

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 NO_x 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-SO₄ in the presence of SO₂ 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.

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

Component	Lean
CH ₄	1000 ppm
C ₂ H ₆	150 ppm
C ₃ H ₈	50 ppm
CO	1000 ppm
*NO	100 ppm
O ₂	10%
H ₂ O	5%
CO ₂	5%
**SO ₂	0
N ₂	Balance

Note: *NO is 100 ppm unless specified.

****SO₂ is 100 ppm during poisoning.**

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 2. Engine specifications

Engine Type	4-cylinder Water cooled	
Cylinder Bore × Stroke	98mm × 110mm	
Engine swept volume	3319cm ³	
Combustion chamber	HCCI	Spark ignition
	Dog dish type	Bowl type
Compression ratio	25	12
Intake air temperature	~80deg C	25deg C

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. NO_x 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 NO_x content.

Table 3. Natural gas composition

Component	Concentrations
CH ₄	88 vol%
C ₂ H ₆	6 vol%
C ₃ H ₈	4 vol%
n-C ₄ H ₁₀	2 vol%
*CH ₃ -S-CH ₃	1.8 ppm
*(CH ₃) ₃ C-SH	1.2 ppm

Note: *Gas odorant.

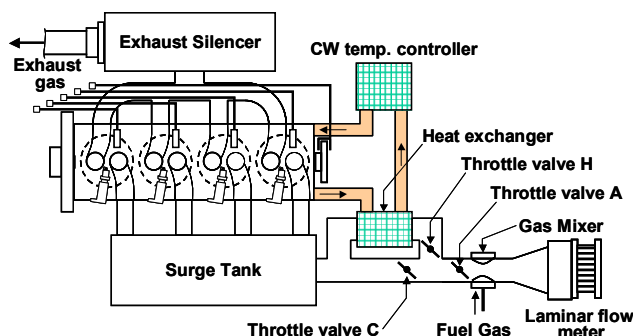


Figure 1. Experimental engine setup.

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_x in the exhaust, and thus the CO oxidation activities in the presence and absence of NO_x are presented for revealing the impact of NO_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_2 , followed by thermal deactivation at 730°C for 1 h in flowing air. The catalytic activities after SO_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_2O_3 , Cordierite substrate, 400 cpsi)

Catalyst ID	PGM	PGM Load g/L_{sub}
Pt	Pt	1
Pd	Pd	5
PtPd	Pt/Pd=1/7	8

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_{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_2O_3 , NO and CO associate with Pt over catalyst Pt/ Al_2O_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_3H_6 and C_3H_8 over Pt/MCM-41 in the absence and presence of NO and found that C_3H_8 oxidation is not obviously affected by the presence of NO in the gas mixture [15].

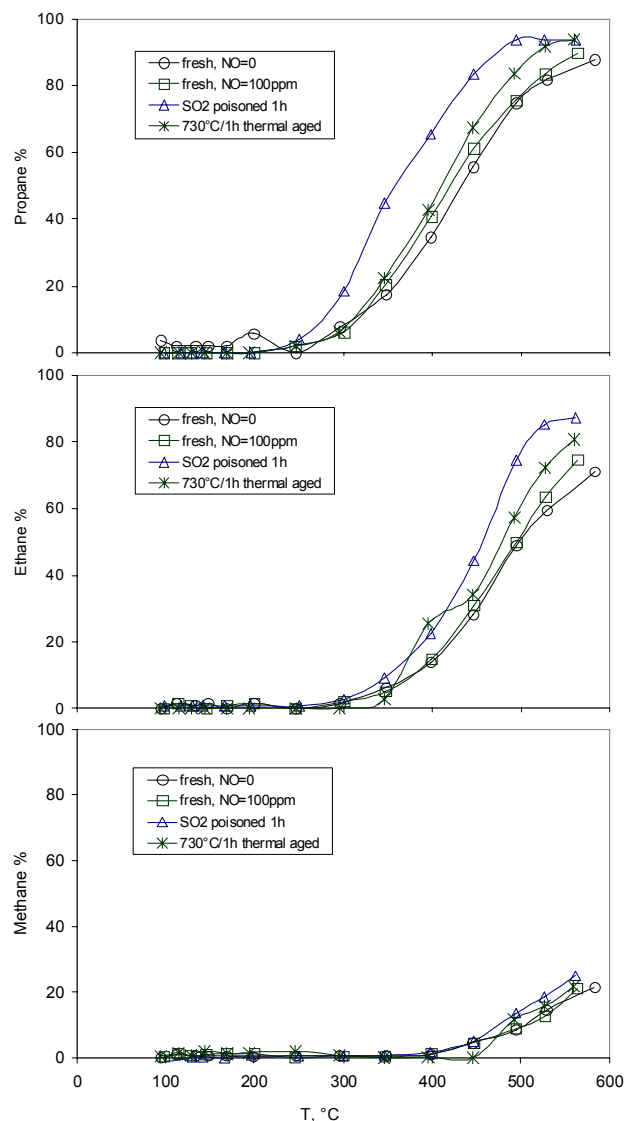


Figure 2. Hydrocarbon oxidation activities of Pt-based monolithic catalyst under various catalyst conditions. SO_2 aging conditions: 100ppm SO_2 , 400°C , the other components see Table 1 ($\text{SV}=100,000 \text{ h}^{-1}$).

