

Pt/Pd Bimetallic Catalyst with Improved Activity and Durability for Lean-Burn CNG Engines

Joonwoo Kim, Eunseok Kim, JaeUk Han, and Hyun Sik Han
Heesung Catalysts

ABSTRACT

Compressed natural gas (CNG) has been regarded as an alternative fuel for current fossil fuels such as gasoline and diesel. Recently the increasing interest in shale gas is drawing more attention to CNG vehicles of which number is expected to increase.

Exhaust gas from CNG engines with lean combustion contains relatively low nitrogen oxides and particulate matters compared to conventional fossil fuel based engines. However, high amount of unburned methane, which has much higher greenhouse warming potential than CO₂, limits the wide use of CNG for many applications. Even though Pd-based catalysts have been popularly studied in order to convert methane, their activity and durability have not been sufficient for practical applications to aftertreatment of lean burn CNG engines and the formation of a new Pd containing.

In the present study, we developed an improved Pd-based catalyst for CNG engines by introducing Pt and promoters to enhance methane oxidation activity at low temperature and long term durability. Pt was more active to oxidize paraffinic hydrocarbons that comprise ~10% of total hydrocarbons in exhaust gas from lean burn CNG engines. Exotherm resulting from the paraffinic hydrocarbon oxidation by Pt could promote the remaining methane oxidation by Pd. Furthermore, potential causes for the deactivation of Pd-based catalyst were investigated from the various points of Pd-sintering by high temperature exposure, PdO decomposition, sulfation and coking, and the formation of new Pd containing compound. Optimal use of support material for Pd/Pt and promoters to keep Pd stable were identified as key factors for the design of more active and durable catalyst.

CITATION: Kim, J., Kim, E., Han, J., and Han, H., "Pt/Pd Bimetallic Catalyst with Improved Activity and Durability for Lean-Burn CNG Engines," *SAE Int. J. Fuels Lubr.* 6(3):2013, doi:10.4271/2013-01-2591.

INTRODUCTION

Providing new alternative energy sources has been requested to solve the lack of conventional fossil fuels and needs of clean energy sources for human beings [1,2]. Compressed natural gas (CNG) has been regarded as an alternative fuel for current fossil fuels such as gasoline and diesel. It's penetration into energy portfolio is growing globally as a clean fuel, especially in urban bus [3].

CNG vehicles have low emissions because it uses an environmentally friendly fuel. Soot and carbon monoxide emissions are less in CNG engine than diesel engine. For the wide application of CNG engines, an aftertreatment system is mandatory to remove unburned methane. Methane has been designated as a greenhouse gas, much stronger than carbon dioxide [1]. Low temperature activity and long term durability of these catalysts are challenging.

Pd-based catalysts have been studied for a long time for the combustion of methane that is a main constituent of CNG. Pd is reported to be more active for combustion of methane as a main, compared to other precious metals. However the durability of Pd-based catalysts has been a concern so far [4, 5, 6].

Deactivation of Pd-based CNG catalyst takes place through various pathways. R.J. Farrauto et al. reported the deactivation was associated with the loss of active sites resulting from PdO decomposition to Pd at high temperature [7]. Sulfation was identified by P. Gelin as the cause of deactivation [8]. Sulfate can be formed by reaction between O₂ and SO₂ from the fuel. R. Burch investigated the effect of products such as CO₂ and H₂O on the activity of CNG catalyst [9]. It was also reported that Pd-based catalysts lost their activity due to the formation of Pd(OH)₂ in the presence of excess H₂O condition.

Accordingly, in this study the root causes for the deactivation was investigated from the points of thermal and non-thermal routes. Based on the investigation a more active and more durable CNG catalyst was developed.

EXPERIMENTAL

Catalysts Preparation and Aging

Reference Pd-based and newly developed CNG catalysts were prepared by applying washcoat onto cordierite honeycomb substrates (400cps/6.5mil). 1Pt/5Pd ratio was adopted for the sample preparation for activity test and characterization. Hydrothermal aging before activity testing was performed at 750 °C for 10hrs with 10% water.

Table 1. Summary of prepared catalysts.

