Oxidation Catalysts for Natural Gas Engine Operating under HCCI or SI Conditions

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ABSTRACT

Oxidation catalyst performances are studied under HCCI (Homogeneous Charge Compression Ignition) and SI (Spark ignited) conditions using a model gas reactor and with natural gas fuelled HCCI and SI engines. The characteristic emissions of HCCI engines are high levels of CO and hydrocarbons, and temperatures as low as 120°C. Conventional oxidation catalysts typically light off at around 200°C, well above these temperatures. The oxidation catalyst for a HCCI engine is required to be active at low temperature, and be durable. Test results will be shown for bench-scale experiments for a series of catalyst formulations. Some catalyst formulations show excellent performance. The HCCI-tailored catalyst exhibits complete conversion of CO under HCCI engine emission conditions with various loads. Under SI conditions, high conversion efficiencies are observed for methane and non-methane hydrocarbons.

INTRODUCTION

Homogeneous charge compression ignition (HCCI) is receiving attention as a new low-emission engine concept. The ignition process in an HCCI engine involves homogeneously premixing the fuel with air in the combustion chamber where the lean mixture is ignited when the piston reaches top dead center (TDC) during the compression stroke. The ignition of the mixture occurs evenly throughout the fuel/air mixture. The flame burns cooler and causes reductions in NOx and particulate matter (PM) emissions. Compared with spark-ignited (SI) gasoline engine, HCCI engines possess a higher thermal efficiency due to the higher compression ratio and its leaner operation. However, several technical barriers must be broken through before HCCI can be implemented in production engines. The largest challenge is to control its smooth and stable operation within the narrow limits between misfiring and knocking [1-3]. Due to the intrinsic constraints, the HCCI combustion can be confined within a relatively small region in the map of load versus speed [4].

HCCI-SI dual-mode combustion system is commonly adopted to expand the operating range of a HCCI engine. An HCCI-SI dual mode combustion system can achieve high mean effective pressure by operating as a conventional SI engine at high loads, and can improve fuel economy by operating in HCCI mode at lower loads.

Low combustion temperatures during HCCI operation result in high levels of CO and hydrocarbons emissions as well as low exhaust temperature. The HCCI combustion generally operates at a very lean charge in order to avoid engine damage and to increase the compression ratio. Therefore, the low combustion temperatures cause incomplete burning of fuel, which leads to high level of CO and HC (hydrocarbon) emissions. The exhaust temperature of HCCI engines remains a concern to the CO and hydrocarbons abatement. The exhaust temperatures of HCCI engines could be extremely low, typically between 125°C and 175°C for idle and 25% load, respectively. Traditionally, oxidation catalysts are used to reduce CO and HC emissions; they typically have higher light-off temperatures (~50°C higher). The challenge is to design a highly active oxidation catalyst with long durability and at a low cost.

The light hydrocarbons content can be up to 10,000 ppm at idle if the HCCI combustion is fuelled with natural gas. The current catalyst technology cannot perform methane oxidation at HCCI exhaust temperatures. However, methane and non-methane hydrocarbons (NMHCs) abatement is possible at SI mode of such engine, at which the exhaust temperature is generally higher than 400°C. It is generally recognized that Pd-based catalysts are poisoned by sulfur, phosphorous etc [5]. The PdO active sites would form Pd-SO$_4$ in the presence of SO$_2$ at ppm level [6-10]. The metallic contaminants, such as Zn and Ca, could mask the active sites and deactivate the catalyst. The origin of these metals is the inorganic remainder of the lubricant oil additives [5, 11-13]. Platinum-based catalyst is not sensitive to sulfur, but it is not as active as Pd catalyst for methane and NMHCs oxidation.
In order to develop catalysts for natural gas fuelled engine operated with HCCI-SI dual-mode combustion system, the catalytic performance of Pt-based, Pd based, and PtPd bimetallic catalysts were systematically investigated in this paper using a model gas reactor equipped with a Fourier Transform Infrared Spectrometer (FTIR). The impact of NO on CO oxidation activity was studied. The catalysts were then poisoned by sulfur dioxide and deactivated at 750°C to investigate their stability and durability. Some of the catalysts were tested using Yanmar natural gas engine. In addition, PtPd-based catalysts are investigated to perform methane and NMHCs abatement at temperatures above 350°C. It is demonstrated by a spark-ignited, Yanmar natural gas engine that the PtPd-based catalyst formulations exhibits excellent activity for methane and NMHCs abatement.

