Zeolite Supported Pd Catalysts for Low Temperature NOx and HC storage

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Johnson Matthey Inc.

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Johnson Matthey

EMISSION CONTROL TECHNOLOGIES

Outline

- Challenges in controlling NOx and HC emissions at low temperatures
- Development of zeolite supported Pd catalysts for low temperature NO/HC storage and conversion
- Characterization of the active sites in zeolite supported Pd catalysts
- Fully formulated catalysts with zeolite supported Pd catalysts
- System demonstration on vehicles
- Modelling study

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Federal Tier 3 and CA LEV III emission standards call for significant reduction of criteria pollutants

Federal Tier 3 standards

Tier 3 Certification Bin Standards (FTP; 150,000 miles)				
Bin	NMOG+NOx	PM*	CO	HCHO
	mg/mi	mg/mi	g/mi	mg/mi
Bin 160	160	3	4.2	4
Bin 125	125	3	2.1	4
Bin 70	70	3	1.7	4
Bin 50	50	3	1.7	4
Bin 30	**30**	**3**	**1.0**	**4**
Bin 20	20	3	1.0	4
Bin 0	0	0	0	0

California LEV III standards

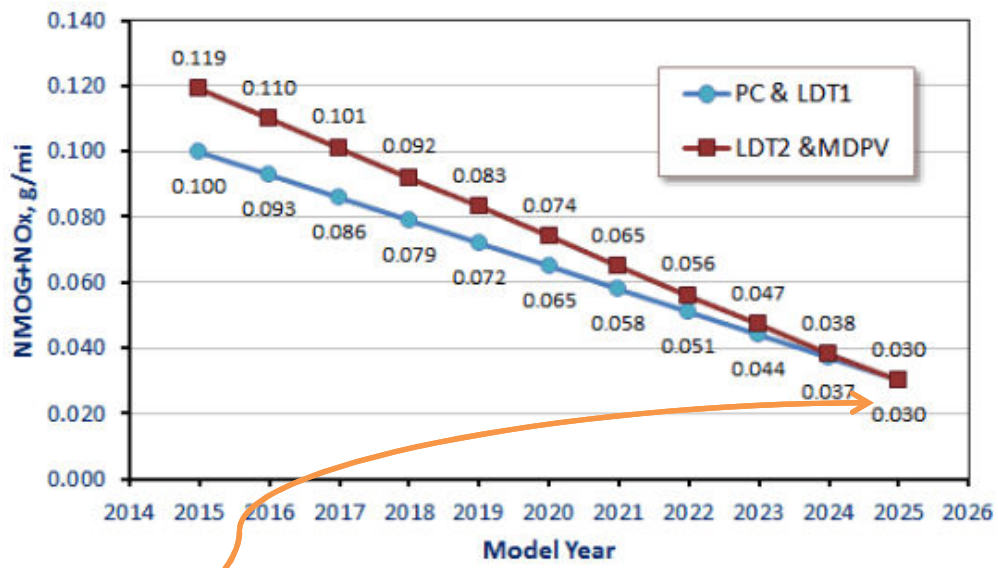


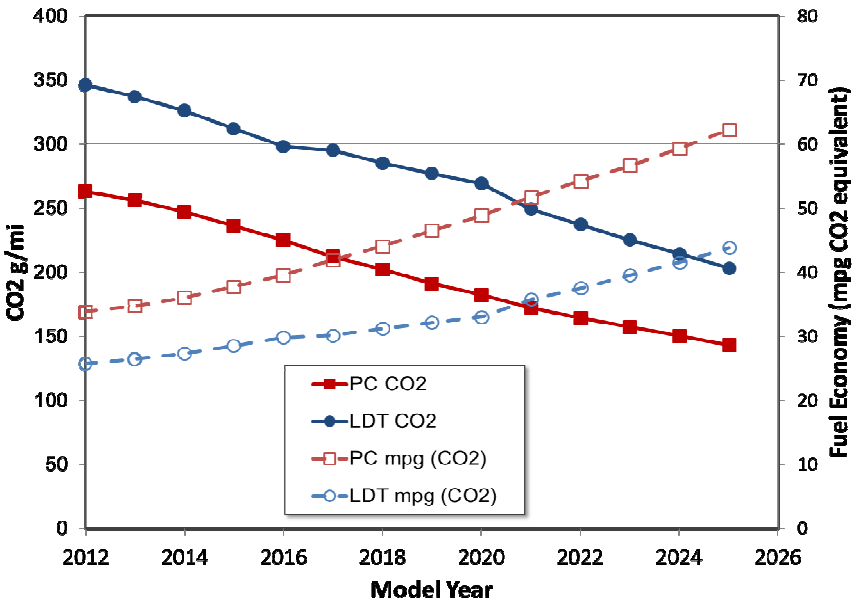
Figure 1. LEV III Fleet Average NMOG+NOx Standards

LDT1: 0-3750 lbs LVW. LDT2: 3751-8500 lbs LVW.

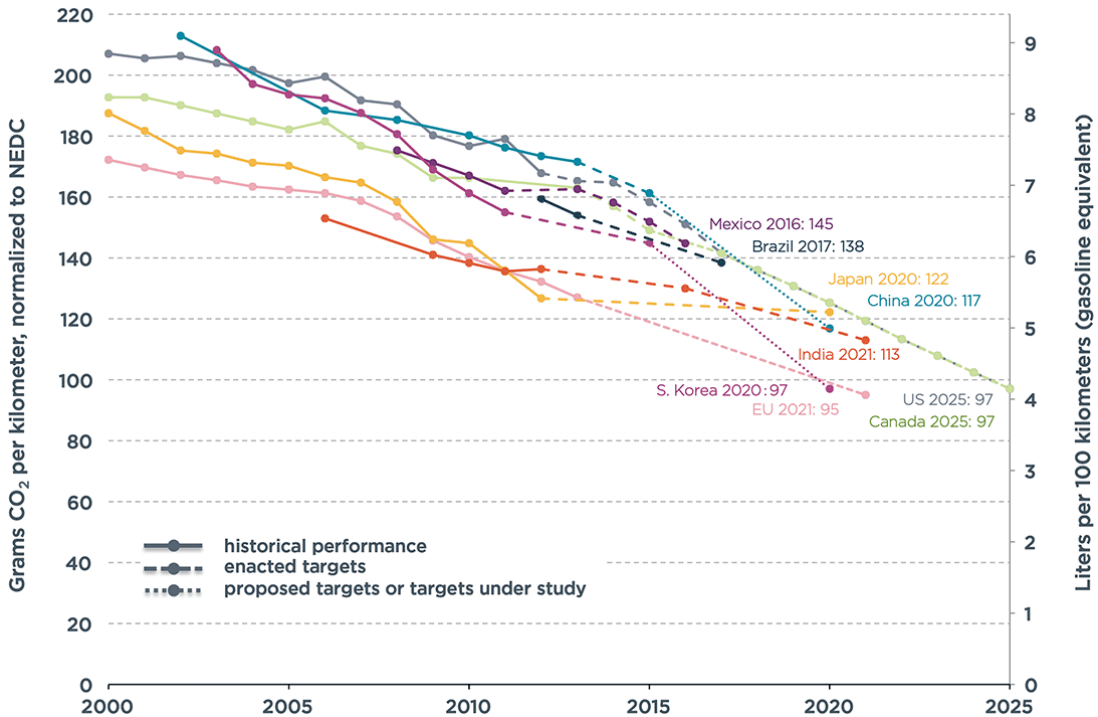
www.dieselnet.com

Fuel economy and Green House Gases (GHG) are also part of the future emission legislations

US



Worldwide



www.theicct.org

Additional GHG limits:

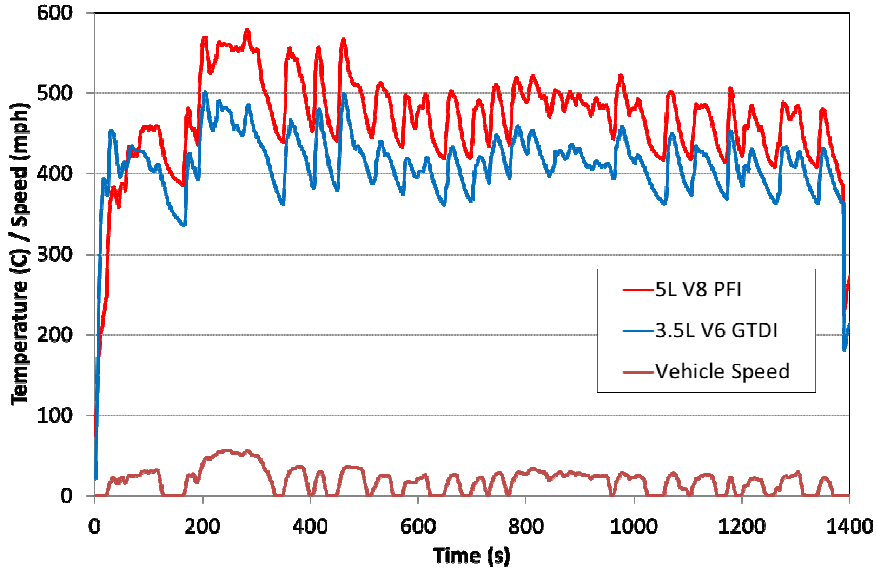
N_2O: 0.010 g/mile

CH_4: 0.030 g/mile

Advanced engines can improve the fuel efficiency, but result in lower exhaust temperatures

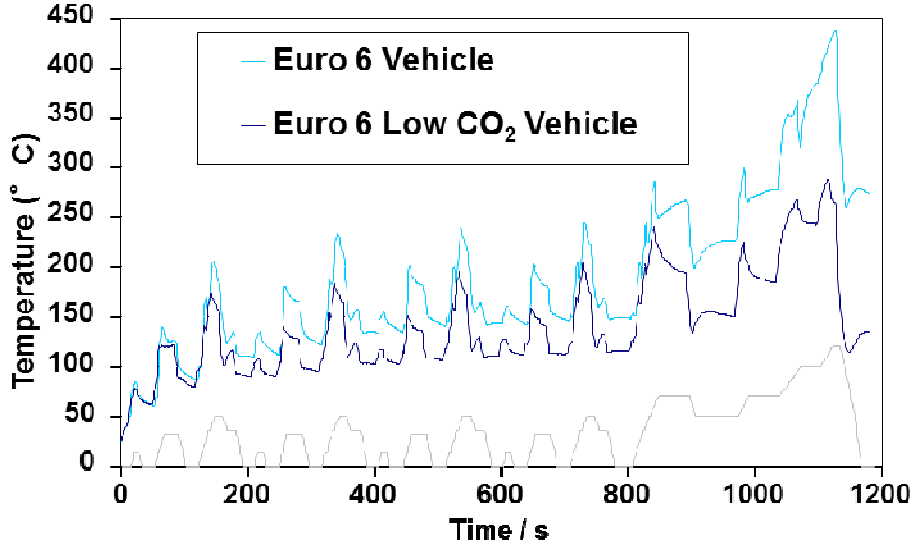
- Advanced combustion, downsizing of engine, turbocharging,

