

Controlling of the Exhaust Emissions of the Natural Gas Vehicles using Palladium Deposited on a Mixture of TiO₂ and ZSM-5

Adi Setiawan

Department of Mechanical Engineering, Faculty of Engineering, Malikussaleh University,
Bukit Indah, Lhokseumawe, 24352, Indonesia
Corresponding Author: adis@unimal.ac.id

Abstract

The exhausts of natural gas vehicles (NGVs) still contain unburned methane and other contaminants such as CO and NO_x while methane has a CO₂ greenhouse gas warming potential (GWP) of 25 over a 100 year time horizon. Successful development of catalytic converters for natural gas vehicles would significantly reduce the greenhouse gas emissions. This work aims to develop a suitable catalytic converter using palladium catalyst supported on zeolite combined with titanium oxide. Prepared sample was tested in a micro tubular stainless steel reactor under condition mimicking the exhaust gas of NGVs. The understanding on the activity and stability of the catalyst were explored by characterizing the catalyst using TPD, analysis as well as N₂-adsorption-desorption analysis. The results suggest that catalyst can fully oxidize methane at reaction temperature below 430 °C. Water vapor produced from reaction does not significantly inhibit the activity of this catalyst. However, co-feeding 4 % vol. water vapor into the feed reduces the methane conversion level up to 40 %.

Keywords: Natural gas vehicles, methane, total oxidation, palladium, zeolite, titanium oxide

Introduction

Natural gas is widely accepted as a prospective energy source to reduce pollution lean-burn natural-gas engines due to its higher thermal efficiencies and cleaner exhaust gases than stoichiometric engines. The exhaust emissions of the natural gas vehicles however, remain contain unburned methane and other contaminants such as CO and NO_x. Compare to diesel vehicles exhaust, NO_x emissions and particulates from NGV exhaust pipe are significantly low. Thus, the only major drawback of the NGVs is unburned methane. Methane is known as a gas with a CO₂ greenhouse gas warming potential (GWP) of 25 over a 100 year time horizon (Solomon, *et al.*, 2007) and development of catalytic converters are required (Gelin and Primet 2002) in order to reduce greenhouse gas emissions associated with NGVs.

In general, the exhaust gas of the NGVs contains ~0.1% CH₄, 10–15 % H₂O, CO₂, SO_x and NO_x in a high excess of oxygen. The temperature of the engine exhaust is ranging from 500 to 550 °C (Gelin and Primet, 2002). Catalytic combustion of methane is a promising solution for methane emission abatement where methane is oxidized to carbon dioxide on a catalytically-active solid surface. This flameless combustion is applicable for highly diluted air-methane streams.

Supported Pd catalysts are considered as excellent catalysts for this reaction (Gelin and Primet, 2002). Poisoning by water and other contaminants can have long-term deleterious effects, and significantly reduce their potential for their use in catalytic converter for NGVs exhaust. Earlier studies reported that the water significantly inhibits the activity of Pd on Al₂O₃ (Burch, *et al.*, 1995, Roth, *et al.*, 2000) and Pd on zeolites (Shi, *et al.*, 2007, Zhang, *et al.*, 2008) at lower temperatures which is due to competition between water and methane for adsorption on the active site (Ribeiro, *et al.*, 1994, Burch, *et al.*, 1995, Roth, *et al.*, 2000). Furthermore, an irreversible deactivation can possibly be induced by the presence of water where the active site (PdO) could transform into a less active site (palladium hydroxide) (Ribeiro, *et al.*, 1994, Burch, *et al.*, 1995, Roth, *et al.*, 2000). Ciuparu, *et al.* (2001) suggested that the hydroxyl groups produced by reaction are bound strongly on the surface and accumulated on the support (Schwartz, *et al.*, 2012). Therefore, when the external water is introduced the surface becomes saturated and the rate of desorption is decreased (Ciuparu, *et al.*, 2001). Attempt to improve the tolerance against water was carried out by choosing TiO₂-SiO₂ as a support to avoid or delay the reaction between Pd and H₂O (Carlo, *et al.*, 2010). Enhanced hydrothermal stability was reported recently by Liu *et al.* (2012) by using Ni-modified alumina as support at a reaction temperature of 600 °C.