EXPERIMENTAL

A model gas reactor and a Yanmar natural gas fuelled engine, operated with HCCI, SI or HCCI + SI mode, are employed to evaluate the catalysts. The catalysts can be classified as Pt, Pd and PtPd-based formulations, which are designed for HCCI and SI engines.

Exhaust gas conditions were simulated using a model gas reactor. The gas compositions are listed in Table 1. The space velocity based on substrate volume is maintained at 100,000 h⁻¹. The temperatures before and after the catalyst are monitored with two thermocouples. The inlet temperature is taken as the reaction temperature in the light-off curve presented later. Prior to entering the reactor, the bulk-premixed gases were preheated to more than 150°C. Water was added using a peristaltic pump after the preheater. The length of tube from the pre-heater to the reactor was heated to more than 100°C using heating tape to prevent condensation of the water. The tubing from the reactor to the exhaust gas analyzer (FTIR) was heated to about 150°C to prevent water condensation. Gas pressure was maintained at around 1 atm over the catalyst.

The wall reaction over the stainless steel reactor was investigated with a uncoated substrate prior to the experiments. No significant wall reaction was observed except for slight CO and NO oxidation at temperatures more than 400°C. The maximum CO conversion is 30% at 550°C for blank tests under the investigated reaction conditions. The maximum NO oxidation was less than 3% observed at 550°C, which was likely gas phase reaction.

The experimental engine setup is shown in figure 1. The specifications of the test engine are shown in Table 2. A 4-stroke 4-cylinder Yanmar natural gas engine, having a displacement of 3.3 liters, was modified for HCCI, SI and HCCI + SI operation. Under HCCI mode the engine was operated with wide-open throttle and intake mixture temperature control (designated HCCI without throttle). Under SI mode, the engine was operated with throttle control, spark ignition and without intake air mixture heating (designated spark ignition with throttle). Under HCCI + spark ignition mode engine operation was with throttle control, intake mixture temperature control and spark ignition (designated HCCI + SI with throttle). The catalyst is located at the exhaust silencer. Further details on the test engine are described in previous papers by Ohtsubo et al [1-3].

### Table 1. Model gas composition (SV=100,000 h⁻¹).

<table>
<thead>
<tr>
<th>Component</th>
<th>Lean</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₄</td>
<td>1000 ppm</td>
</tr>
<tr>
<td>C₂H₆</td>
<td>150 ppm</td>
</tr>
<tr>
<td>C₃H₈</td>
<td>50 ppm</td>
</tr>
<tr>
<td>CO</td>
<td>1000 ppm</td>
</tr>
<tr>
<td>*NO</td>
<td>100 ppm</td>
</tr>
<tr>
<td>O₂</td>
<td>10%</td>
</tr>
<tr>
<td>H₂O</td>
<td>5%</td>
</tr>
<tr>
<td>CO₂</td>
<td>5%</td>
</tr>
<tr>
<td>**SO₂</td>
<td>0</td>
</tr>
<tr>
<td>N₂</td>
<td>Balance</td>
</tr>
</tbody>
</table>

Note: *NO is 100 ppm unless specified. **SO₂ is 100 ppm during poisoning.

The test fuel is commercial natural gas that is purchased from Osaka Gas Co, and its composition is shown in Table 3. Exhaust emissions are measured by model NBY701DERG that is made by Best Sokki. NOₓ is measured by a chemiluminescent analyzer. CO and CO₂ are determined by TCD. THC is measured by FID. O₂ is measured by a paramagnetic analyzer. Water in exhaust gas is removed using an electrical cooler. However THC is measured under wet condition. Supplied intake air is always kept at 25°C with a relative humidity of 60% to maintain NOx content.