  all result in lower exhaust temperatures



Gasoline vehicles

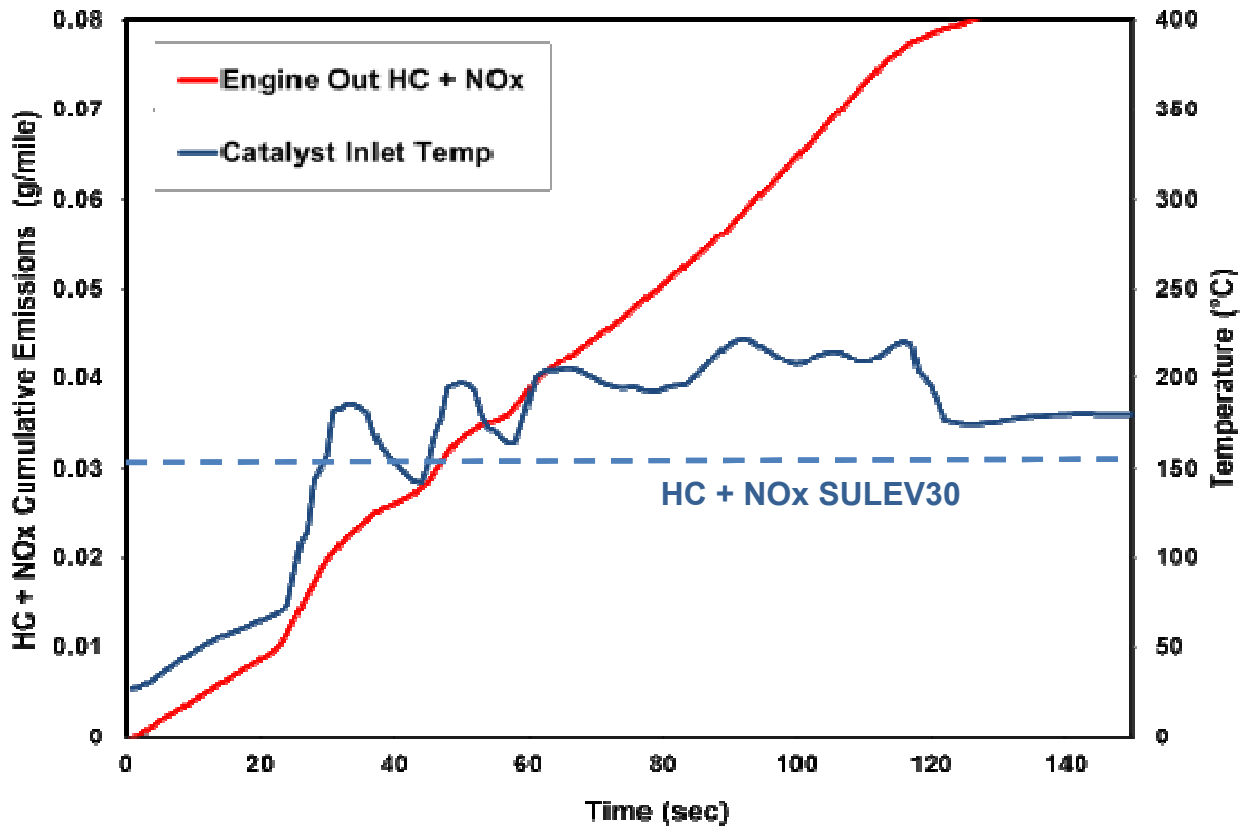
- Diesel CO_2 reduction leads to even lower exhaust temperatures



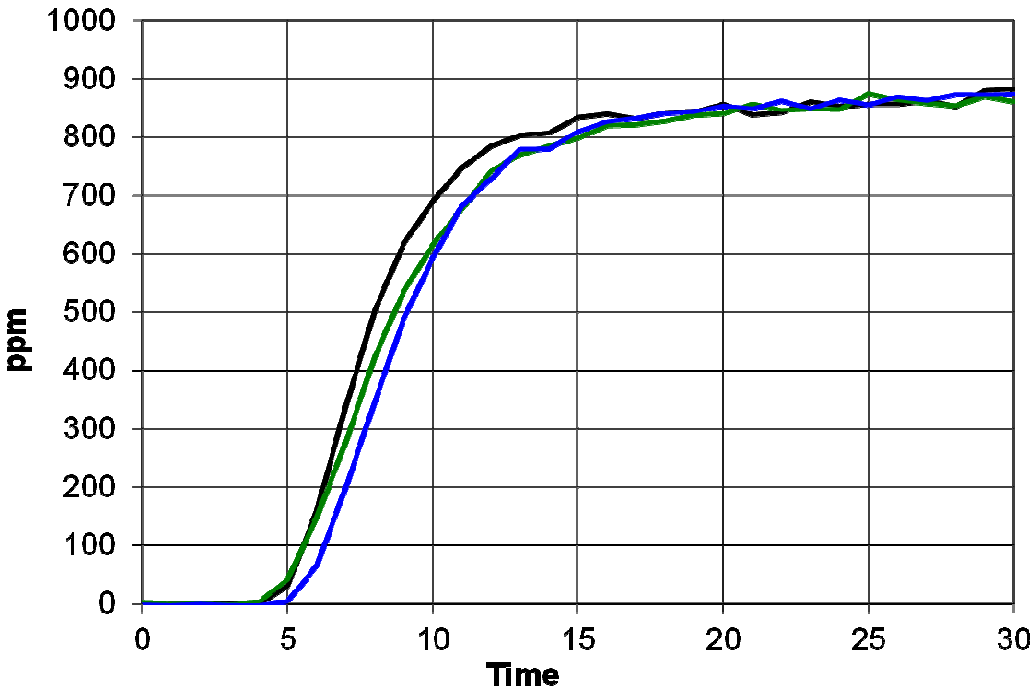
Diesel vehicles

Control of cold-start emissions is crucial to meet the future emission regulations

- e.g. SULEV30 (HC +NOx = 30 mg/mile)
  - Current TWC, DOC, SCR, NAC catalysts function at >~200°C
  - ~100-200s for these components to reach the operating temp
  - Engine-out HC/NOx emissions exceed SULEV30 during the cold start period



Zeolite based HC traps can storage HC's at low temperatures, but release them too earlier



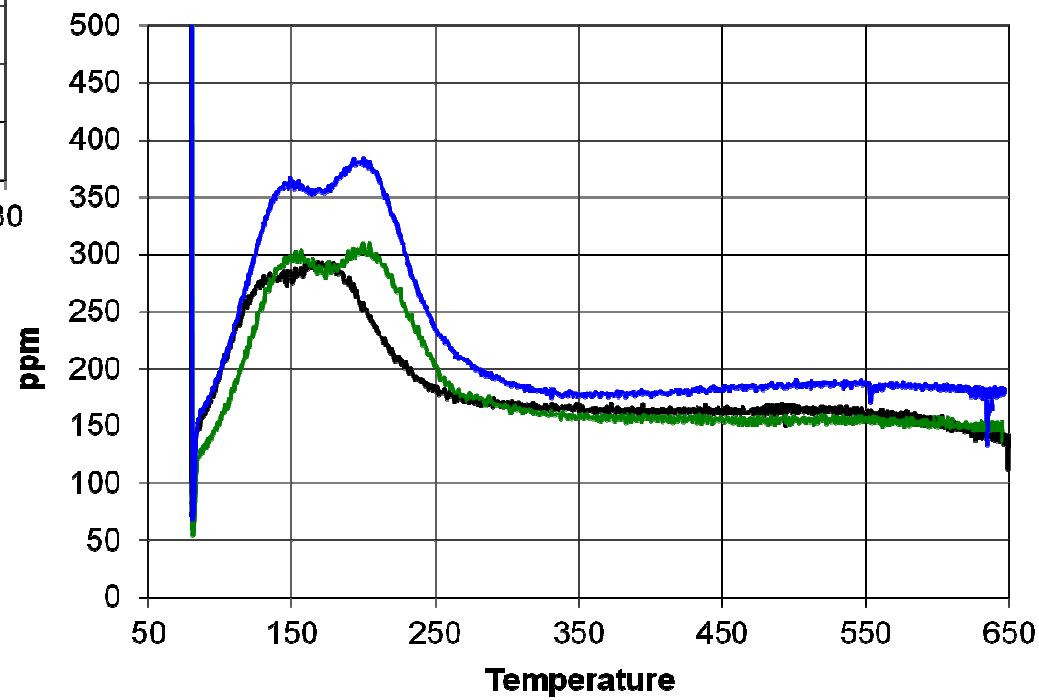
HC storage at 80C
1500ppm HC inlet

HC release
Temp ramping
rate 40C/min

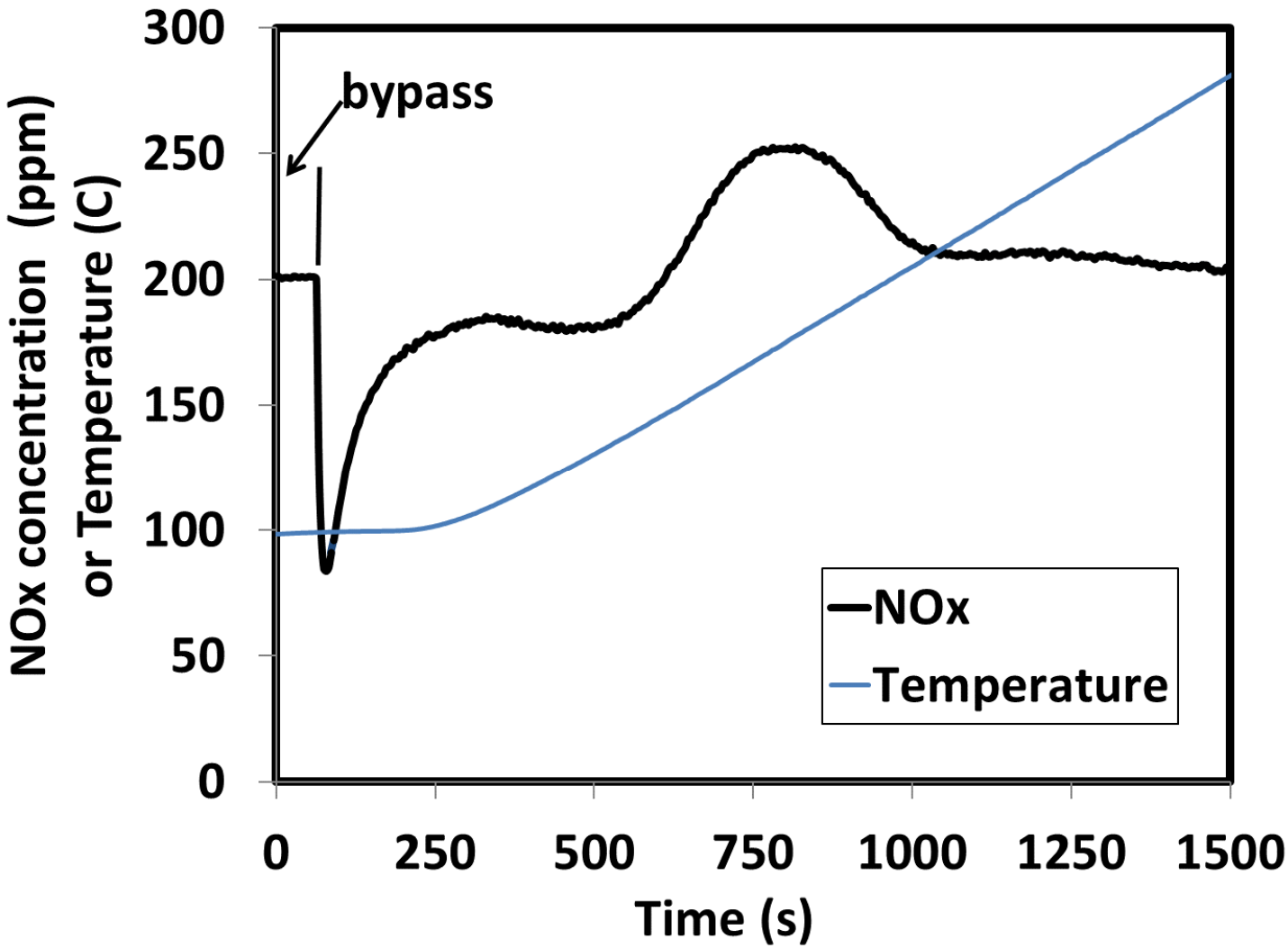
Zeolite

Zeolite/M1

Zeolite/M2



Conventional NACs store NO at LT but with low trapping efficiency, oxidation of NO to NO_2 is kinetically limited at LT



