

where C_{inlet} and C_{outlet} indicate CH₄ concentrations at the inlet and outlet of catalyst.

3.2 Catalyst characterization

In order to consider the relationships Pd loading and CH₄ oxidation activity of Pd catalysts, the relationship between Pd loading and active sites where CH₄ oxidation reaction is preceded was investigated. The active sites are represented by Pd surface area. To measure Pd surface area of the samples in this study, volumetric CO chemisorption (V_{co}) on Pd surface area was measured by CO pulse chemisorption¹⁰⁾. The CO pulse chemisorption were carried out in a BEL-METAL-3 (MicrotracBEL Corp.). The samples were pretreated in accordance with the Ref¹⁰⁾. The Pd surface area (A_m) and CO chemisorbed particle size (d_{co}) can be determined by following equations, using a stoichiometry of Pd/CO=1 because it is assumed that all adsorption sites for the chemisorbed CO are still occupied¹¹⁾.

$$A_m = \frac{V_{co} \cdot 6.02 \times 10^{23} \cdot \sigma_m \times 10^{-18}}{22414 \cdot m_c}, \quad (2)$$

$$d_{co} = \frac{6000}{\rho A_m}, \quad (3)$$

where σ_m is cross-sectional area per atom of Pd: 0.0787 nm², ρ is density of Pd: 12.02 g/cm³¹¹⁾. In addition, in order to confirm the accuracy of d_{co} , the Pd particle size on the Pd catalysts were also

analyzed by an XRD (X ray diffraction) analysis instrument (Rigaku, RINT-2550VB1L). Measurement conditions and analysis of the diffraction pattern to identify the peaks of Pd are based on the Ref.⁷⁾ XRD analyzed particle size (d_{XRD}) was estimated from the Scherrer equation which relates the crystallite size to the width of a given peak at integral breadth⁸⁻⁹⁾. Polyvinylpyrrolidone (PVP)-protected Pd nanocolloid (Tanaka Kikinzoku Kogyo K.K.), which have 4 nm as the mean particle size of Pd, was analyzed by XRD as a reference sample for the validation of d_{XRD} of Pd particles.

4. Results and Discussion

4.1 Catalytic activity tests

To confirm the effects of water vapor on the CH₄ oxidation activity of Pd catalysts, the CH₄ conversion at steady state in the micro reactor was investigated by using the simulated exhaust gas of a lean burn gas engine. Figure 2 shows the light-off curves, the relationships between temperature and η over 0.5 mass%, 1.0 mass% and 2.0 mass% Pd/Al₂O₃ in dry and wet conditions. The tests were conducted in twice for each condition and the plots in the figure mean the average. The maximum error of η was within 5 percentage point, but the

Figure 2 Light-off curves of CH₄ oxidation activity over Pd catalysts with/without H₂O

maximum error of CH₄ concentration was in the measurement error margin. The H₂O concentration of wet condition is set to 10 %. This graph shows that, in the dry condition, the methane conversion started at 473 K and η reached to approximately 80% at 573 K for all the Pd catalysts. In addition, 2.0 mass% Pd/Al₂O₃ show the highest activity at the same temperature with the amount of Pd on the catalyst increased. On the other hand, in the wet condition, the light-off curves shifted to approximately 100 K higher temperature than those in the dry condition. 2.0 mass% Pd/Al₂O₃ also show the highest activity in the wet concentration. It is indicated that, in the wet condition, Pd catalyst exhibited the similar tendency and the light-off curves shifted to higher temperature with increased H₂O concentration¹²⁾. It is also reported that the inhibition effects distinguished at the temperature under 723 K due to a low H₂O desorption rate because the adsorption and desorption of H₂O from the Pd catalyst surface reaches equilibrium at temperature above 723 K¹³⁾.

If the Pd catalysts are applied to the slipped methane reactor for the marine lean burn gas engine as marine power system, this inhibition effects by H₂O vapor can bring several difficulties to reducing the slipped methane of marine lean burn gas engine. Because exhaust gas temperature of 4-stroke lean burn gas engines can attain approximately 673 K in high load condition, the CH₄ oxidation activity of Pd catalysts can be little influenced by the inhibition effects. However, when the 4-stroke lean burn gas engine is operated at partial load in the coastal area or the large bore 2-stroke lean burn gas engine is installed to achieve the higher efficiency, the exhaust gas temperature can decrease less than 673 K. It can therefore be hard to maintain the high CH₄ oxidation activity of Pd catalysts.