### Table 2. Engine specifications

<table>
<thead>
<tr>
<th>Engine Type</th>
<th>4-cylinder Water cooled</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cylinder Bore × Stroke</td>
<td>98mm × 110mm</td>
</tr>
<tr>
<td>Engine swept volume</td>
<td>3319cm³</td>
</tr>
<tr>
<td>Combustion chamber</td>
<td>HCCI, Spark ignition</td>
</tr>
<tr>
<td>Compression ratio</td>
<td>25, 12</td>
</tr>
<tr>
<td>Intake air temperature</td>
<td>~80deg C, 25deg C</td>
</tr>
</tbody>
</table>

### Table 3. Natural gas composition

<table>
<thead>
<tr>
<th>Component</th>
<th>Concentrations</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₄</td>
<td>88 vol%</td>
</tr>
<tr>
<td>C₂H₆</td>
<td>6 vol%</td>
</tr>
<tr>
<td>C₃H₈</td>
<td>4 vol%</td>
</tr>
<tr>
<td>n-C₄H₁₀</td>
<td>2 vol%</td>
</tr>
<tr>
<td>*CH₃-S-CH₃</td>
<td>1.8 ppm</td>
</tr>
<tr>
<td>*(CH₃)₂C-SH</td>
<td>1.2 ppm</td>
</tr>
</tbody>
</table>

Note: *Gas odorant.
RESULTS AND DISCUSSION

The catalytic performance of Pt, Pd and PtPd based catalysts was first investigated to choose the active components of the catalysts for CO or hydrocarbon abatement. The catalyst compositions are listed in Table 4. The washcoat is La stabilized gamma alumina. As mentioned above, the HCCI combustion produces virtually no NO\textsubscript{x} in the exhaust, and thus the CO oxidation activities in the presence and absence of NO\textsubscript{x} are presented for revealing the impact of NO\textsubscript{x}. In addition, engine misfire and traces of sulfur species in the natural gas may cause temperature jump and catalyst poisoning, respectively. Therefore, the catalysts were poisoned with SO\textsubscript{2}, followed by thermal deactivation at 730°C for 1 h in flowing air. The catalytic activities after SO\textsubscript{2} poisoning and thermal aging are compared with that of the fresh catalysts. It is expected that these tests could offer some information for the catalyst design.

Table 4. Catalyst composition (Washcoat Al\textsubscript{2}O\textsubscript{3}, Cordierite substrate, 400 cpsl)

<table>
<thead>
<tr>
<th>Catalyst ID</th>
<th>PGM</th>
<th>PGM Load g/L\textsubscript{sub}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt</td>
<td>Pt</td>
<td>1</td>
</tr>
<tr>
<td>Pd</td>
<td>Pd</td>
<td>5</td>
</tr>
<tr>
<td>PtPd</td>
<td>Pt/Pd=1/7</td>
<td>8</td>
</tr>
</tbody>
</table>

PT-BASED CATALYST

The performance of the Pt catalyst is presented in Figures 2 and 3. The difference in hydrocarbon conversions is negligible with and without 100 ppm NO in the gas stream. The presence of NO slightly enhances the oxidation of propane, with about 10°C lower shift in light-off curve of propane or T\textsubscript{50} (the temperature at 50% conversion). However, the CO light off curve shifts about 30°C higher in the presence of 100 ppm NO in the gas stream, indicating that the CO and NO compete for the same adsorption sites (Pt sites) on the catalyst surface. In situ infrared spectra of adsorbed NO and hydrocarbons revealed that nitrate species associate with Al\textsubscript{2}O\textsubscript{3}, NO and CO associate with Pt over catalyst Pt/Al\textsubscript{2}O\textsubscript{3} under reaction conditions [14]. Temperature programmed desorption of NO revealed that most of NO desorbed from Pt catalyst at temperatures above 350°C, leaving low surface coverage of NO [15]. Therefore, above 350°C the competition of NO unlikely exists and the presence of NO in the reactant gas mixture has little effect on the oxidation of hydrocarbons. Shen et al also investigated the conversion of C\textsubscript{3}H\textsubscript{6} and C\textsubscript{3}H\textsubscript{8} over Pt/MCM-41 in the absence and presence of NO and found that C\textsubscript{3}H\textsubscript{8} oxidation is not obviously affected by the presence of NO in the gas mixture [15].

