Natural Resources Canada / Ressources naturelles Canada

CanmetENERGY
Leadership in ecoInnovation

Enhanced Pd catalyst for abatement of methane emissions from natural gas vehicles

Gianni Caravaggio, Lioudmila Nossova, Raymond Burich and Nicola Maffei

Natural Resources Canada, CanmetENERGY, Ottawa, ON, Canada

Introduction

- Natural gas (NG) has received increased interest in the transportation sector as a low carbon fuel (abundant and inexpensive).
- Lean burn natural gas engines are similar in performance to diesel engines.
- Natural gas engines provide a cleaner option, with estimated 15-20% lower greenhouse gas (GHG) emissions [1], than gasoline and diesel engines but have methane (CH_4) slip emissions.
- It is projected in the next 10 years CH_4 emissions will surpass those of CO_2 [2].
- CH_4 has a global warming potential 21 times greater than CO_2.
- Reduced CH_4 emissions can be achieved by using catalytic converters [3].
- The best known methane oxidation catalysts contain Pd which is highly active for the low temperature oxidation of methane but is a relatively expensive noble metal.
- **Objective:** Develop a methane oxidation catalyst active in the range of NG lean burn engine exhaust temperature (300-480°C), with a reduced amount of noble metal.

Catalyst Synthesis, Characterization and Testing

Pd supported catalysts were synthesized by incipient wetness impregnation (IWI) on alumina supports: An aqueous solution of metal nitrates was prepared, then added to supports in the quantity required to fill the pore volume.

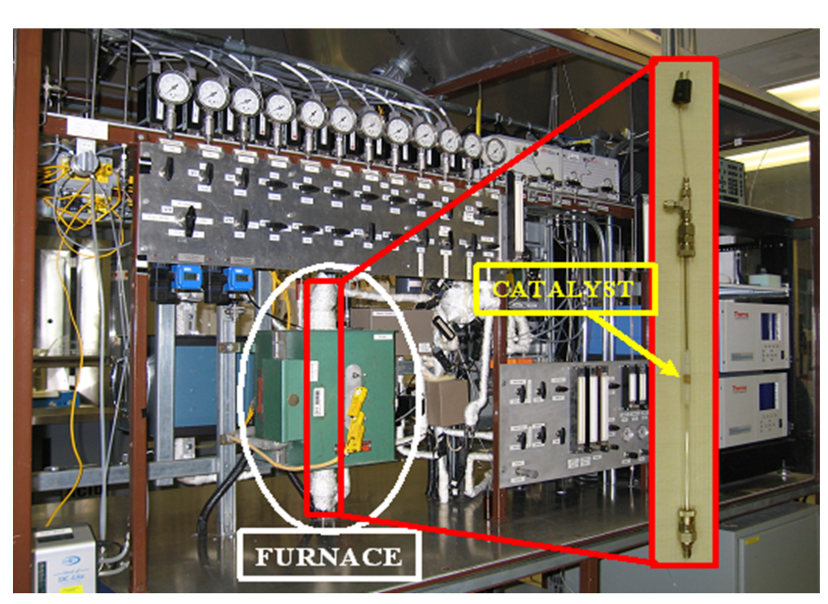
Catalyst Characterization

- Surface area: BET Micromeritics ASAP 2010 analyzer
- Composition: SEM/EDX, Hitachi S3400N VP-SEM with an Oxford INCA EDX detector system operating at 20 kV and 80-90 mA
- Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS)
  - Pretreatment for 1hr @ 400°C with N_2 flow 50 mL/min and 30 min @ 350°C under a N_2 flow of 50 mL/min
  - Flow of 50 mL/min of 1% CH_4 and 10% O_2 balance of He

Catalyst Activity

Temperature Programmed Oxidation (TPO)
- Micromeritics Autochem II 2920 with TCD
- Temperature ramp: 50-600°C at 10°C/min.
- Sample size: 50 mg
- Feed gas: 1% CH_4, 10% O_2, balance He.
- Flow: 50 mL/min

Catalyst testing unit (CTU) (test with water)
- In house testing unit with FT-IR Detector
- Temperature ramp: 150-600°C at 3°C/min.
- Sample size: 500 mg
- Feed gas: 1% CH_4, 10% O_2, 6% CO_2, 10% H_2O, balance N_2, Flow: 500 mL/min, ~55K (GHSV)



Catalyst testing unit (CTU)