In this work, we prepare palladium supported on a mixture of TiO_2 in ZSM-5 catalyst for lean-methane combustion. The nature of water involved in the reaction is investigated based on catalyst characterization. Hydrothermal stability of the Pd/ TiO_2 -ZSM-5 catalysts is evaluated in time-on-stream experiment under dry and humid conditions.

Experimental

Catalyst preparation

Pd based catalyst (1.1% g/g) was prepared by an incipient wetness technique. As a support, 5 wt. % of titanium (IV) oxide (Sigma-Aldrich) was physically mixed with NH_4 -ZSM-5 (Zeolyst International) in methanol (0.1 M) and stirred overnight at room temperature. The solid was collected after evaporation of methanol in a rotary evaporator and then dried in the oven at 110 °C for 20 h. Pd (II) nitrate solution (Sigma-Aldrich) was then added drop-wise and mixed with TiO_2 -ZSM-5. The dried catalyst was ground, pressed and sieved to 250–425 μm . Prior to measuring the catalyst activity, samples were pre-treated in-situ in air at 500 °C for 2 h.

Catalyst characterization

The surface area of catalysts was measured by nitrogen adsorption at 77 K using Gemini 11 2370 surface area analyzer according to the Brunauer-Emmet-Teller (BET) method. Temperature-programmed desorption (TPD) analysis was performed using a Pfeiffer prisma quadrupole mass analyzer. The palladium and TiO_2 loadings were quantified using Varian 715-ES inductively coupled plasma optical emission spectrometer (ICP-OES).

Catalytic activity measurement

Catalytic activity measurements were performed in a tubular stainless steel micro reactor. The inlet methane concentration was set at 0.5 % balanced with air at GHSVs between 15,000 and 200,000 h^{-1} . The inlet and outlet mixtures were analyzed using an online gas chromatograph equipped with a thermal conductivity detector (TCD) and concentric packed column (Alltech CTR-I). For humid feed experiments, the reactant mixture was passed through a saturator operated at 25 °C \pm 3 °C and a humidity probe was installed at the outlet. The actual reaction temperatures were observed by placing a K-type thermocouple into the reactor close to the catalyst bed.

Results and Discussion

The loading of palladium and TiO_2 quantified by ICP-OES resulted in 1.1 wt. % for Pd and 5.7 wt. % for TiO_2 , respectively. The catalytic activity test of Pd/ TiO_2 -ZSM-5 catalyst was performed by feeding the reactor tube with 5,000 ppm methane (balance air) at gas hourly space velocity (GHSV) of 15,000 h^{-1} . The light-off curves were recorded at temperatures from 200 to 450 °C. A preliminary blank experiment was carried out prior to catalytic activity test and confirmed that no observable methane conversion was detected until a temperature of 650°C (Setiawan, Kennedy et al. 2014). Figure 1 shows methane conversion as a function of temperature where 10 % conversion (T_{10}) is achievable at 200 °C which indicates an active catalyst at low temperature. The total oxidation of methane was observed at 420 °C which is within the range of engine exhaust temperature of NGVs.

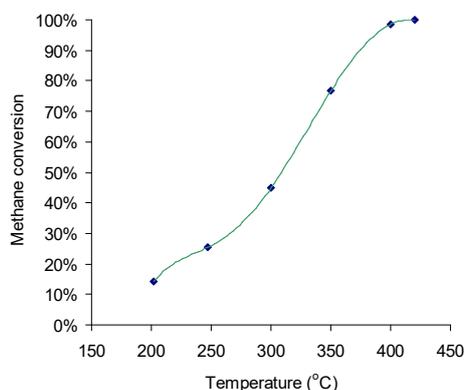


Figure 1. Methane conversion as a function of reaction temperature of methane oxidation over Pd/ TiO_2 -ZSM-5. Feed = 0.5 vol. % CH_4 balanced air, GHSV = 15,000 h^{-1} .

Catalytic activity evaluation of Pd supported on TiO₂-ZSM-5 catalyst was performed in a time-on-stream experiment under dry feed at 400 °C with results plotted in Figure 2. Zhang et al. reported previously that the activity of Pd/ZSM-5 without water shown rapidly decreased from 100 % to 82 % (Zhang, *et al.*, 2008). Interestingly, no significant deactivation was observed within 20 h from our catalyst indicating the addition of TiO₂ into zeolite enhances the thermal stability.