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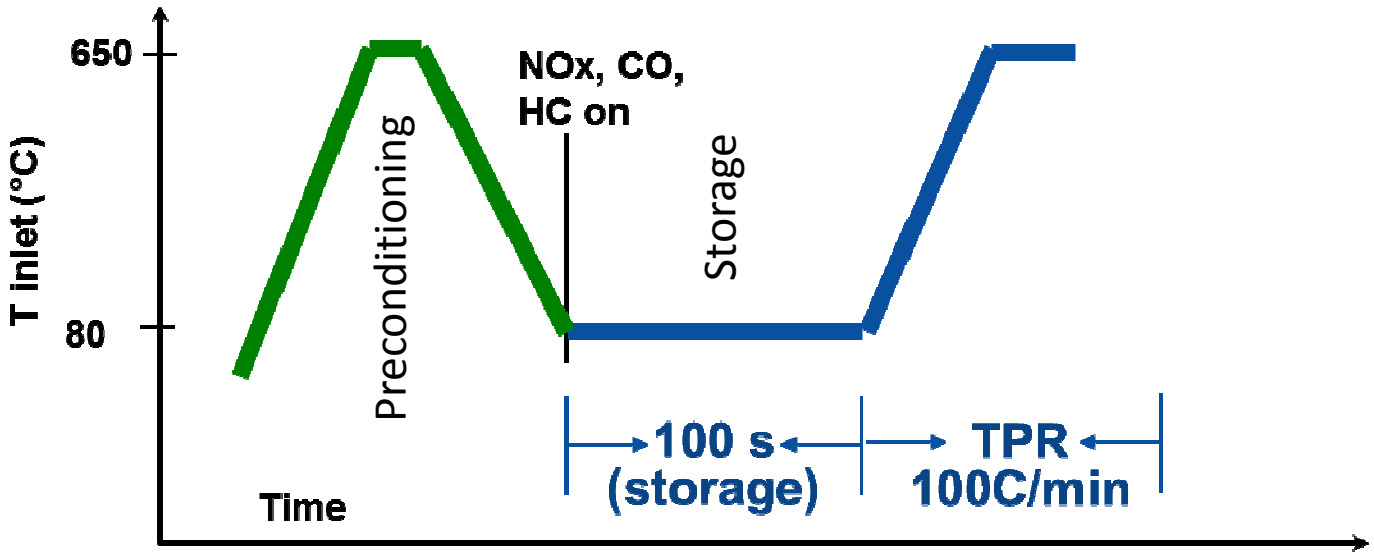
Laboratory evaluation protocol

- NO/HC storage, release, and conversion testing



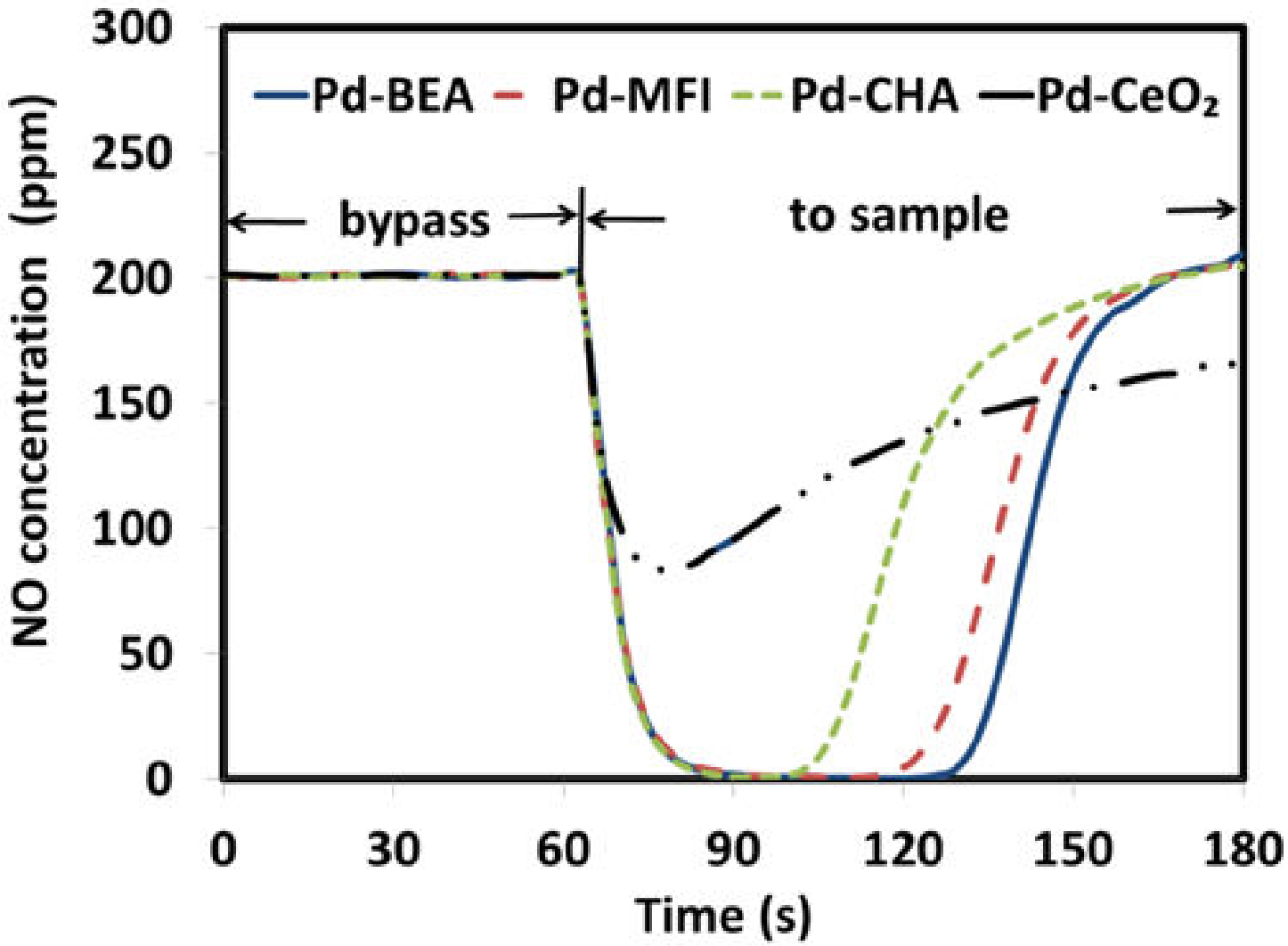
: 10% O_2 / 5% H_2O / 5% CO_2

: 200 ppm NO/200 ppm CO/500 ppm (C_1) $C_{10}H_{22}$/10% O_2 / 5% H_2O / 5% CO_2

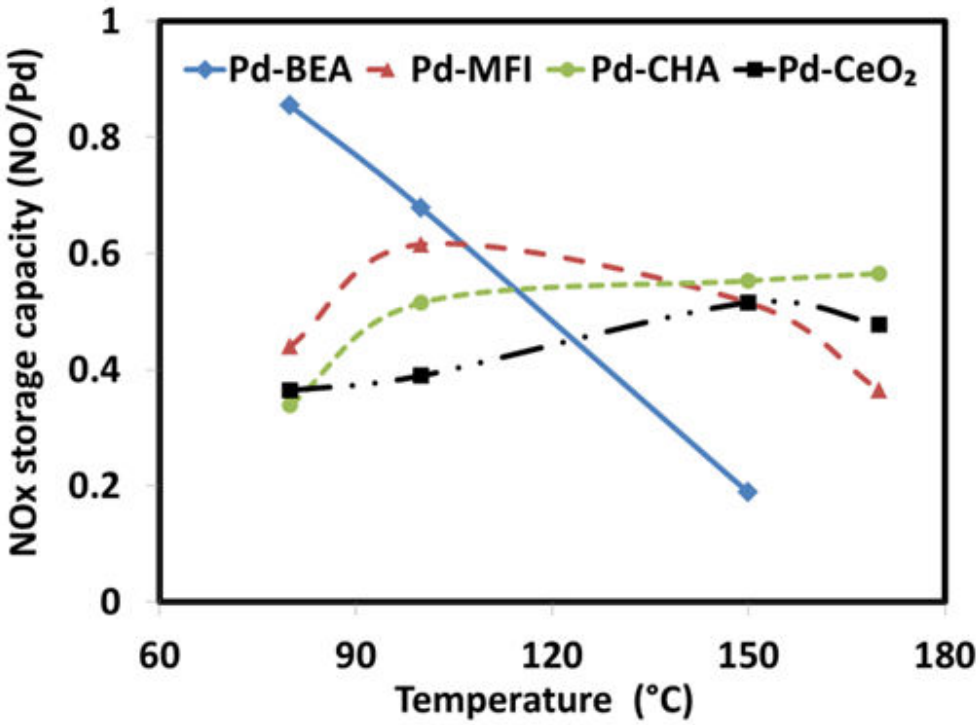
S.V. : 30,000 hr^{-1}
(Flow rate = 21.2 L / min)

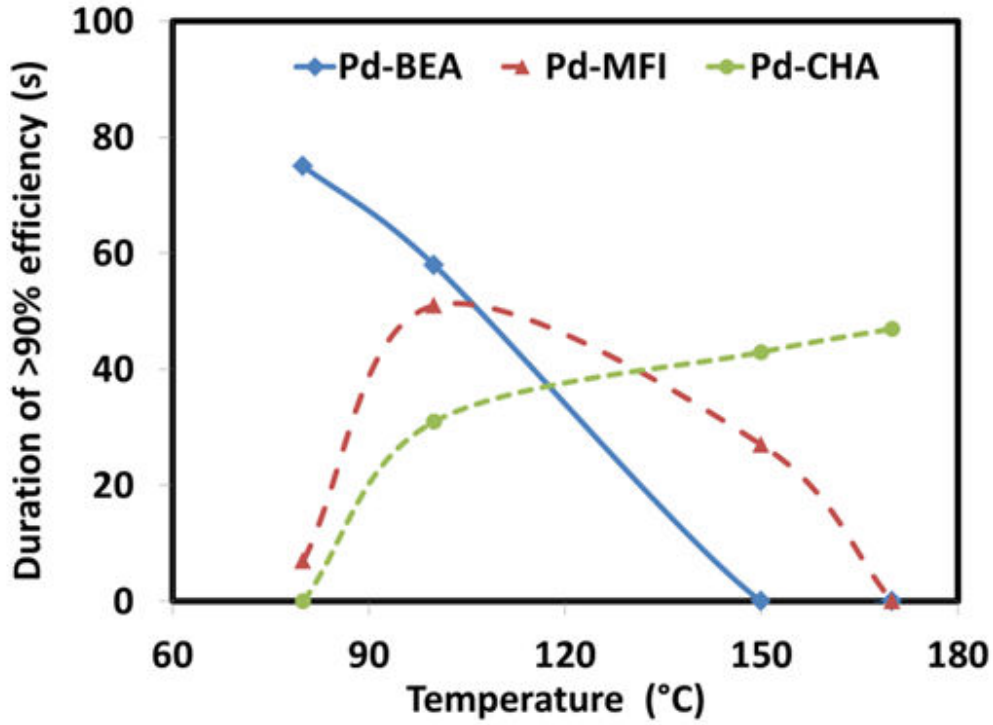
Hydro-thermally aged 750°C/5% H_2O/16h

Zeolite supported Pd catalysts exhibit high NO storage capacity with nearly 100% trapping efficiency