Results

Characterization and activity (by TPO) of Pd catalysts on various supports

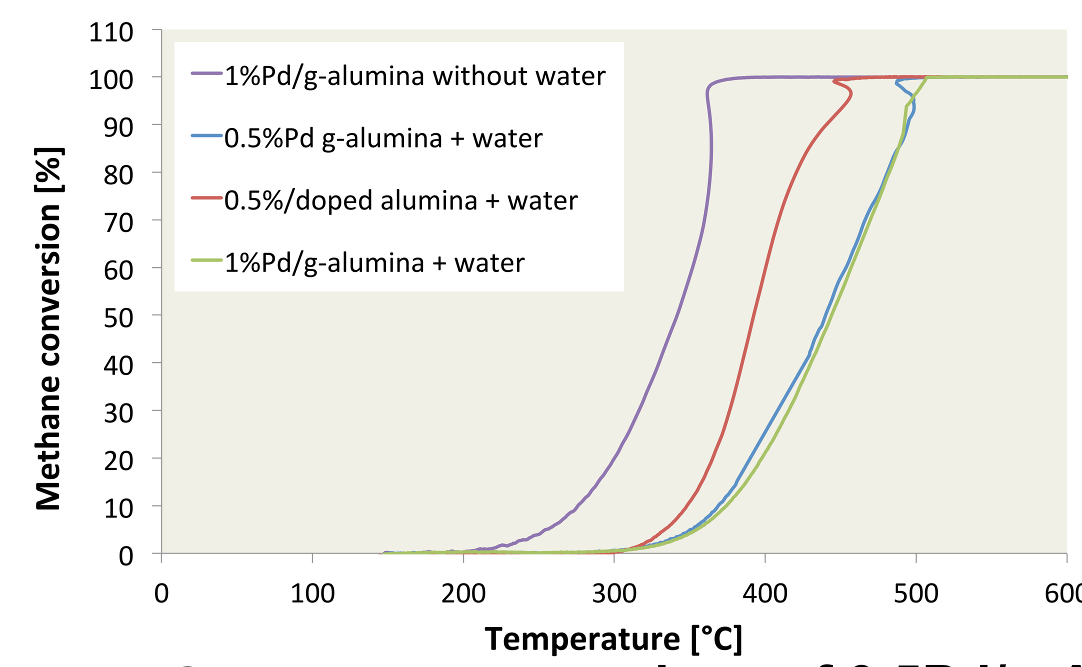
Name (composition)	Active metal content Nominal/SEM EDX (wt%)			Surface area (m^2/g)	T_{50}[1] (°C)
	Pd	Zr	Ti		
0.5Pd/g-Al_2O_3[2]	0.50/0.52	-	-	275	374
1Pd/g-Al_2O_3[2]	1.0/1.1	-	-	240	354
0.5Pd/doped alumina[3]	0.50/0.52	-	-	149	357
0.5Pd/1Zr/doped alumina[3]	0.50/0.47	1.0/1.0	-	145	348
0.5Pd/1Ti/doped alumina[3]	0.50/0.57	-	1.0/0.67	146	375
0.5Pd/1Zr/g-Al_2O_3	0.50/0.47	1.0/1.0	-	246	361
0.5Pd/1Ti/g-Al_2O_3	0.50/0.58	-	1.0/0.73	230	407
0.5Pd/Silica[4]	0.50/0.56	-	-	199	376
0.5Pd/1Zr/Silica[4]	0.50/0.53	1.0/0.52	-	194	371
0.5Pd/1Ti/Silica[4]	0.50/0.59	-	1.0/0.64	204	370

[1] Temperature at 50% methane conversion
[2] g-Al_2O_3 prepared in –house
[3] Commercial support
[4] Commercial silica

- Surface area is not necessarily an indicator of catalytic performance
- Composition has a greater effect on catalytic activity
- Pd supported on commercial doped alumina exhibits highest activity