3.2 Cylinder pressure and temperature

In order to compare catalytic activity of the Pd catalysts, the inhibition effects on CH₄ oxidation activity of Pd catalysts were evaluated based on kinetic analysis. In lean burn gas engine exhaust gas condition, CH₄ oxidation process on Pd catalyst depends on a following reaction:

In this study, it is assumed that difference of O₂ concentration is negligible because the order of CH₄ concentration (ppm) is much lower than that of O₂ concentration (%). CH₄ oxidation rate is thus defined as a pseudo-first order approximation and indicated in a following equation:

$$\frac{d[CH_4]}{dt} \approx -k[CH_4]. \quad (5)$$

The kinetic constant is obtained from the results of light-off curves, using a following equation:

$$k = -SV \ln(1 - \eta). \quad (6)$$

In addition, the kinetic constant is also analyzed by Arrhenius plots to determine the kinetic parameters, fitting to the following Arrhenius equations:

$$k = k_0 \exp\left(-\frac{E}{R T}\right), \quad (7)$$

$$\ln(k) = -\frac{E}{R T} + \ln(k_0). \quad (8)$$

Figure 3 shows the Arrhenius plots of CH₄ oxidation activity on Pd catalysts in the dry and wet conditions. In the same figure, all the plots show the average of experimental results in each condition and the solid lines are fitting results by the equation (8). For each Pd catalyst, the Arrhenius plots can be fitted to the linear function and all the correlation coefficients is over 0.97. The results thus explain that the assumption, in which CH₄ oxidation process is regarded as the pseudo-first order approximation, is suitable and other oxidation processes can be negligible.

Figure 3 Arrhenius plots of CH₄ oxidation activity on Pd catalysts in the dry and wet conditions

In addition, Table 2 also demonstrates the results of the kinetic parameters obtained from the fitting to equation (8). The same table shows that activation energy and k_0 are decreased with increasing Pd load. The results can explain that, because Pd active sites where is CH₄ reacted with O₂ are increased, CH₄ oxidation activity is increased with increasing Pd loading. Moreover the same table presented that activation energy was not influenced by H₂O vapor. On the other hand, the same table shows that, with increasing Pd load, frequency factor is decreased. The results can account that, because activation energy is decreased, the required CH₄ concentration to maintain k_0 is decreased. However, it is remarkable that, because k_0 was sharply dropped in wet condition, k_0 was influenced by H₂O vapor.

Table 2 Kinetic parameters of methane oxidation

	Pd loading [mass %]	E [kJ/mol]	k_0 [1/h]
dry	0.5	110(±2)	6.67×10^{14} (±17%)
	1.0	100(±2)	1.04×10^{14} (±28%)
	2.0	96(±4)	6.81×10^{13} (±54%)
wet	0.5	107(±9)	8.57×10^{12} (±80%)
	1.0	101(±6)	4.43×10^{12} (±67%)
	2.0	98(±2)	4.07×10^{12} (±35%)

4.3 Characterization of Pd catalysts

To confirm the relationships Pd loading and active sites of Pd catalysts in this study, volumetric CO chemisorption measurements by the CO pulse chemisorption were carried out. Figure 4 shows the relationships between Pd loading, A_m and V_{co} .

The measurements were conducted in twice for each condition and the plots in the figure mean the average. The maximum error in all the results was within 5% for the each average value. The same figure explains that A_m and V_{co} are increased with increased Pd loading. The order of Pd surface area is similar to that in the article¹⁴⁾. In addition, in order to valid the results of Pd surface area, XRD analyzed particle size of Pd catalysts are examined. The results are shown in Table 3. The measurements were conducted in twice for each condition and the values in the same table mean the average and its error exhibits in the parenthesis.

Figure 4 Relationships between Pd loading, Pd surface area and volumetric CO chemisorption

Table 3 Comparisons of Pd particle size on Pd catalysts

Pd loading [mass %]	d_{co} [nm]	d_{xrd} [nm]
0.5	4.3(±0.1)	3.7(±0.2)
1.0	4.2(±0.1)	3.5(±0.1)
2.0	4.4(±0.0)	4.6(±0.1)

In addition, in order to valid the results of Pd surface area, XRD analyzed particle size of Pd catalysts are examined. The results are shown in Table 3. As the validation of XRD analyzed particle

size of Pd, PVP-protected Pd as the reference sample which have 4 nm as the mean particle size of Pd, was analyzed by XRD. The same table indicated that, because XRD analyzed Pd particle size of PVP-protected Pd was 3.8 (± 0.05) nm, the estimations of XRD analyzed particle size and CO chemisorbed particle size on the Pd catalysts can be reasonable, respectively.

4.4 Case studies on CH₄ oxidation converter

If Pd catalysts are applied to CH₄ oxidation catalysts in the slipped methane reactor for the marine lean burn gas engine, it is useful for the decision of design and arrangements in machinery space in the gas fueled ships that the geometric size of the slipped methane reactor is considered by using the kinetic parameters obtained from this study. In this section, when the Pd catalysts using in this study is applied to CH₄ oxidation catalysts in the slipped methane reactor as an after-treatment system of exhaust gas of 400 kW lean burn gas engine with pre-chamber spark ignition^[15], the case study was examined.

Table 4 shows specifications of the 4-stroke lean burn gas engine with a turbocharger, using for this case study. Operation condition is set as a full load condition; the output is 400 kW at 1800 min⁻¹.