Time-on-stream catalyst performance in dry and humid conditions is plotted in Figure 3 at 425 °C. Under humid conditions, the methane conversion decreases slowly from ca. 90 % to 50 % and stays constant until 20 h. This saturated stream sample was then analyzed in TPD. The effect of water on palladium supported on TiO₂-containing-zeolite catalyst was also investigated using TPD analysis. Water has been selected as an adsorbate with the purpose of investigating the interactions between water, active sites and the support material. Before adsorption, sample was pre-heated for 1 h at 500 °C with a heating rate of 5 °C·min⁻¹ to remove any pre-adsorbed compounds. Water was adsorbed at 110 °C to avoid any weakly bound adsorbate retained on the sample. The spectra of water desorbed from the used sample are plotted in Figure 4. Interestingly, the maximum intensity of water dissociated from this catalyst occurs at 105 °C, far below our reaction temperature. However, a little amount of hydroxyl is strongly bonded on the catalyst which is thought to be responsible for catalyst deactivation.

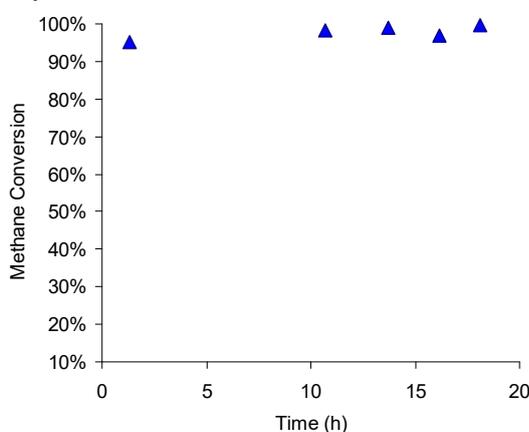


Figure 2. Evaluation of time-on-stream behavior at 400 °C over Pd/TiO₂-ZSM-5. Feed = 0.5 vol. % CH₄ balanced air, GHSV = 15,000 h⁻¹.

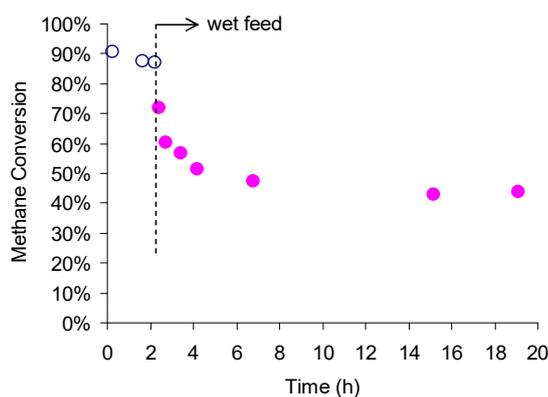


Figure 3. Time-on-stream behavior under dry and wet feed conditions over Pd/TiO₂-ZSM-5 catalyst at 425 °C, GHSV = 100,000 h⁻¹, CH₄ inlet = 0.6 vol. %, H₂O = 4 %, balanced air.

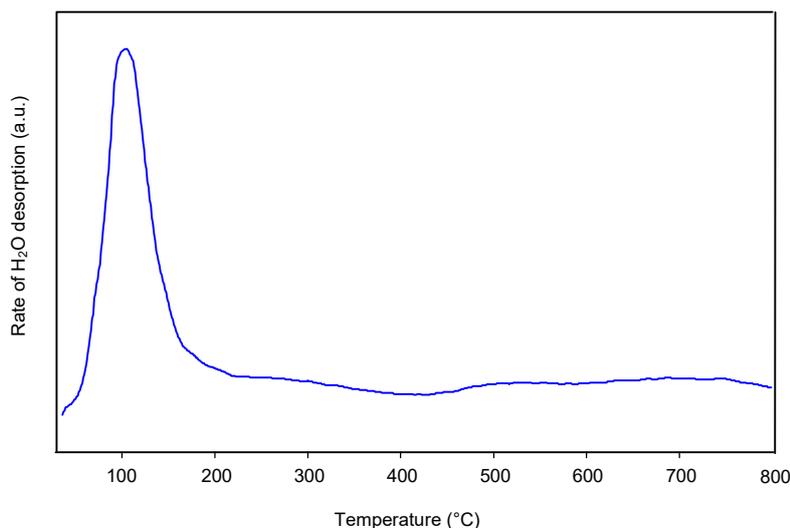


Figure 4. TPD curves of water desorption from Pd/TiO₂-ZSM-5 catalyst. Water was adsorbed at 110 °C at a heating ramp of 5 °C·min⁻¹.