The SO\textsubscript{2} poisoning of Pt-based catalyst led to an enhancement in the activity for combustion of hydrocarbons. In contrast, the oxidation activity of CO and NO was suppressed. The propane light off curve shifts 80°C higher after 1 h of 100 ppm SO\textsubscript{2} treatment at
400°C. We believe that the promoting effect by SO\(_2\), and more slightly by NO\(_x\), is due to the formed sulfates and nitrates that would increase the acidity of support alumina. The surrounding acidic sites will interact with metal particles and modify the electronic properties of the PGM particles [16]. These results are consistent with some publications [17-19]. The oxidation of propane in the absence and the respective presence of SO\(_2\) in the feed gas was studied over 1 wt% Pt/Al\(_2\)O\(_3\) using transient experiments and in situ DRIFT spectroscopy [18]. The transient experiments confirmed the promoting effect of SO\(_2\) on the conversion of propane and, moreover, showed an inhibiting effect from SO\(_2\) on the conversion of the intermediate products propene and CO. The promoting effect by SO\(_2\) on the conversion of propane is ascribed to the formation of an acidic site at the Pt/Al\(_2\)O\(_3\)/SO\(_4^{2-}\) interface. However, works by other researchers showed the support acidity is not a major contributing factor for lower alkane combustion [19], and the increase in activity by SO\(_2\) is due to a more subtle effect in which the possible role of perimeter sites at the metal-support interface is emphasized [17].

The thermal aging of the SO\(_2\)-aged Pt catalyst led to a significant loss of activity for both hydrocarbons and CO/NO oxidation, compared with the same catalyst after aging by SO\(_2\). The thermal aging at 730°C could cause sulfates decomposition [20], surface area loss and Pt particles agglomeration. The degree of sintering is mostly dependent on the aging temperature and is increased by temperature. Decrease in platinum dispersion is usually taking place at temperatures over 600°C for Pt/Al\(_2\)O\(_3\) in the oxidizing atmosphere [21]. The activity loss likely caused from one or the combination of the three influential factors. It should be noted that the activity of the thermal aged for hydrocarbon oxidation is still higher than the fresh catalyst, indicating the sulfates was not eliminated on the catalyst surface even after the thermal aging. The residual sulfates in the thermal aged catalyst may account for the slight enhanced activity for hydrocarbon oxidation over the fresh catalyst.

### PD-BASED CATALYST

The catalytic performance of the Pd-based catalyst was also investigated with the results shown in Figures 4 and 5. Similar to the Pt catalyst, NO in the gas phase has little effect on the oxidation of hydrocarbons, but inhibits the oxidation of CO.

![Figure 3](image.png)

**Figure 3.** CO and NO oxidation activities of Pt-based monolithic catalyst under various catalyst conditions. SO\(_2\) aging conditions: 100ppm SO\(_2\), 400°C, the other components see Table 1 (SV=100,000 h\(^{-1}\)).

The thermal aging of the SO\(_2\)-aged Pt catalyst led to a significant loss of activity for both hydrocarbons and CO/NO oxidation, compared with the same catalyst after aging by SO\(_2\). The thermal aging at 730°C could cause sulfates decomposition [20], surface area loss and Pt particles agglomeration. The degree of sintering is mostly dependent on the aging temperature and is increased by temperature. Decrease in platinum dispersion is usually taking place at temperatures over 600°C for Pt/Al\(_2\)O\(_3\) in the oxidizing atmosphere [21]. The activity loss likely caused from one or the combination of the three influential factors. It should be noted that the activity of the thermal aged for hydrocarbon oxidation is still higher than the fresh catalyst, indicating the sulfates was not eliminated on the catalyst surface even after the thermal aging. The residual sulfates in the thermal aged catalyst may account for the slight enhanced activity for hydrocarbon oxidation over the fresh catalyst.

![Figure 4](image.png)

**Figure 4.** Hydrocarbon oxidation activities of Pd-based monolithic catalyst under various catalyst conditions. SO\(_2\) aging conditions: 100ppm SO\(_2\), 400°C, the other components see Table 1 (SV=100,000 h\(^{-1}\)).

In contrast to the Pt catalyst, a significant deactivation was observed for the oxidation of all the components, including hydrocarbons, CO and NO, over Pd catalyst after SO\(_2\) aging. Sulfur poisoning and regenerating of Pd
catalyst was systematically investigated and discussed in previous papers [8, 10, 13]. It is generally accepted that PdO is the active site for oxidation under lean-burn conditions, and SO$_2$ can be oxidized by excess oxygen in the gas stream and form less active Pd-SO$_x$ with the PdO [6-9].

Thermal aging at 730°C likely removed some sulfate species, and thus increased the activity as shown in Figures 4 and 5. Thermal aging at 730°C may be sufficient for a partial or complete decomposition of PdSO$_4$, but not for that of Al$_2$(SO$_4$)$_3$, according to thermal analysis [20, 22] and thermodynamic equilibrium calculation [12].