The SO_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_2 treatment at 400°C . We believe that the promoting effect of SO_2 on hydrocarbon oxidation is due to the formed sulfates and more slightly by NO_x , is due to the formed sulfates and

nitrate 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% $\text{Pt}/\text{Al}_2\text{O}_3$ 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 $\text{Pt}/\text{Al}_2\text{O}_3/\text{SO}_4^{2-}$ 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].

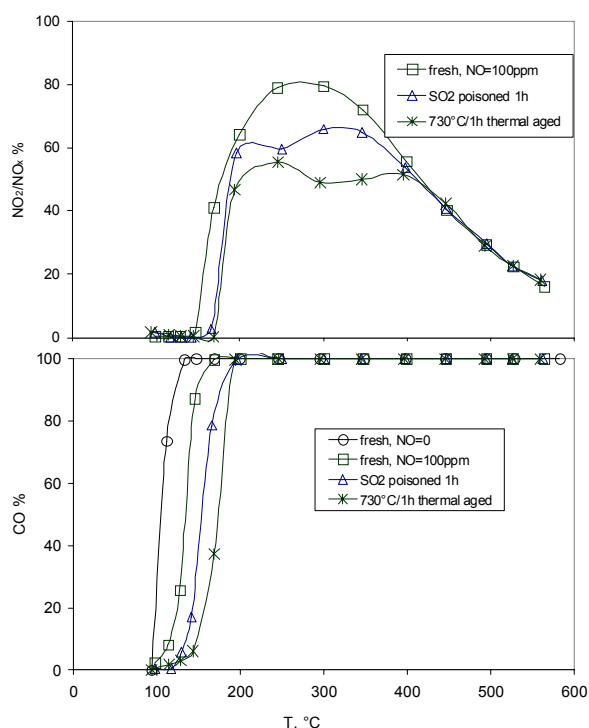


Figure 3. CO and NO oxidation activities of Pt-based monolithic catalyst under various catalyst conditions. SO_2 aging conditions: 100ppm SO_2 , 400°C, the other components see Table 1 ($\text{SV}=100,000 \text{ h}^{-1}$).

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 $\text{Pt}/\text{Al}_2\text{O}_3$ 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.

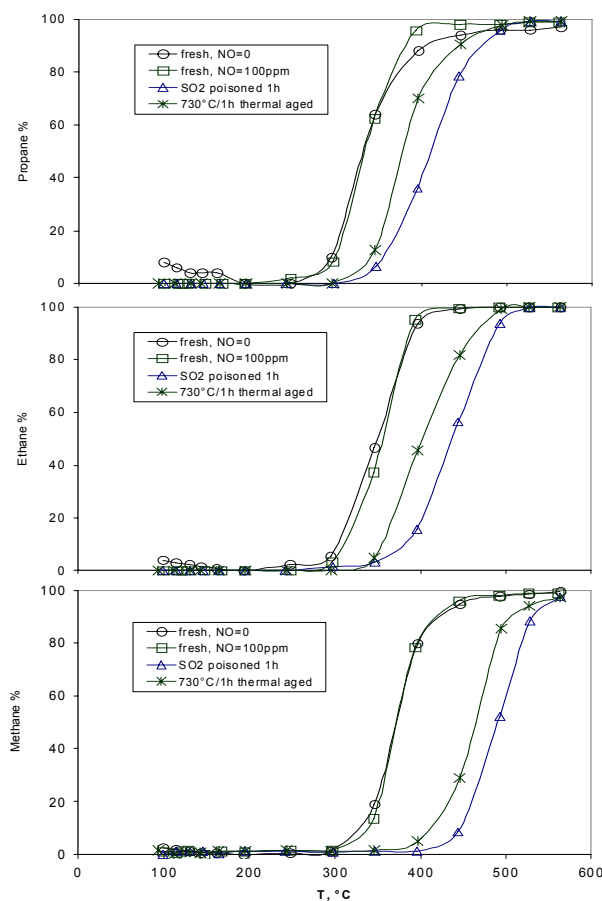


Figure 4. Hydrocarbon oxidation activities of Pd-based monolithic catalyst under various catalyst conditions. SO_2 aging conditions: 100ppm SO_2 , 400°C, the other components see Table 1 ($\text{SV}=100,000 \text{ h}^{-1}$).

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