Table 4 Model engine for the case study

Maker/Model	YANMAR/AYG20L-SE
Type	4-stroke cycle gas engine
Cylinders	6
Bore/ Stroke [mm]	155/ 180
Fuel	City gas
Output [kW]	400
Speed [min ⁻¹]	1800

In this condition, the temperature of outlet of turbo charger is approximately 643 K and the volume rate of exhaust gas is approximately 2000m³/h (normalized at 273 K, 101 kPa). To estimate the required volume of Pd catalysts in this condition, the equation (7) is substituted for equation (6) to get required SV as a following equation (9):

$$SV = \frac{-k_0 \exp\left(-\frac{E}{R T}\right)}{\ln(1-\eta)} \quad (9)$$

Based on the equation (9) and the kinetic parameters of three Pd catalysts using in this study, the required SV (SV_c) and volume of Pd catalysts (V_c) which attain 80% reduction of CH₄ ($\eta=0.8$) in wet exhaust gas in this condition, can be estimated. Table 5 shows the results of SV_c and V_c in this condition for three Pd catalysts.

Table 5 Required SV and volume of Pd catalysts

Pd loading [mass%]	SV_c [1/h]	V_c [m ³]
0.5	9000	0.22
1.0	18000	0.11
2.0	27000	0.07

The same table explains that 0.5 mass% Pd catalyst requires 3 times as catalysts volume as 2.0 mass% Pd catalyst in comparisons between 0.5 mass% and 2.0 mass% of Pd catalysts. It is noted that the results of V_c means the minimum volume of required volume of catalyst in this condition because other parameters, such as geometry of catalysts, back pressure or temperature difference between inlet and outlet of catalysts, are not considered in this stage. In actual design of the slipped methane reactor, it needs therefore further consideration.

5. Conclusion

The authors investigated on the CH₄ oxidation activity of Pd catalysts to reduce the slipped methane from marine lean burn gas engines, dealing with global warming. This study indicated that the issues in operations of marine lean burn gas engine when Pd catalysts are applied for the slipped methane reactor of marine lean burn gas engine, through the investigation of CH₄ oxidation performance and characterizations of Pd catalyst. The main findings in this paper can be summarized as follows:

- (1) Pd catalysts have a potential of CH₄ oxidation activity in the temperature of exhaust gas from lean burn gas engine. On the other hand, in the wet condition, the light-off curves of CH₄ oxidation reaction shifted to approximately 100 K higher temperature than those in the dry condition. It can be therefore hard to maintain the high CH₄ oxidation activity when the marine lean burn gas engine is operated at partial load or its bore size is larger.
- (2) The results of kinetic analysis conducted the equation to estimate the required volume of Pd catalysts when considering geometric size as a designed parameter of the CH₄ converter using Pd catalyst for marine lean burn gas engine to reduce the slipped methane.
- (3) The case study which was the consideration of geometric size of CH₄ converter for lean burn gas engine to reduce the slipped methane at 643 K, revealed that 0.5 mass% Pd catalysts required the 3 times larger catalyst space than that of 2.0 mass% Pd catalyst.

In near future, the power systems in the gas fueled ships are hoped to be installed CH₄ oxidation catalysts to reduce total amount of GHG. Because Pd catalyst have a high CH₄ oxidation activity, it can be suitable as CH₄ oxidation catalyst for reduction of methane slip from marine lean burn gas engines installed in the gas fueled ship. On the other hands, Pd catalysts need further investigation to clarify the mechanism and countermeasures for the inhibition effects by H₂O vapor.

Acknowledgments

We would like to express grateful thanks to Dr. Hidenori Sekiguchi for your considerable efforts and helpful discussions.

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k_0	Pre-exponential factor, [1/h]
E	Activation energy, [kJ/mol]
R	Gas constant, [kJ/mol K]
T	Absolute temperature, [K]
SV_c	Required SV for 80% reduction of CH_4 in wet exhaust gas, [1/h]
V_c	Required volume of Pd catalysts for 80% reduction of CH_4 in wet exhaust gas, [m ³]

subscript

<i>outlet</i>	: At the outlet of catalyst
<i>inlet</i>	: At the inlet of catalyst
<i>XRD</i>	: XRD analyzed
<i>CO</i>	: CO chemisorbed
<i>c</i>	: Catalyst

Nomenclature

SV	Gas hourly space velocity, [1/h]
η	CH_4 conversion [-]
C	CH_4 concentration at the outlet of catalyst, [ppm]
d	Particle size [nm]
V_{co}	Volumetric CO chemisorption, [cm ³ /g]
A_m	Pd surface area, [m ² /g]
m_c	Mass of catalysts of Pd [g]
σ_m	Cross-sectional areas per atom of Pd, [nm ²]
ρ	Density of Pd, [g/cm ³]
k	Kinetic constant, [1/h]