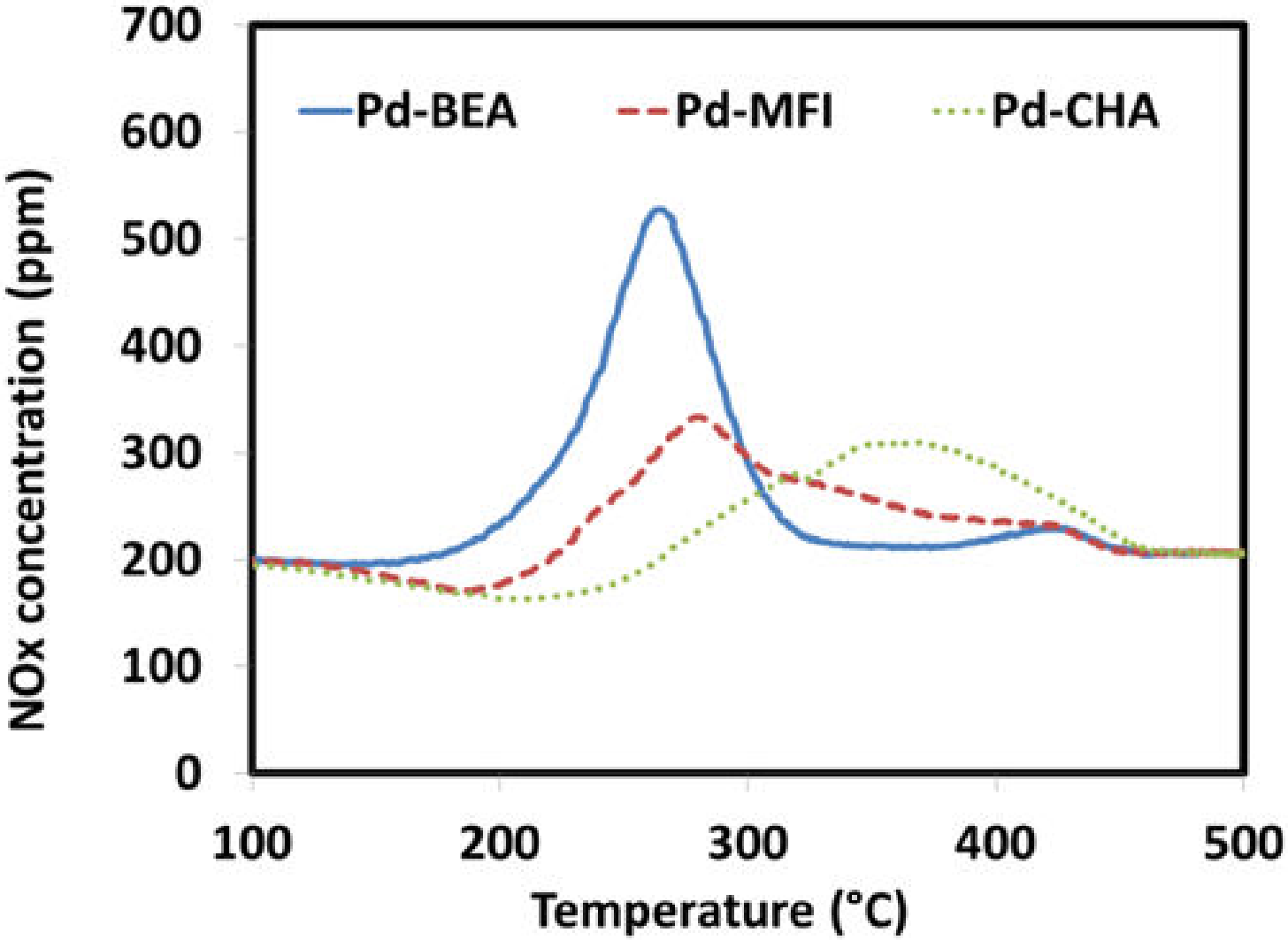


Zeolite structures have a strong influence on the temperature profiles of the NOx storage capacity

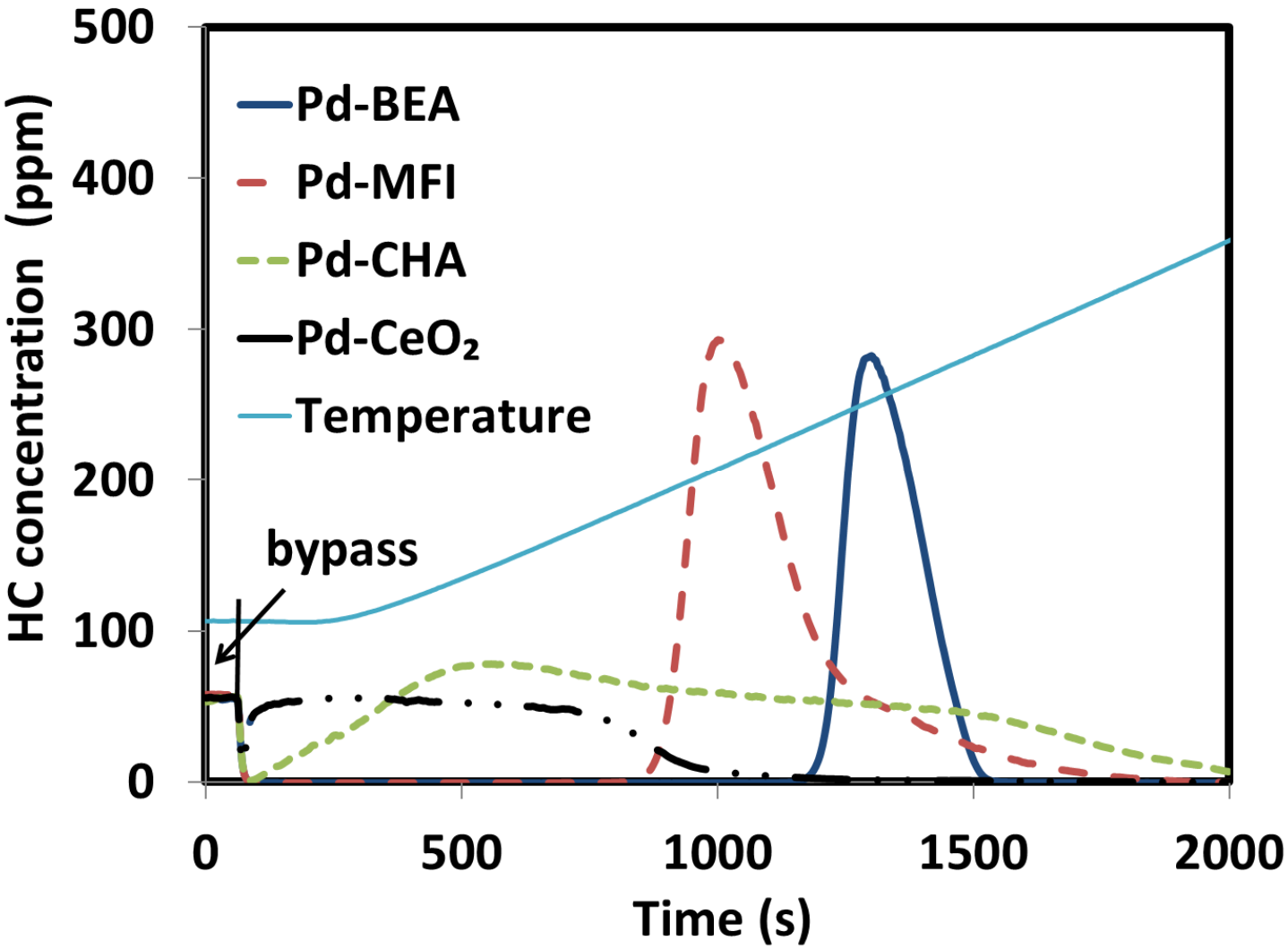




Zeolite structures also affect the NOx release profiles



Zeolite structures affect the HC storage and release profiles – the larger the pores, the higher HC storage capacity



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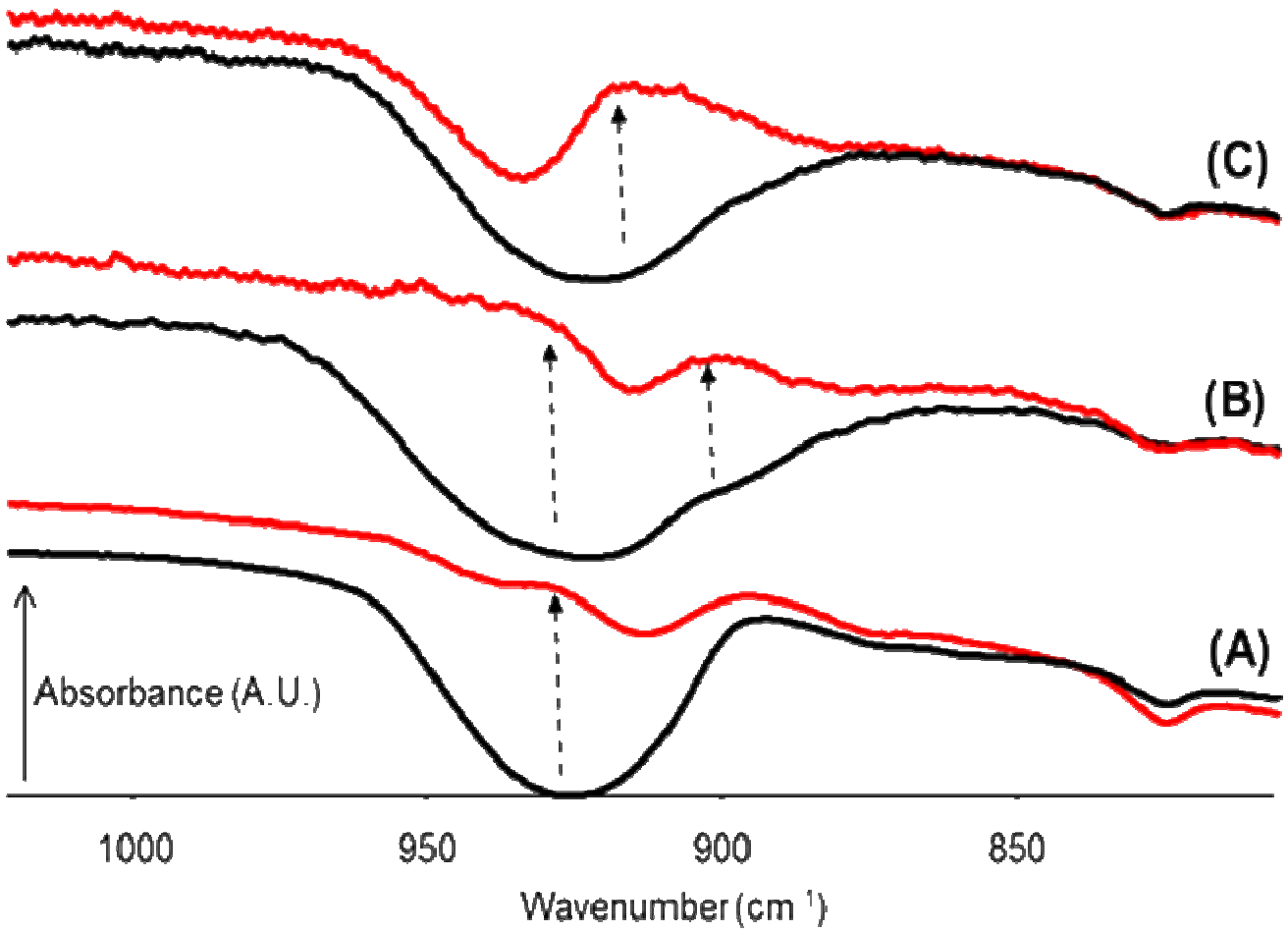
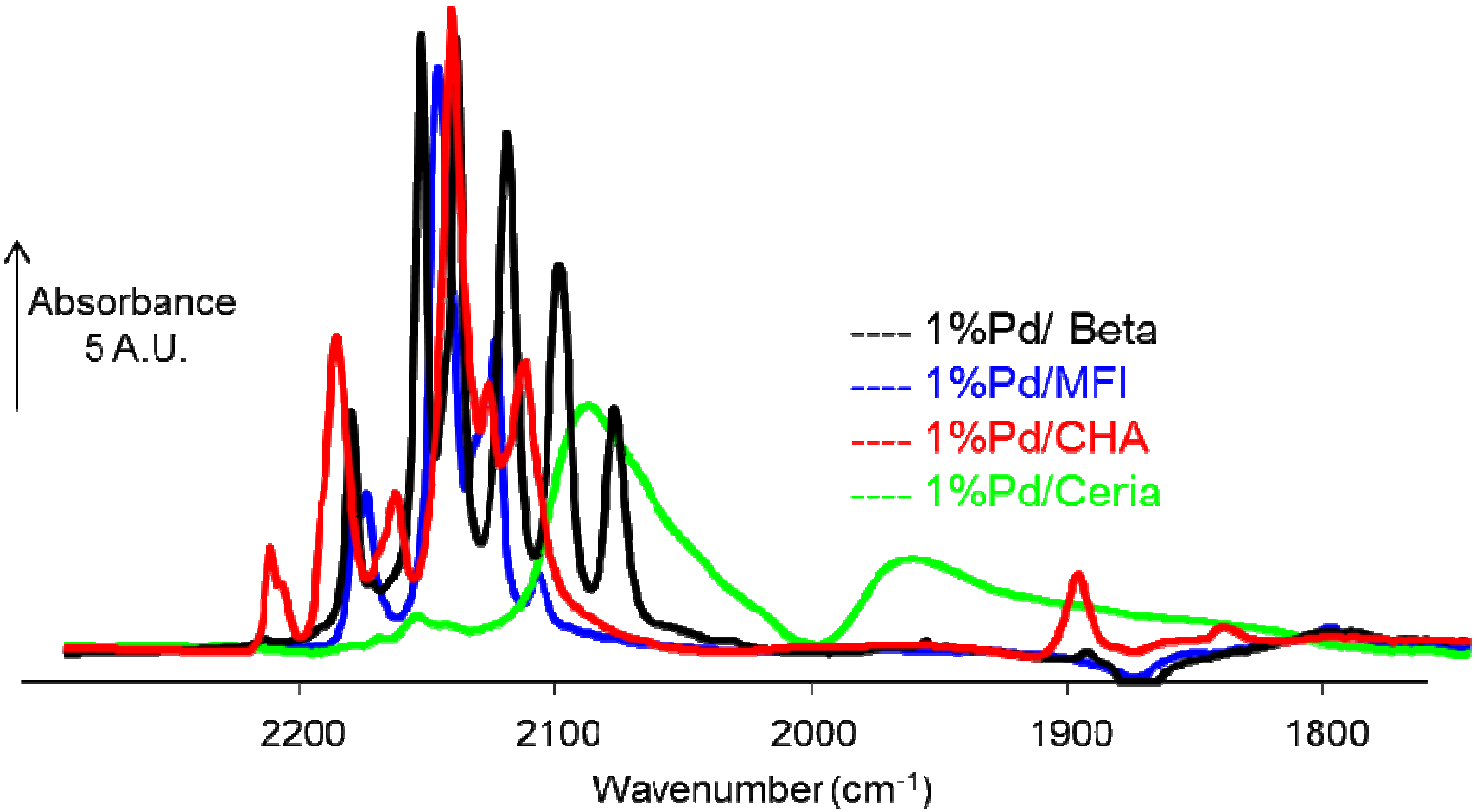
Pd is located at the exchange sites of the zeolite supports