Catalyst	Key concept
Ref. CNG	Reference
CNG-A	Optimal Pt/Pd location
CNG-B	CNG-A + new support
CNG-C	CNG-B + Optimal OSC
CNG-D	CNG-C + additive

Catalytic Activity Test

Catalytic activity tests were performed in a fixed-bed reactor equipped with an electrically heated furnace. Cored catalysts with 1" diameter and 2" length were located vertically in the rig. Temperatures were monitored using a K-type thermocouple placed in the inlet and outlet position of the cored catalyst. Main feed condition of CH₄ oxidation was 5000ppm CH₄, 10% O₂, 5% H₂O, 5% CO₂ under N₂ balance and GHSV=50,000 1/h. Feed condition were also adjusted when needed. Catalyst inlet temperature was heated from room temperature to 500°C for CH₄ light-off test and maintained at 450°C for durability test. Total HC was detected using FID equipped analyzer (Thermo, 51C-HT, USA). NDIR equipped analyzer (Simens Oxymat6) was used for CO and NO_x measurement.

Catalyst Characterization

Diffuse Reflectance Infrared Fourier Transform (DRIFT) spectra of the samples were recorded using a Nicolet 6700 spectrometer equipped with a MCT detector and a diffuse reflectance cell (Harrick CHC-CHA-3). The spectra of 64 scans were collected with a resolution of 2 cm⁻¹. About 20 mg of the catalyst powder was placed in the cell and pretreated at 400°C for 30 min in a flow of N₂ (40 ml/min) in order to remove water in the catalyst. The system was cooled down to room temperature and the background spectrum was recorded. The catalyst was then subjected to feed stream for methane oxidation reaction, CH₄ 5000 ppm, 10 vol.% O₂, N₂ balance.

CO-chemisorption was performed using BELCAT instrument in order to measure the PGM dispersion. About 50 mg of catalyst powder was used for the experiment.

Two kinds of TG/DSC experiments were performed. First one was a consecutive heating-up and cooling-down test for PdO decomposition study. Secondly soot oxidation test using mixture of 0.2g catalyst powder and 0.04g soot was placed into a crucible. Soot burning temperature was determined by increasing temperature to 900°C.

RESULT AND DISCUSSION

Durability of Pd-Based CNG Catalyst

The durability of Pd-based CNG catalyst with 10.6g/L, PGM ratio 1Pt/5Pd, 10.5"×6"(400/6.5) was evaluated at 6L CNG engine using Seoul-10 as shown in Figure 1. Used evaluation mode has 3 phases with difference engine speed and load rate. Maximum temperature during on cycle test of Seoul-10 mode was about 600°C. THC conversion was monitored with Seoul-10 aging time. The THC conversion dropped significantly as the aging time increased from 100% at fresh state to 40% after 50-hrs aging (Figure 2).

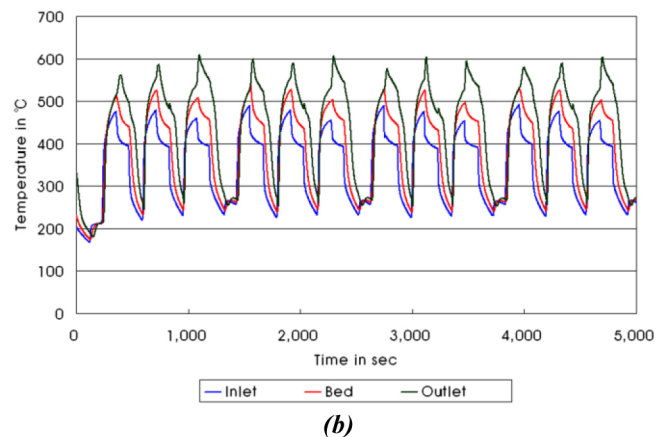
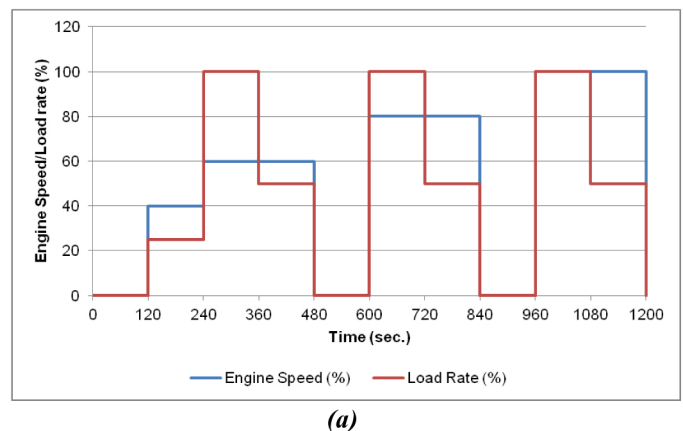


Figure 1. (a) Seoul-10 mode for evaluation and (b) temperature profiles of Seoul-10 mode for aging