PTPD-BASED CATALYST

NO has little effect on the hydrocarbon oxidation over the PtPd bimetallic catalyst, but suppresses the oxidation of CO, as shown in Figures 6 and 7. Compared with NO-free reactant gas, the T$_{50}$ of CO (the temperature required for 50% conversion) shifts 20°C higher in the presence of NO.

The sulfur poisoning causes dramatic deactivation of the catalyst. The extent of light off shift after SO$_2$ exposure depends on the type of hydrocarbon component. The T$_{50}$ of methane after SO$_2$ aging moves 130°C higher relative to the fresh, while light off temperatures of ethane and propane shift 90°C and 80°C, respectively. This is consistent with Pd catalyst aging test results on a lean burn natural gas engine [7]. These authors report the deactivation of PdO by sulfur oxides is due to both a decrease in the chemisorption of hydrocarbons on PdO-SO$_x$ and a decrease in the availability of oxygen from PdO-SO$_x$ [9]. The PdO-SO$_x$ sites are still active in propane oxidation, but not sufficient to activate methane molecules. Therefore, the light-off shift of propane is not so large as methane after SO$_2$ poisoning.

The similarity to single Pd catalyst in catalytic performance suggests that Pd or PdO$_x$ species locate in the outer shell of the bimetallic particles. The formation of bimetallic Pt-Pd particles with segregation of the palladium to the particles surfaces was evidenced by XPS and bombardment with argon cations [23]. Under lean burn conditions, the particles in Pd-Pt/Al$_2$O$_3$ are split into two different domains: one with PdO on surface, and the other likely consisting of an alloy of Pd and Pt in the core. The ejected Pd from the core is oxidized into PdO. The amount of PdO depends on the oxidation time and temperature [24].
Figure 7. CO and NO oxidation activities of PtPd-based monolithic catalyst under various catalyst conditions. SO\textsubscript{2} aging conditions: 100ppm SO\textsubscript{2}, 400°C, the other components see Table 1 (SV=100,000 h\textsuperscript{-1}).

The thermal treatment at 730°C of SO\textsubscript{2}-aged Pt-Pd bimetallic catalyst improved the activity for the oxidation of hydrocarbons, NO and CO. The improvement is even greater than the Pd-based catalyst. For example, the T\textsubscript{50} of methane shifted 50°C lower after thermal aging for the PtPd catalyst, compared to 25°C for the Pd catalyst. In contrast, the SO\textsubscript{2}-poisoned Pt catalyst deactivated after the thermal aging, with 50°C higher shift for T\textsubscript{50} of propane. Therefore, the addition of Pt improves the thermal stability of the Pd catalyst. A considerable number of papers have also shown that the activity of the bimetallic Pd-Pt catalysts is improved in comparison to monometallic palladium catalysts, as well as the stability [24].

CATALYST SELECTION FOR ENGINE TESTS

In order to provide a clear comparison, the oxidation activity of various catalyst formulations is shown in Figures 8-15, including the oxidation activity for each of the components over the fresh or aged catalysts.

Figure 8. Hydrocarbon oxidation activities of fresh catalysts with different PGMs. Model gas compositions see Table 1, without NO in the gas stream (SV=100,000 h\textsuperscript{-1}).

The activity for hydrocarbon oxidation is presented in Figures 8, 10, 12, and 14. The catalyst formulation for hydrocarbon oxidation should be Pd-based, or contain Pd, based on the testing results shown in the Figures 8 and 10. When the catalysts are fresh, the methane conversion is only less than 10% at 500°C over the Pt catalyst, compared with more than 80% at 400°C over the Pd or PtPd catalyst. These Pd-based catalysts remain one of the most actively studied and most promising for oxidation of methane and other light alkanes under lean conditions [6].
Figure 9. CO oxidation activities of fresh catalysts with different PGMs. Model gas compositions see Table 1, without NO (SV=100,000 h⁻¹).

Figure 10. Hydrocarbon oxidation activities of fresh catalysts with different PGMs. Model gas compositions see Table 1 (SV=100,000 h⁻¹).