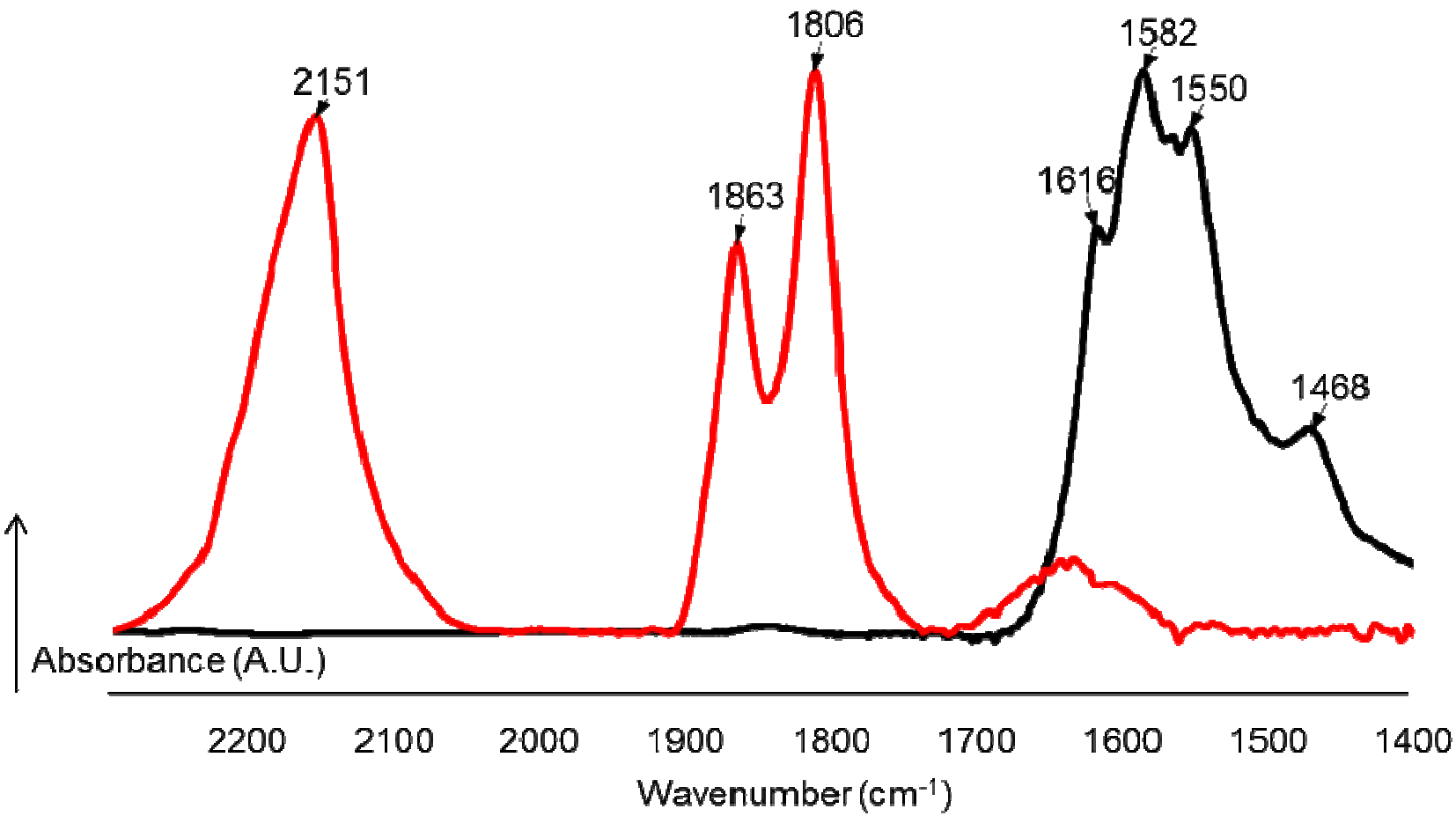
IR spectra of 1%Pd/Zeolite (red) and bare zeolite (black) samples after dehydration at 400 °C under 6%O_2/Helium for 2 hours; (A) BEA, (B) MFI; (C) CHA

CO adsorption experiments confirm that Pd is at the exchange sites



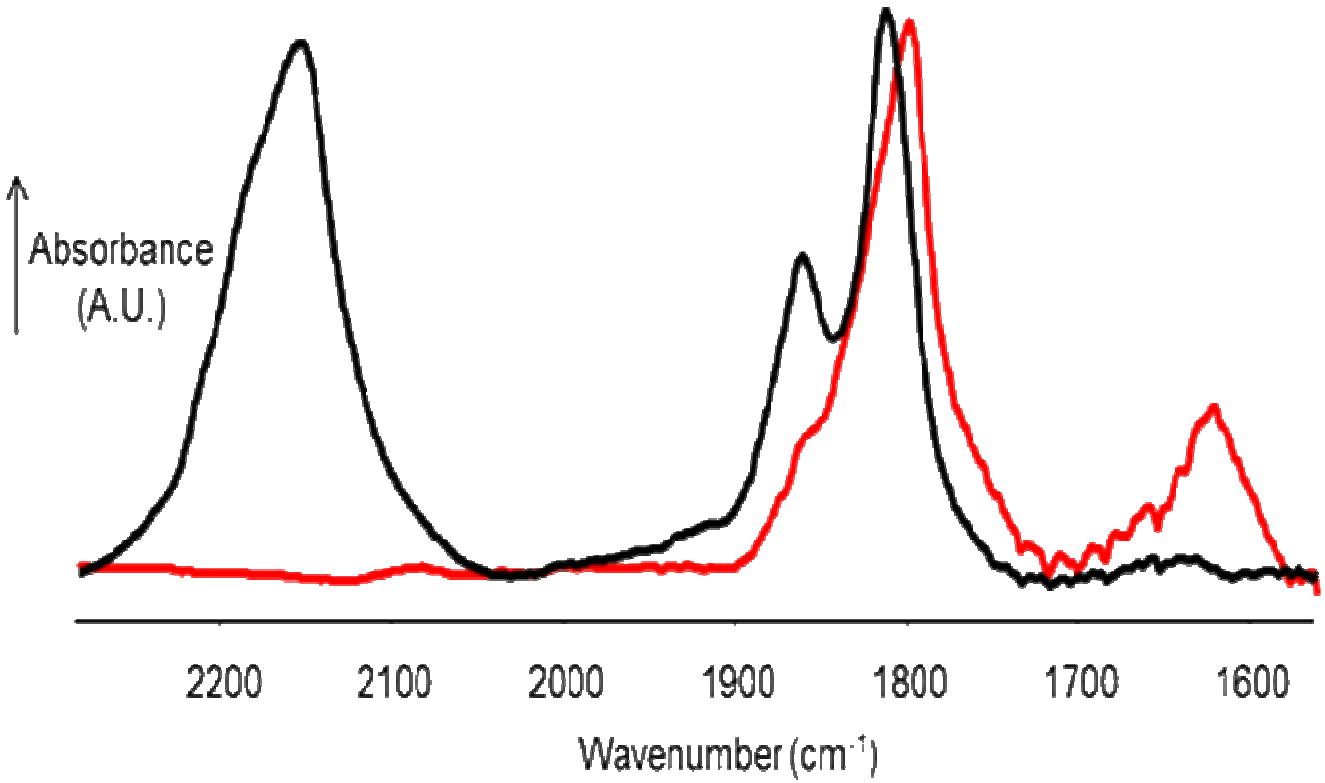
Transmission spectra of CO adsorbed on Pd/Zeolites and Pd/Ceria

Pd at the exchange sites adsorbs NO directly, other non-zeolite supported Pd catalysts need formation of nitrates



Transmission IR spectra of NO adsorption on 1%Pd/CHA (red) and 1%Pd/Alumina (black) [samples were dehydrated at 400 °C under 6%O_2/Helium for 2 hours; spectra recorded after 15 min exposure to 500ppm NO/Helium at 100°C]

