Regeneration of Palladium Based Catalyst for Methane Abatement

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Introduction

• Methane is a green house gas \[1 \text{t}_{\text{CH}_4} \sim 20 \text{t}_{\text{CO}_2}\]
• A 4 MW lean burn engine emits up to 300 tonnes of methane per year, or 6000 tonnes of CO2
• If we were able to oxidize this methane with a catalyst, we could generate a € 30,000 credit
• Furthermore, in case of co-generation application, heat resulting for methane slip oxidation will be recovered in the exhaust, thus improving overall system efficiency
• Problem: methane is most stable hydrocarbon, therefore most difficult to oxidize with a catalyst
• How can we get 90% CH4 conversion?
CH4 Oxidation with Platinum catalyst

Operating window yields to little conversion
Need to install catalyst upstream of turbo
Need to use another type of catalyst
Pre-turbo catalyst

Higher conversions will require a different catalyst
Pd catalyst can provide fairly high conversions of CH4
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Deactivation with time

Aging with 5 ppm SO2
Role of sulfur in catalyst deactivation

- $\text{SO}_2$ adsorbs strongly on Pd
- The resulting $\text{PdO-SO}_3$ sites possess low activity for HC oxidation

- Methane is the most sensitive to SO2 poisoning
What do we do next?

- Pd based catalyst is an interesting alternative but has serious durability issues
- Need to frequently replace catalyst
- Need to regenerate catalyst on a regular basis
  - Similar strategies have been developed for NOx storage catalysts in GDI engines
  - Use of Diesel NOx storage catalysts also require periodic catalyst regeneration
  - Will need system approach between engine OEM and catalyst supplier
- Can we actually regenerate methane catalyst?
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Methane catalyst regeneration

- Thermal regenerations
- Rich regeneration strategies
  - With oxygen cuts
  - With H2
  - With H2 & CO
  - With gas mixtures
Thermal regeneration is not an option.
Rich regeneration (oxygen cuts)

Oxygen Cuts (45s, 90s)

T: 540 °C,
112ppm CH₄, 10% O₂, 5ppm SO₂, 6% H₂O

CH₄ Conversion(%)

Time (s)

0 200 400 600 800 1000 1200 1400 1600

45s, oxygen cut
90s, oxygen cut

Time = 0, after 12 hrs of aging with 5 ppm SO₂

Oxygen cut is an option but is not practical
Regeneration considerations

- From literature, H$_2$ is a good chemical for regenerating Pd catalysts
- H$_2$ could be produced by the engine when $\lambda < 1$
- CO can also be used as a reducing agent but is less efficient than H$_2$
Regeneration results

Methane conversion

- **Mixture 1**: 1% H₂
- **Mixture 2**: 0.25% H₂ & 0.75% CO
- **Mixture 3**: 70 ppm H₂, 200 ppm CH₄, 3 ppm SO₂, 500 ppm CO, 6% H₂O, Balance N₂
Results

• Mixture 1: complete regeneration
• Mixture 2: partial regeneration
• Mixture 3: partial/lower regeneration than mixture 2

• In actual engine conditions (mixture 3), catalyst will have to be exposed longer to regeneration conditions
Questions?