However, the Pd-based catalysts have poor stability for methane conversion in the presence of water and poisons. The poisons may refer to sulfur, phosphorous and some metals in the exhaust of natural gas fuelled engines [12]. The Pd and PtPd catalyst can hardly ignite methane at 400°C after SO₂ aging as shown in Figure 12, compared with more than 80% methane conversion at 400°C when the catalysts were fresh (Figure 10). Even at 500°C, the methane conversion were less than 60% over the SO₂ aged Pd or PtPd catalyst. The initial high activity drops significantly during operation, resulting in increasing difficulty in igniting the methane at exhaust temperatures [6-9]. It has been reported that sulfur causes serious activity drop of Pd catalysts for oxidizing methane and other light alkanes [7-9]. The sulfur poisoning of Pd catalyst is attributed to the formation of PdSO₄, and is irreversible. The activity for methane oxidation cannot be fully recovered after high temperature treatment or regeneration [8, 22, 25].

The thermal-aged PtPd catalyst performed better than either Pt or Pd catalyst in the oxidation of hydrocarbons, as shown in Figure 14. The T₅₀ of methane over the PtPd catalyst is about 30°C lower than the Pd catalyst, and the Pt catalyst could not ignite methane until the temperature reached 500°C. The PtPd catalyst likely possesses better stability than Pd catalyst for methane oxidation, which has been reported in many papers [24].
Therefore, the PtPd bimetallic catalyst is likely more promising for the abatement of methane and other light alkanes for the natural gas fuelled dual mode engines under the spark-ignition mode.

The three catalyst formulations exhibited similar activity for CO oxidation, with a light-off difference less than 20°C in all the cases. The Pt catalyst is better when the catalyst is fresh or SO₂ poisoned, but slightly worse after the thermal aging than the Pd or PtPd catalyst which has a higher PGM loading.

Below the catalysts were evaluated under HCCI and SI mode operations using an engine at the Yanmar R&D center. Engine tests were performed under fresh
conditions (where indicated), otherwise all emission measurements were performed after 10 hours of aging. This aging simulates the catalyst deactivation observed with sulphur poisoning.

Figure 15. CO and NO oxidation activities of thermal-aged catalysts with different PGMs (SV=100,000 h⁻¹). Thermal aging conditions: 730°C, 1 h, flowing air with moisture. The catalysts had been poisoned by SO₂ prior to thermal aging.

COMPARISON BETWEEN HCCI AND SI MODE

Gas engines conventionally use spark ignition to combust the fuel. However, HCCI initiates combustion by precise control of the inlet temperature of the gas mixture. This control on the mixture quantity results in HCCI exhaust temperatures being lower than under SI conditions (Figure 16). The quantity of exhaust gas is constant over the full range of throttle positions. Typically, exhaust concentrations of THC and CO under HCCI conditions are very high. While NOₓ levels under HCCI operation are very low and with a thermal efficiency that is 3 points higher than SI under high load.

However combining HCCI with spark ignition can result in lower inlet air temperatures at low loads and higher exhaust temperatures than with HCCI only. SI is effective at low load because it can run using low temperature mixtures and low maximum pressure. This allows the mixture to be ignited using spark ignition at low inlet temperatures.

ENGINE OPERATION WITH HCCI AND HCCI WITH SPARK IGNITION MODE

Initially, the cold start ignition performance of the high loading PtPd catalyst was tested under HCCI mode. Figure 17 shows the test result of the catalysts under fresh conditions. In this case, the engine is run under wide-open throttle. Exhaust temperatures are observed to increase due to the gradual increase in BMEP. After 0.15 hours from engine start, the engine load maintains 0.34 MPa and exhaust temperature before the catalyst is stable at 350°C.

Figure 16. Comparison of exhaust composition between SI, HCCI and HCCI with spark ignition. Engine speed N = 1700 min⁻¹. Nomenclature: Exh = exhaust, ave = average, Texh = exhaust temperature, Tin = intake mixture temperature, THC = total hydrocarbons, η = thermal efficiency of engine.

Figure 18 shows the exhaust gas conditions of the natural gas engine running under HCCI mode, 1700 min⁻¹, and Brake Mean Effective Pressure (BMEP) ranges from 0 to 0.55 MPa. For the BMEP range between 0 to 0.55 MPa, the exhaust temperature changes from 120 to 260°C, and the exhaust O₂ content drops from 18.5 to 11.5%. The CO emission decreases with the increasing BMEP, from an initial concentration of 10000 ppm (over range of the detector) to 1000 ppm. NOₓ level is very low with NOₓ after catalyst rising slightly at high BMEP. The Pt catalyst used here has a CO light off range between 130 to 180°C. Under light load engine conditions, the temperature of the exhaust is 150°C. In
In this case, the CO began to convert at exhaust temperature around 150°C.