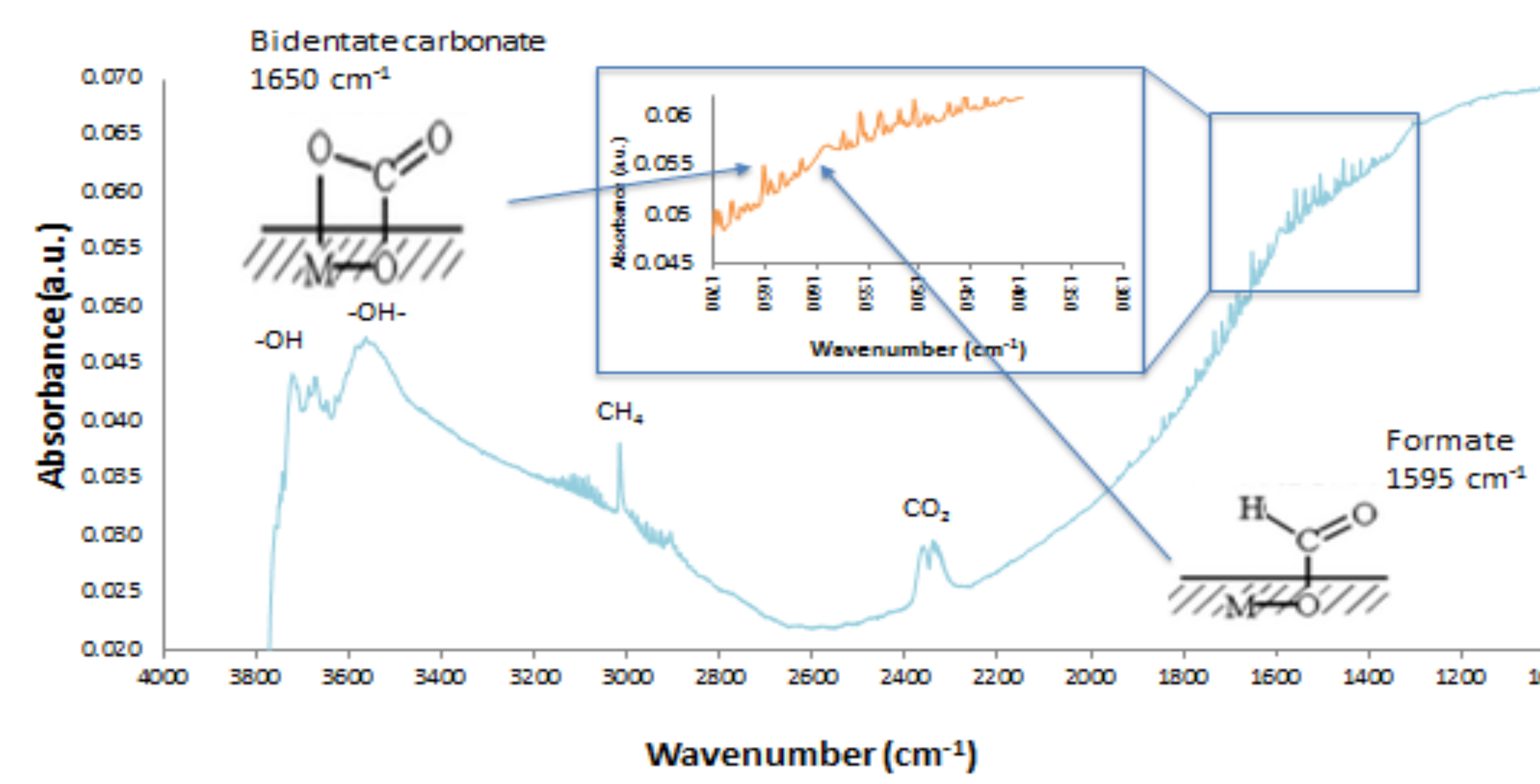
Results (Cont.)

Methane oxidation activity evaluation in presence of water (CTU)

