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Development of a test protocol for evaluation of methane oxidation catalysts

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Introduction

- Natural gas (NG) has received increased interest in the transportation sector as a low carbon fuel since it is abundant and relatively inexpensive.
- Natural gas vehicles (NGV) can provide a cleaner option, with estimated 15-20% lower greenhouse gas (GHG) emissions.
- NG engines can be either stoichiometric or lean burn. Lean burn NG engines are more efficient than stoichiometric and are similar in performance to diesel engines. However, they have methane slip (CH_4) emissions that occur when unburnt methane from the engine is released in the exhaust.
- Methane is a more potent GHG than CO_2 (86x more) thus CH_4 slip is a concern since it can significantly minimize or negate the NGV GHG advantage.
- The catalytic combustion of methane is considered an effective method to reduce methane emissions at NGV exhaust temperatures (350 - 500°C).
- Typical methane oxidation catalysts are prone to deactivation by water inhibition, hydrothermal sintering and sulfur poisoning. Since lean burn NGV exhaust contains high water content and sulfur contaminants (NG odorant, lube oil), it is essential to develop methane oxidation catalysts that are sulfur and water-resistant.
- In this work, a testing protocol with performance metrics was developed for assessing CH_4 oxidation activity of catalysts under simulated heavy-duty lean burn NGV exhaust.

Flow bed reactor (Catalyst activity evaluation)

SYSTEM DESCRIPTION

- 11 mass flow controllers (MFCs) produce simulated NGV exhaust
- Water added to feed by calibrated low flow rate dual syringe infusion/ withdrawal pump
- Primary standard (NIST traceable) flowmeter (Bios DryCal DC-Lite model DCL-L) used to measure flows for each MFC
- Two three-zone furnaces used to heat quartz sample reactor tube (6.12 mm nominal ID by 40.00 cm)
- Catalyst powder (500 mg) or mini-cores (12 cells)
- Flow range: 500 to 1000 ml/min (GHSV of 25k to 150k h^{-1})
- MKS MultiGas 2030 FTIR analyzer used to analyze gases

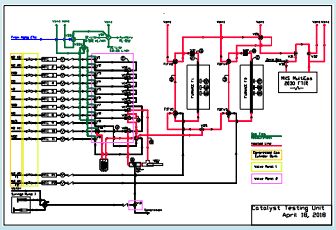


Figure 1. Flow bed reactor schematic

TESTING CONDITIONS

Gradient run procedure

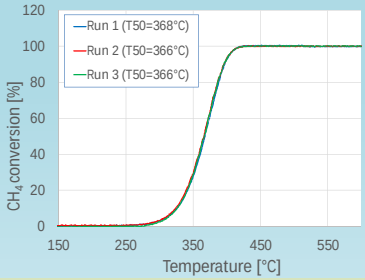
(Determination of temperature at 50% conversion, T_{50})

- Temperature ramp: 150-600°C at 3°C/min
- Sample size: 500 mg
- Sample pressed into wafers (16 mm dia.), 7 tons of force
- Lightly crushed wafers sieved: 80 to 120 mesh
- Feed gas: 1000 ppm CH_4, 10% O_2, 6% CO_2, 10% H_2O, (10 ppm SO_2 added for simulated sulfur compounds in NGV exhaust), balance N_2, Flow: 500 mL/min, GHSV ~55k h^{-1}

Aging conditions

- Temperature: 500°C
- Time: 40 h, 100 h, 200 h, 500 h
- Feed gas: 1000 ppm CH_4, 10% O_2, 6% CO_2, 10% H_2O, 10 ppm SO_2, balance N_2,
- GHSV: 55k h^{-1}

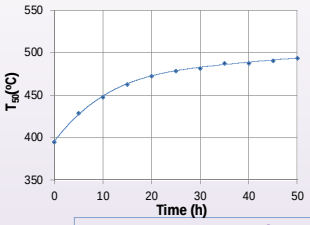
Evaluation of flow bed reactor reproducibility



A catalyst was tested three times under the same NGV simulated exhaust conditions using the gradient run procedure:

- **The T_{50} values are within 2°C showing high system reproducibility**

Establishing short term aging procedure for catalyst screening



1. Run catalyst using gradient procedure to establish initial T_{50}
2. Age catalyst for 5 h at 500°C using same process gas as gradient run procedure, cool to 150°C
3. Run catalyst using gradient procedure to determine aged T_{50}
4. Repeat process (step 2 to 3) until T_{50} does not change more than ± 3°C
5. **40 h was determined as sufficient time for short term aging procedure as T_{50} between runs was < 3°C**

Short Term Aging Procedure

- Run catalyst using gradient procedure to establish fresh T_{50}
- Age catalyst for 40 h at 500°C: 1000 ppm CH_4, 6% CO_2, 10% O_2, 10% H_2O balance N_2, GHSV=55k h^{-1}, cool to 150°C
- Run catalyst again using gradient procedure to establish T_{50} of aged catalyst
- If T_{50} of aged catalyst is < 500°C (upper temperature limit of lean burn NGV exhaust), the catalyst is chosen for longer term aging in preparation of engine test

Reproducibility of short term aging procedure with and without SO_2 in simulated NGV exhaust

Run #	T_{50} (°C) (Without SO_2)	T_{50} (°C) (With SO_2)
1	436	434
2	441	436

- Fresh catalysts of the same composition were aged with or without SO_2 using short term aging procedure to evaluate reproducibility of method
- SO_2 was added to gas flow mixture to simulate sulfur compounds found in lean burn NGV exhaust
- **In both cases T_{50} values are within 5°C showing high reproducibility of short term aging procedure**

Long term aging procedure to establish candidate catalyst for engine test in prototype converter

- Catalysts that "pass" initial T_{50} requirements of short term aging procedure with SO_2 in stream (T_{50} < 500°C after 40 h), need to be aged further under the same conditions for a total of 500 h with T_{50} evaluation at 100 h, 200 h and 500 h
- **Catalyst with T_{50} < 500°C after 500 h aging were chosen for engine test in prototype converter**

Catalyst evaluation using aging procedure

Catalyst T_{50} after short- and long-term aging procedures

Catalyst	Aging time (h)	T_{50} (°C)
Catalyst A	fresh	365
	40	481
	100	500
Catalyst B	fresh	350
	40	508
Catalyst C	fresh	362
	40	449
	100	456
	200	460
	500	**452**

- **Catalyst A:**
  - Passed short term testing requirements
  - Further aged
  - Failed 2nd segment
  - No further testing
- **Catalyst B:**
  - Failed short term testing requirements
  - No further testing
- **Catalyst C:**
  - Passed short term testing requirements
  - Further aged up to 500 h
  - **Chosen as candidate for engine test**

Conclusions

- A test protocol was developed to screen methane oxidation catalysts under lean burn NGV exhaust conditions and to select a suitable candidate for engine testing in prototype converter
- Using the developed protocol, a catalyst was chosen and successfully tested on a lean-burn NG engine

Acknowledgements

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