![Figure 17](image1.png)

**Figure 17.** Cold start performance with the fresh PtPd catalyst under HCCI mode (SV~50,000 h⁻¹). Engine speed N = 1700 min⁻¹.

Exhaust temperatures increased from 120°C (HCCI) to 225°C (HCCI +SI) at BMEP 0 MPa. As can be seen in Figure 16, the exhaust flow rates decrease dramatically after the throttle is applied, particularly when the BMEP is low. In this case the space velocity through the catalyst (Pt) became lower with throttle application. The lower space velocity cause the exhaust temperatures after the catalyst to go up from 223°C to 275°C. CO conversion was 100% over the catalyst for all loads. O₂ concentrations after catalyst were lower than before catalyst. CO level after the catalyst are zero showing complete CO conversion. Little effect is seen on THC after the catalyst, a result of no conversion of the major component (methane) in the exhaust.

![Figure 19](image2.png)

**Figure 19.** The exhaust gas conditions of the natural gas fuelled engine operated with HCCI and Spark ignition mode (Pt catalyst, SV~50,000 h⁻¹). Engine speed N = 1700 min⁻¹.

**ENGINE OPERATING AT SI MODE**

Exhaust conditions and compositions before and after the PtPd catalyst are shown in Figure 20 when the engine is operated under spark-ignition only. The BMEP varied from 0 to 0.7 MPa, exhaust temperature increases from 380°C to 520°C, which makes it possible for the PtPd catalyst to perform methane oxidation. The exhaust before the catalyst contains 4-8% oxygen. On average the oxygen consumption used in oxidation of CO and the hydrocarbons is about 2000 ppm giving an exhaust temperature rise across the catalyst of about 20°C.

The PtPd catalyst showed excellent activity toward CO, methane and NMHC oxidation. Complete conversion of CO was observed during the whole operating range. The total hydrocarbon (THC) concentration at the inlet of the
catalyst ranges from 2200 ppm at idle (BMEP of ~0) to 900 ppm at BMEP 0.7 MPa. The THC conversion across the catalyst is greater than 98% for all operating conditions.

The engine testing results show the catalyst is very promising for this dual mode SI and HCCI with spark ignition operation. Further testing is proceeding to address the long-term stability of the catalyst. The current Japanese regulation requires less than 600 ppm of CO, less than 150 ppm of NOx, and has no THC requirement. Although no regulations exist, the PtPd catalyst gives excellent THC conversion efficiency providing the opportunity to implement THC regulations in the future and also meets the current requirements.

![Figure 20. The exhaust gas conditions of the natural gas fuelled engine operated with lean-burn spark-ignited mode (the PtPd catalyst, SV~50,000 h⁻¹). Engine speed N = 1700 min⁻¹.](image)

CONCLUSIONS

Our study of the activity of methane, NMHCs, CO/NO conversion over the Pt, Pd and PtPd catalysts with Al₂O₃ coated cordierite substrate using a model gas reactor under simulated natural gas engine exhaust conditions, as well as the experimental results tested on a natural gas engine operated under HCCI or SI mode, has led to the following conclusions:

- NO molecule is an apparent inhibitor for CO oxidation due to competitive adsorption of these two molecules on Pt/Pd sites. The inhibiting effects can be observed at temperatures below 200°C.
- The monometallic Pd catalyst shows very little activity for NO oxidation. It is interesting to note that the NO oxidation is strongly suppressed by Pd in the PtPd catalyst under the simulated engine emission conditions, whether the catalyst is fresh or not.
- The Pd and PtPd catalysts were severely poisoned by SO₂ in the gas stream.
- The activity of the Pt catalyst increased after SO₂ aging, likely due to the increase of the support acidity caused by the sulfates around the Pt particles.
- The PtPd bimetallic catalyst exhibited excellent activity of THC oxidation when the natural gas engine was operating under SI mode. Complete conversion of CO was obtained over the Pt catalyst when the engine was running under HCCI with spark ignition mode. The engine testing results are consistent with those of the model gas reactor.

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