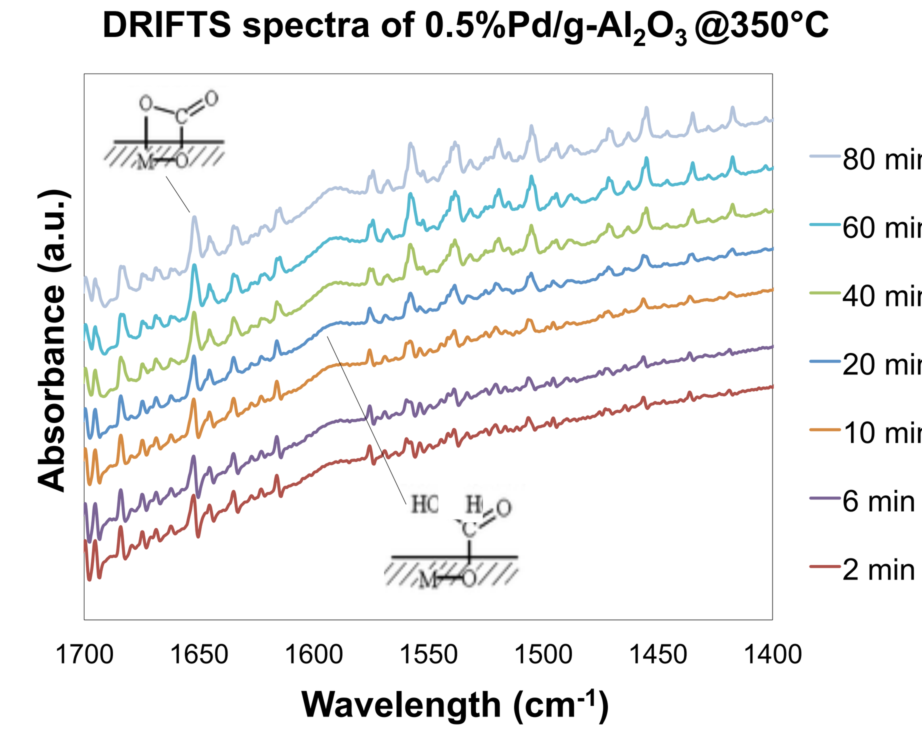


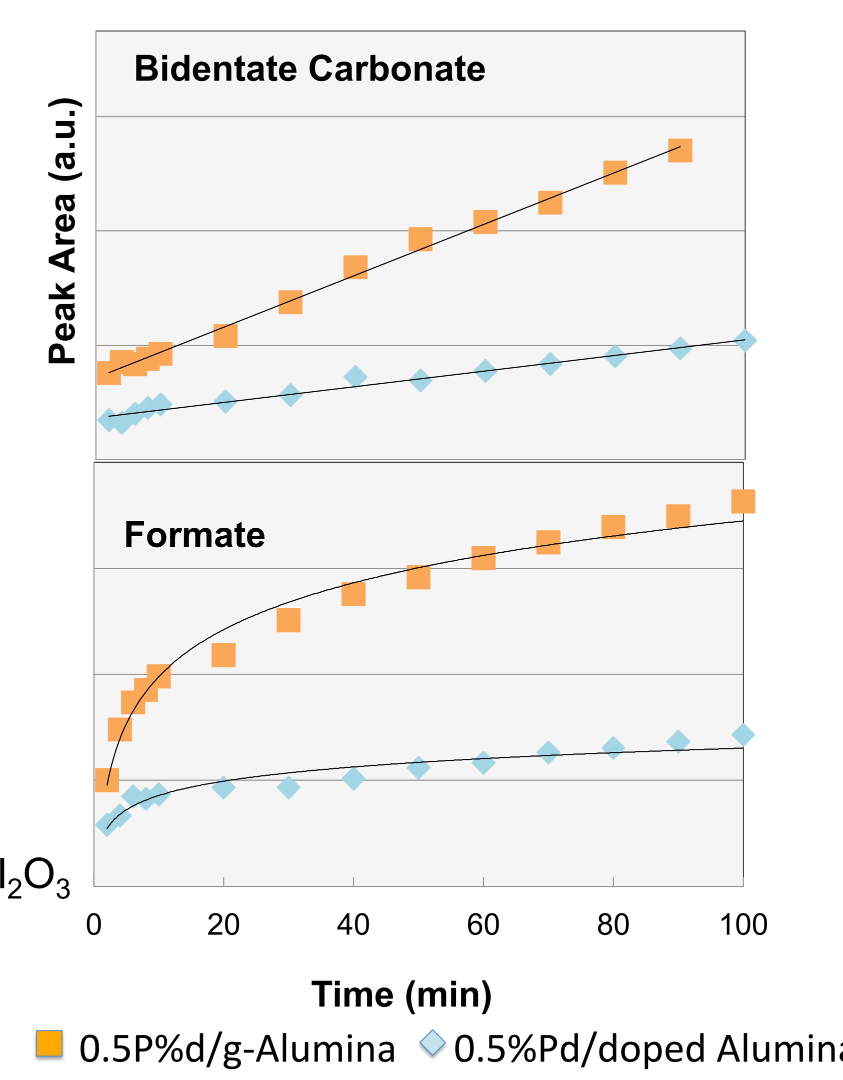
- Water adversely affects methane oxidation activity
- Methane oxidation activity of Pd/doped alumina catalyst has enhanced activity compared to Pd/g-Al_2O_3 catalyst with half the amount of palladium

DRIFTS Analysis: comparison of 0.5Pd/g-Al_2O_3 and 0.5Pd/doped alumina



DRIFTS spectra of 0.5%Pd/g-Al_2O_3 @350°C





- Formate and bidentate carbonate peak area increased with time
- Oxidation is more rapid on doped alumina than g-Al_2O_3
- Dopant may cause structural defects which:
  - Supply a larger amount of lattice oxygen
  - Allow for a faster oxidation of surface species
  - Liberate active sites

Conclusions

- Pd on commercially available doped alumina is the most active catalyst
- DRIFTS identified differences in intermediate surface species emergence
- Dopant in support may provide more lattice oxygen oxidizing surface species and liberating active sites

Future Work

- Aging studies in the presence of water to determine hydrothermal stability
- Test catalyst in presence of sulphur to establish sulphur resistance

Acknowledgements and References

Funding for this project was provided by the Government of Canada Program on Energy Research and Development (PERD), AFTER1 Project.

canmetenergy.nrcan.gc.ca

References:
[1] "Study of Opportunities for Natural Gas in the Transportation Sector"; Marbek: Ottawa, ON, March 2010.
[2] Johnson, J. Chemical & Engineering News, 92:27:10-15, 2014.
[3] DOE Report, http://www.afdc.energy.gov/vehicles/natural_gas_emissions.html

Canada