The presence of H_2O has little impact on NO adsorption on Pd sites

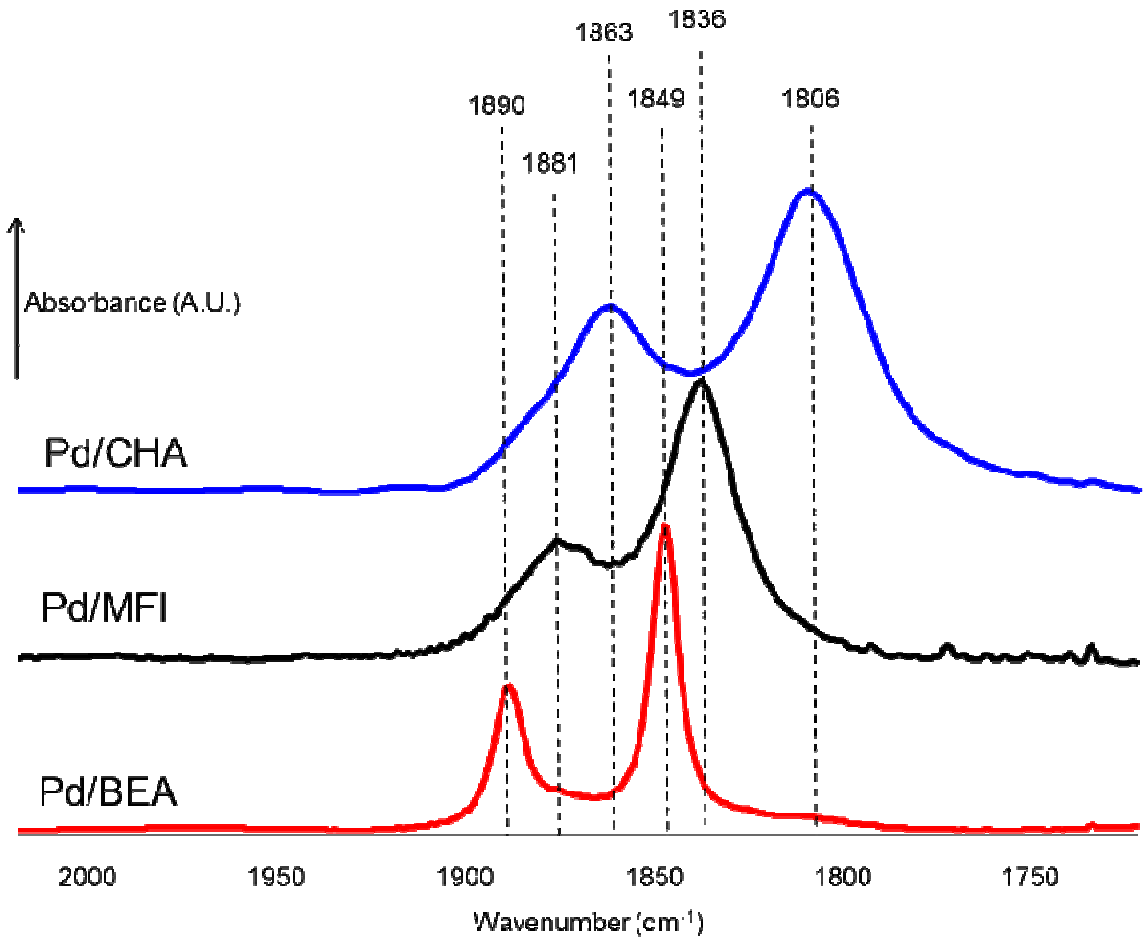


---- 300ppm NO+3%O_2/He

---- 300ppm NO+3%O_2+1.75%H_2O/He

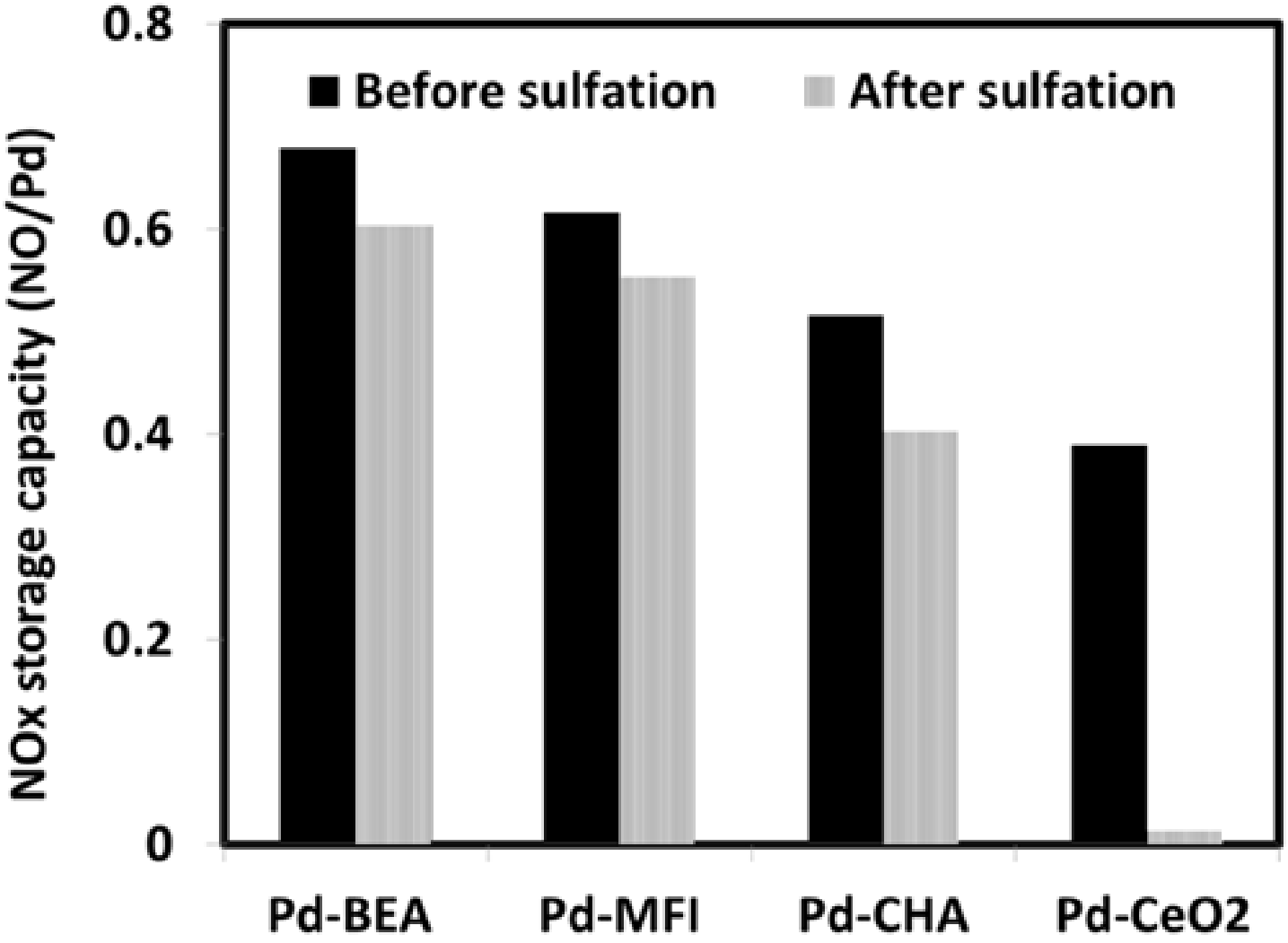
DRIFTS spectra recorded at 100 °C for Pd-CHA after exposure to (NO + O_2) with or without H_2O in the gas mixtures

Zeolite structures affect the NO bonding strength



Transmission spectra of NO adsorption on Pd/Zeolites

Pd/zeolite show good sulfur tolerance and can be desulfated at >600C under lean conditions



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dCSC™ technology utilizes Pd/zeolite providing combined functions of NOx trap, HC trap, and DOC

NOx Trap

- Store NOx during cold start
- Thermal release of NOx
- Low temperature NOx conversion activity
- N_2 selectivity

HC Trap

- Improved HC storage capacity
- Additional HC conversion activity

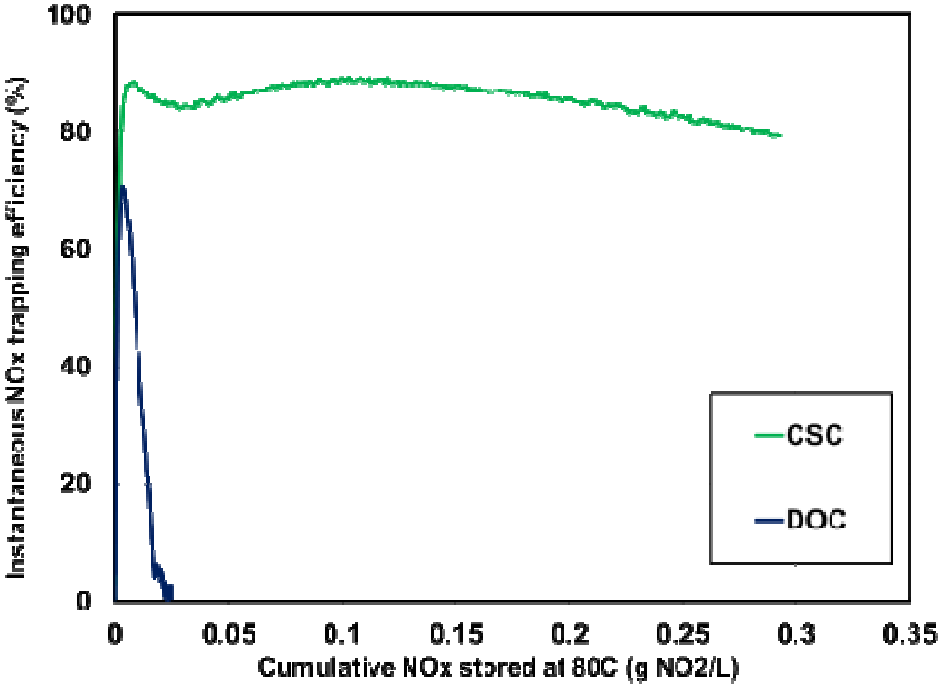
DOC

- Improved CO/HC light-off activity
- Comparable NO to NO_2 activity

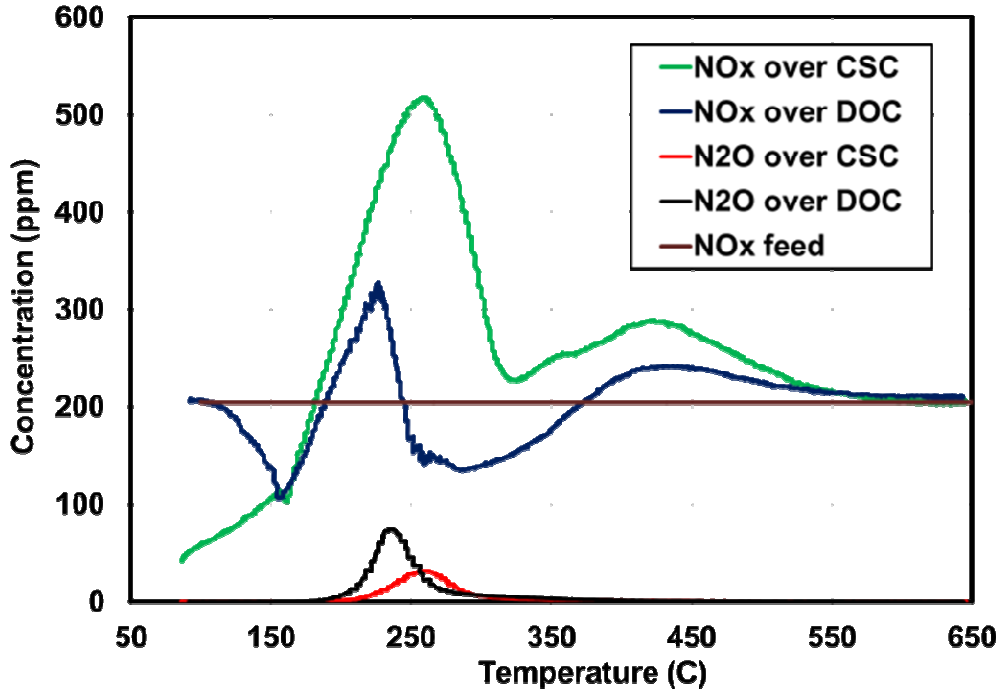
dCSC™ technology

dCSC™ catalysts exhibit high NOx storage capacity/efficiency, NOx thermally release at ~200-350°C