Conclusions

Pd supported on TiO₂ and ZSM-5 catalyst have been prepared and studied in order to explore a new strategy for improving the stability and activity of catalyst for NGVs emission control. This Pd-based catalyst can fully oxidize methane at reaction temperature below 430 °C. It shows that water produced from reaction does not significantly inhibit the activity of this catalyst. However, adding 4 % water vapor into the feed reduces ca. 40 % of methane conversion.

Acknowledgements

Financial support from Faculty of Engineering, Malikussaleh University, is duly acknowledged.

References

- Burch, R., F. J. Urbano and P. K. Loader (1995). "Methane combustion over palladium catalysts: The effect of carbon dioxide and water on activity." *Applied Catalysis A: General* 123(1): 173–184.
- Carlo, G. D., G. Melaet, N. Kruse and L. F. Liotta (2010). "Combined sulfating and non-sulfating support to prevent water and sulfur poisoning of Pd catalysts for methane combustion." *The Royal Society of Chemistry* 46: 6317–6319.
- Ciuparu, D., N. Katsikis and L. Pfefferle (2001). "Temperature and time dependence of the water inhibition effect on supported palladium catalyst for methane combustion." *Applied Catalysis A: General* 216(1–2): 209–215.
- Gelin, P. and M. Primet (2002). "Complete oxidation of methane at low temperature over noble metal based catalysts: a review." *Applied Catalysis B: Environmental* 39: 1–37.
- Liu, Y., S. Wang, T. Sun, D. Gao, C. Zhang and S. Wang (2012). "Enhanced hydrothermal stability of high performance lean fuel combustion alumina-supported palladium catalyst modified by nickel." *Applied Catalysis B: Environmental* 119–120(0): 321–328.
- Ribeiro, F. H., M. Chow and R. A. Dallabetta (1994). "Kinetics of the Complete Oxidation of Methane over Supported Palladium Catalysts." *Journal of Catalysis* 146(2): 537–544.
- Roth, D., P. Gélín, M. Primet and E. Tena (2000). "Catalytic behaviour of Cl-free and Cl-containing Pd/Al₂O₃ catalysts in the total oxidation of methane at low temperature." *Applied Catalysis A: General* 203(1): 37–45.
- Schwartz, W. R., D. Ciuparu and L. D. Pfefferle (2012). "Combustion of Methane over Palladium-Based Catalysts: Catalytic Deactivation and Role of the Support." *The Journal of Physical Chemistry C* 116(15): 8587–8593.

- Setiawan, A., E. M. Kennedy, B. Z. Dlugogorski, A. A. Adesina, O. Tkachenko and M. Stockenhuber (2014). "Evidence of the formation of surface palladium carbide during the catalytic combustion of lean methane/air mixtures." *Energy Technol.* 2.
- Shi, C., L. Yang and J. Cai (2007). "Cerium promoted Pd/HZSM-5 catalyst for methane combustion." *FUEL* 86(1–2): 106–112.
- Solomon, S., D. Qin, M. Manning, R. B. Alley, T. Berntsen, N. L. Bindoff, Z. Chen, A. Chidthaisong, J. M. Gregory, G. C. Hegerl, M. Heimann, B. Hewitson, B. J. Hoskins, F. Joos, J. Jouzel, V. Kattsov, U. Lohmann, T. Matsuno, M. Molina, N. Nicholls, J. Overpeck, G. Raga, V. Ramaswamy, J. Ren, M. Rusticucci, R. Somerville, T. F. Stocker, P. Whetton, R. A. Wood and D. Wratt (2007). Technical summary. *Climate change 2007: the physical science basis. contribution of working group I to the fourth assessment report of the intergovernmental panel on climate change.* S. Solomon, D. Qin, M. Manning et al. Cambridge, United Kingdom and New York, NY, USA 996.
- Zhang, B., X. Wang, O. M'Ramadj, D. Li, H. Zhang and G. Lu (2008). "Effect of water on the performance of Pd-ZSM-5 catalysts for the combustion of methane." *Journal of Natural Gas Chemistry* 17(1): 87–92.