NOx storage at 80°C



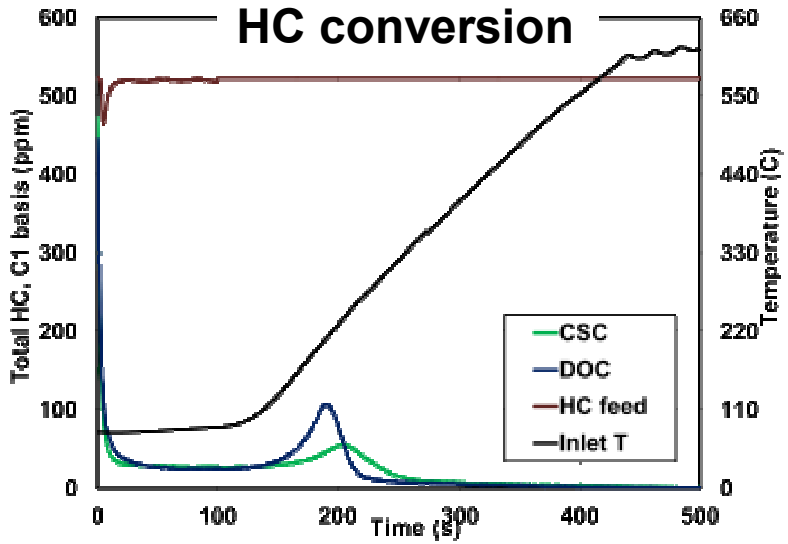
NOx release in the subsequent temperature ramp

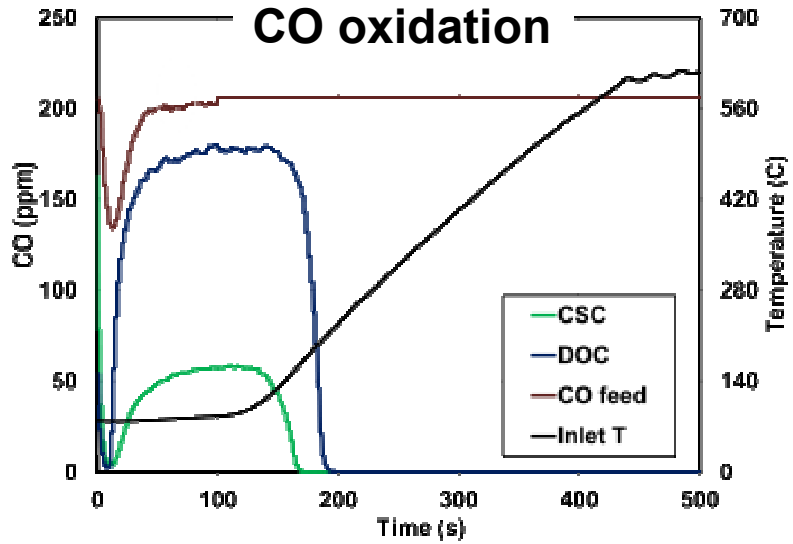


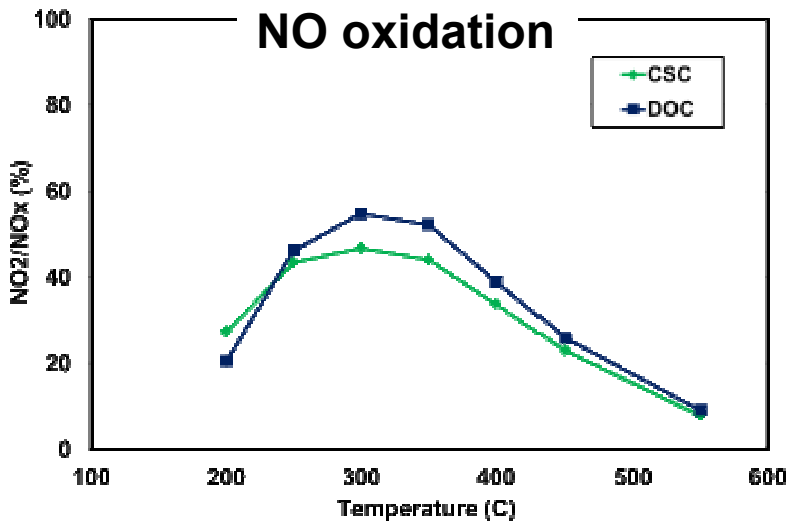
DOC @ Pt70:Pd35	= Diesel oxidation catalyst
CSC @ Pt50:Pd90	= New concept cold start catalyst

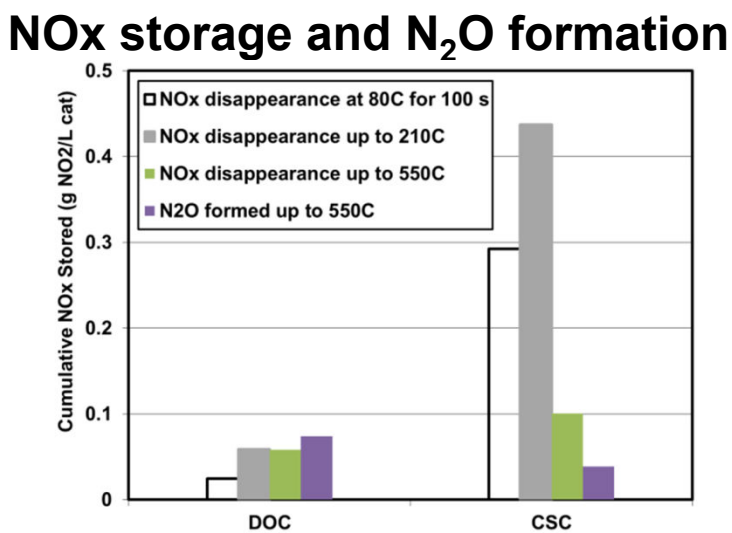
H.-Y. Chen, et al., SAE 2013-01-0535

dCSC™ catalysts also show improved HC/CO conversion, less N_2O formation, and similar NO oxidation activity





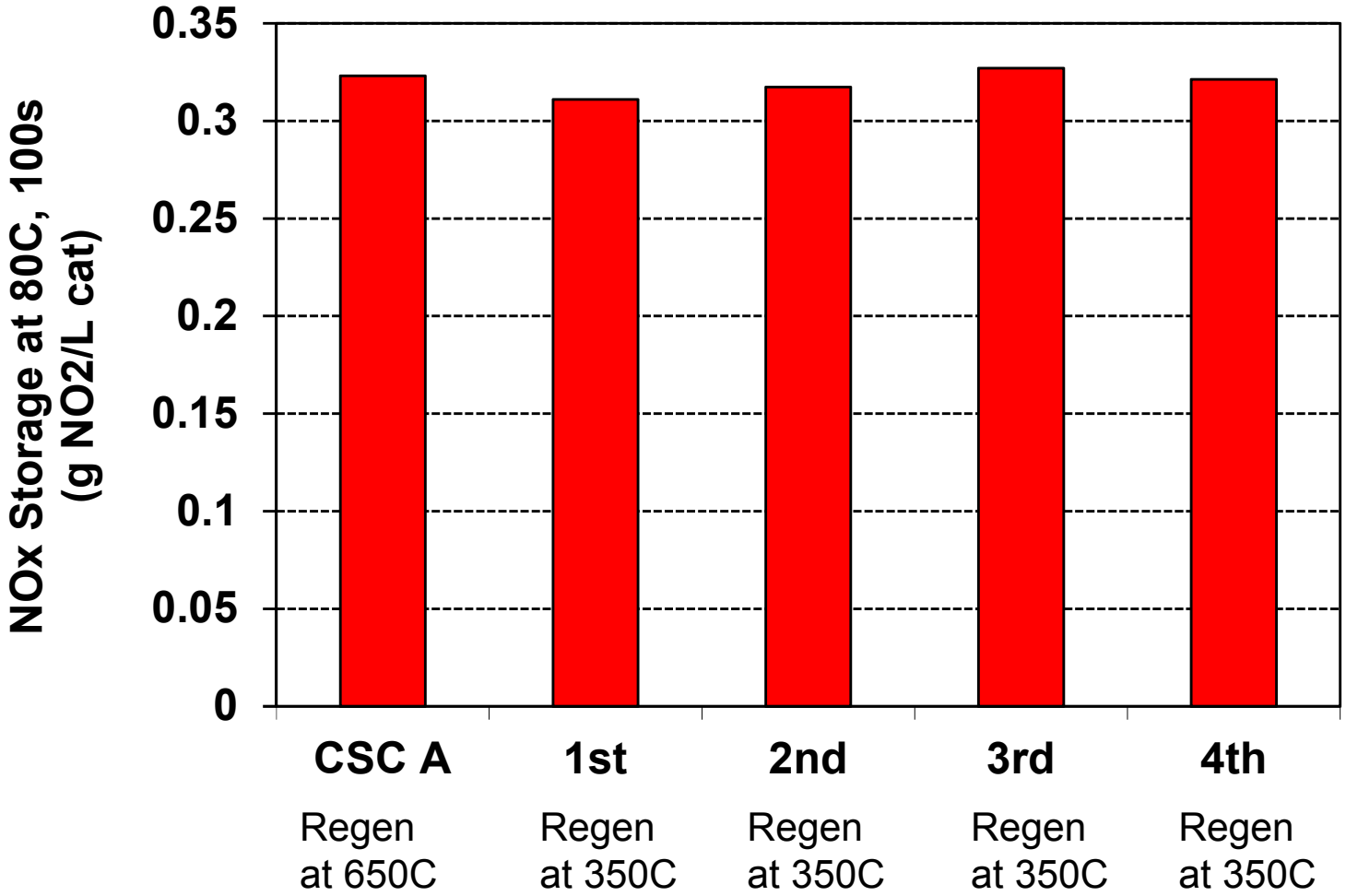




H.-Y. Chen, et al., SAE 2013-01-0535

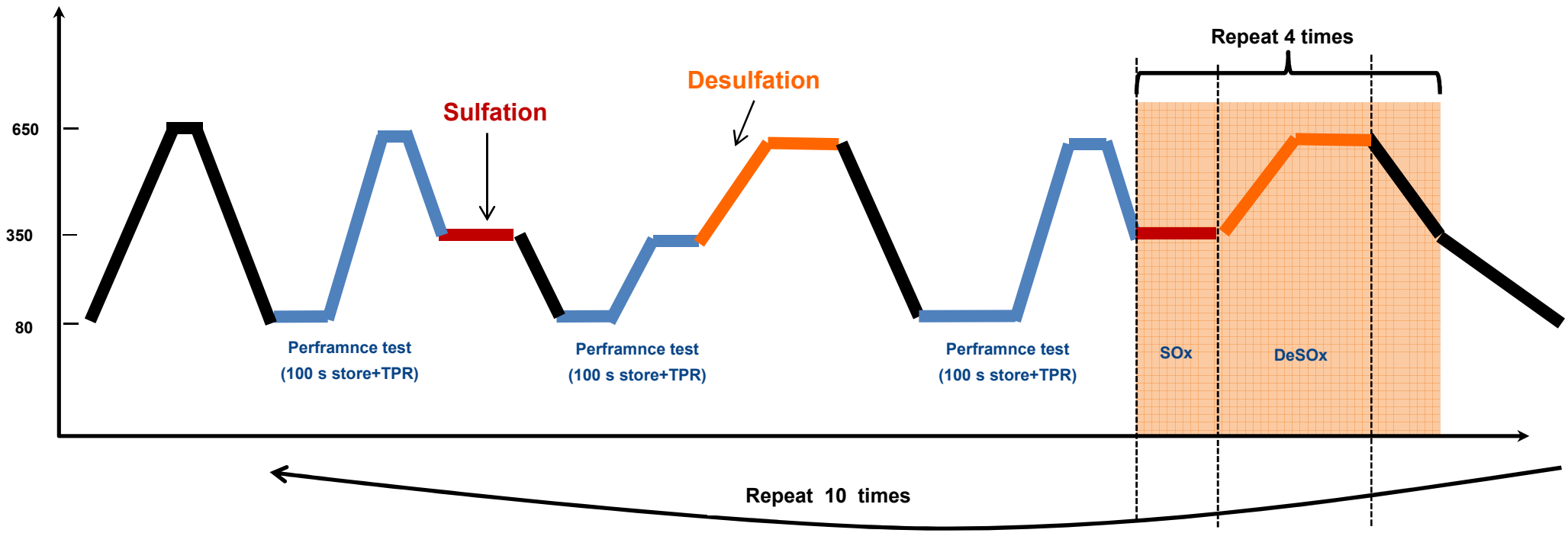
dCSC™ catalysts can be regenerated at ~350C

(750°C/5%H_2O/16h aged, SV=30K, NO, CO=200ppm, C10=500 ppm, 10% O_2)



H.-Y. Chen, et al., SAE 2013-01-0535

Long-term sulfur tolerance and desulfation properties of the dCSC ™ catalyst were evaluated by SOx/DeSOx cycle test



: 10% O_2 / 5% H_2O / 5% CO_2

: 200 ppm NO/200 ppm CO/500 ppm (C_1) $C_{10}H_{22}$/10% O_2 / 5% H_2O / 5% CO_2

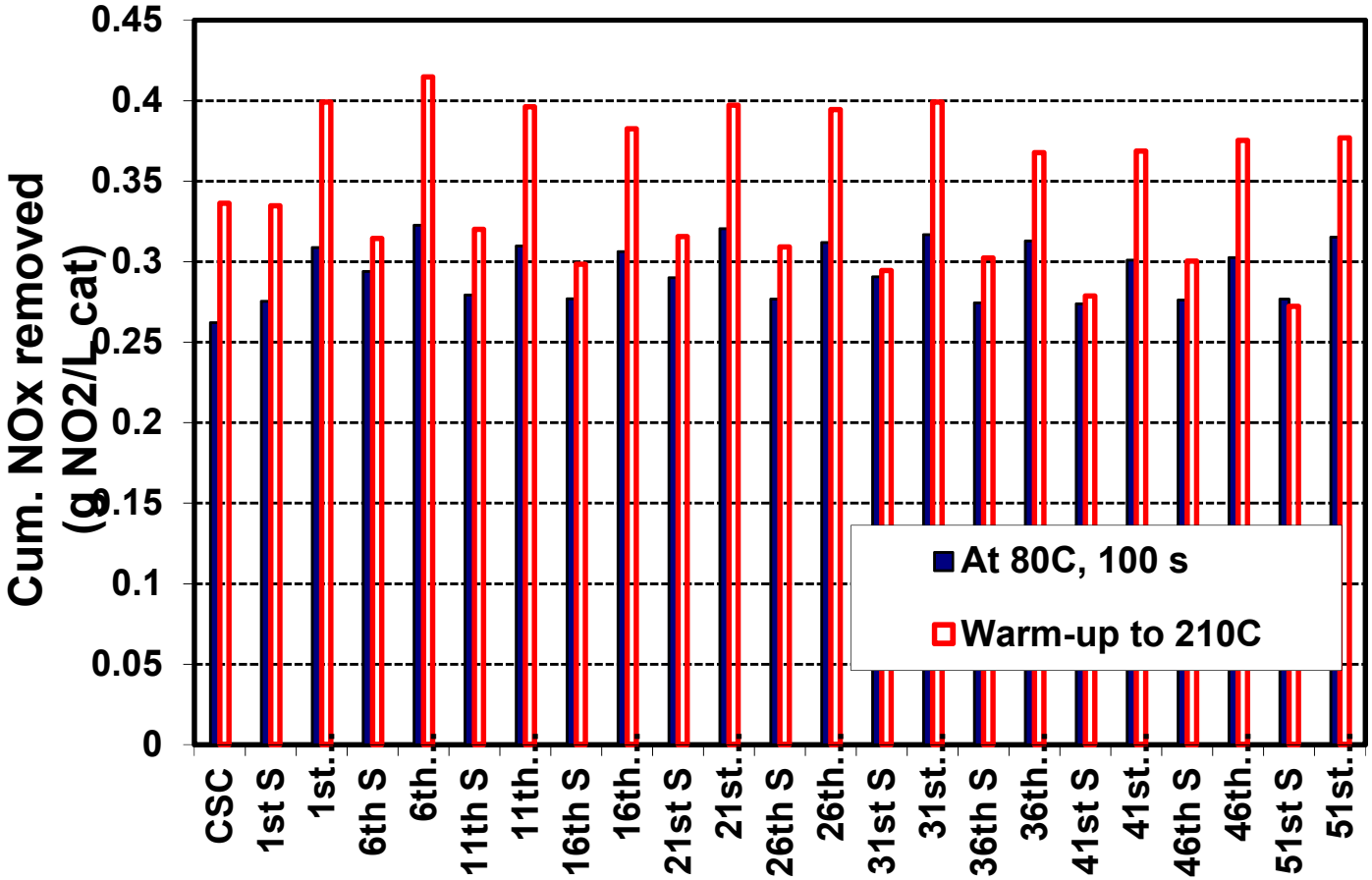
: 200 ppm NO/200 ppm CO/1% (C_1) C_3H_6/10% O_2 / 5% H_2O / 5% CO_2

: 10 ppm SO_2 /200 ppm NO/200 ppm CO/500 ppm (C_1) $C_{10}H_{22}$ /10% O_2 / 5% H_2O / 5% CO_2

SO_2 = 10 ppm @ 350C for 70 min (0.5 g S/L cat)

S.V. : 30,000 hr^{-1} (Flow rate = 21.2 L / min)

The dCSC™ catalyst has good sulfur tolerance is stable after long-term sulfation/desulfation testing



Sulfation was carried at 350°C with an exposure level of 0.5g sulfur /L catalyst

Desulfation was carried at 650°C gas inlet (~720°C catalyst bed) temperature under lean conditions for 15 minutes

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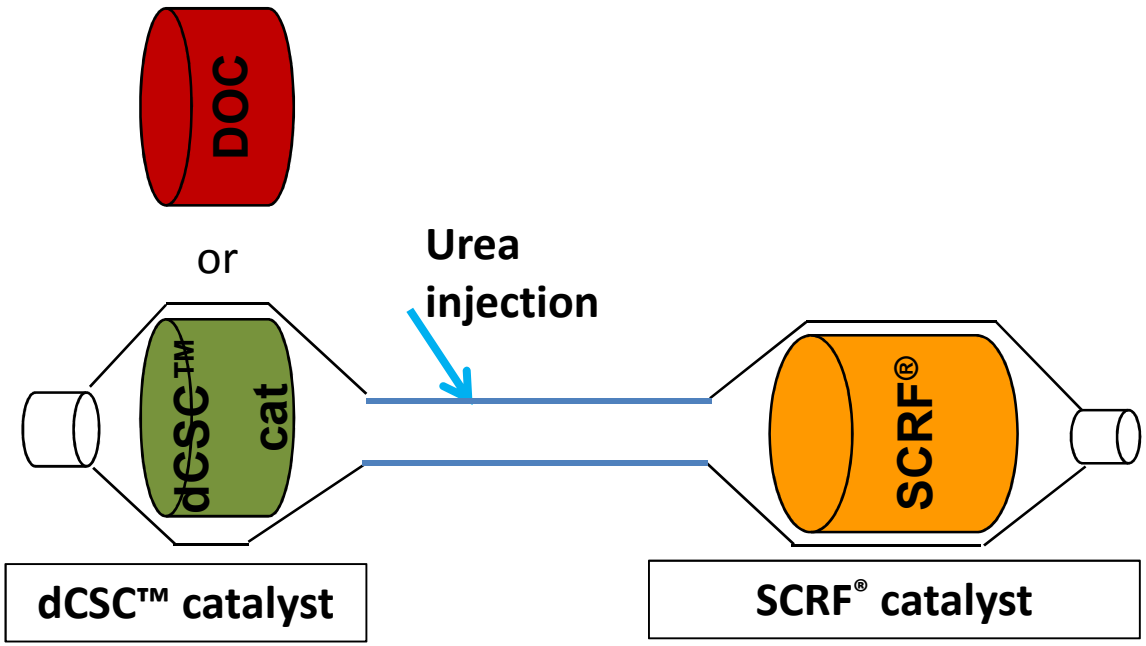
dCSC™ catalyst vehicle testing on EU LDD

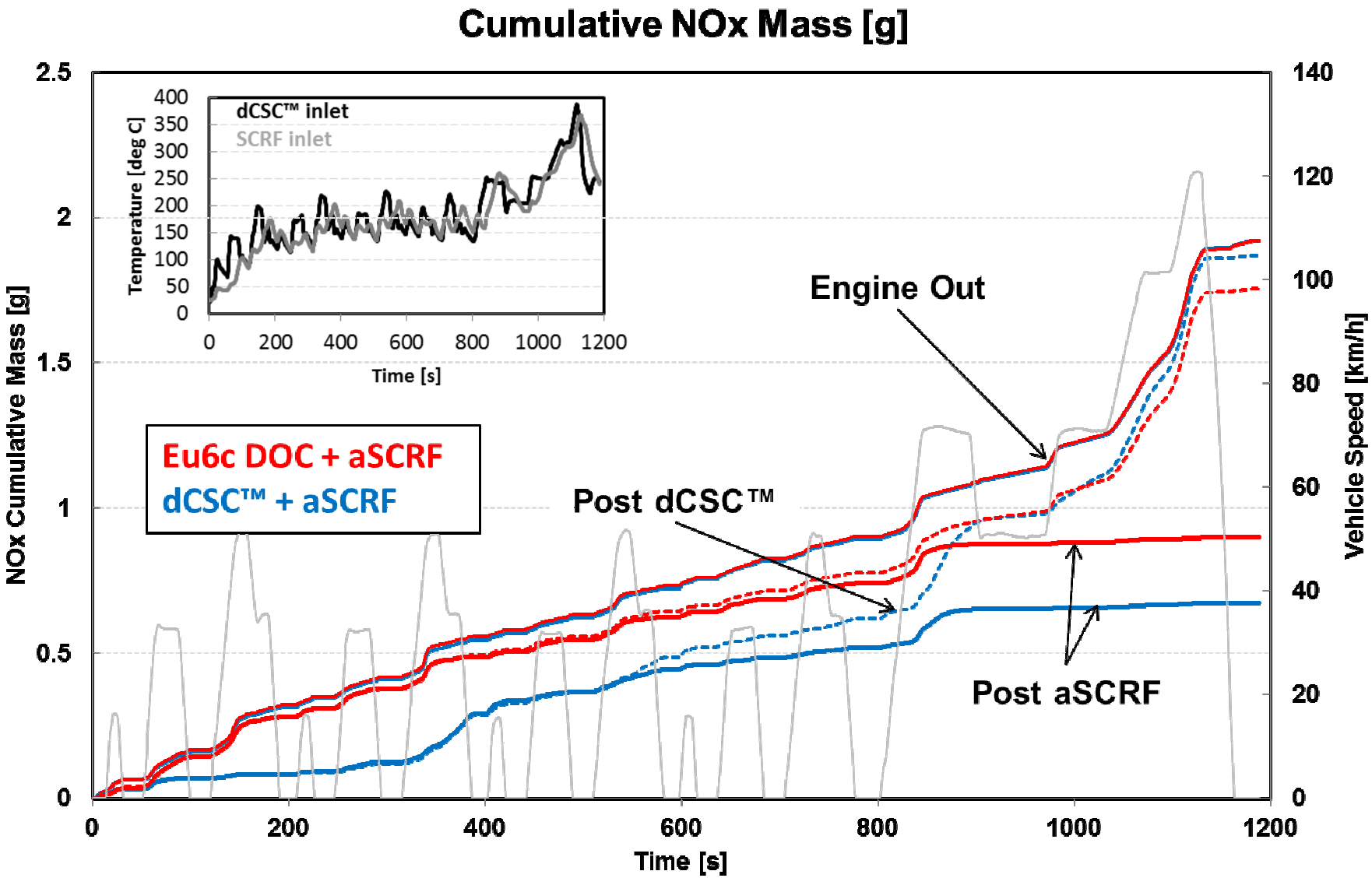
- **Eu6 3.0L engine**



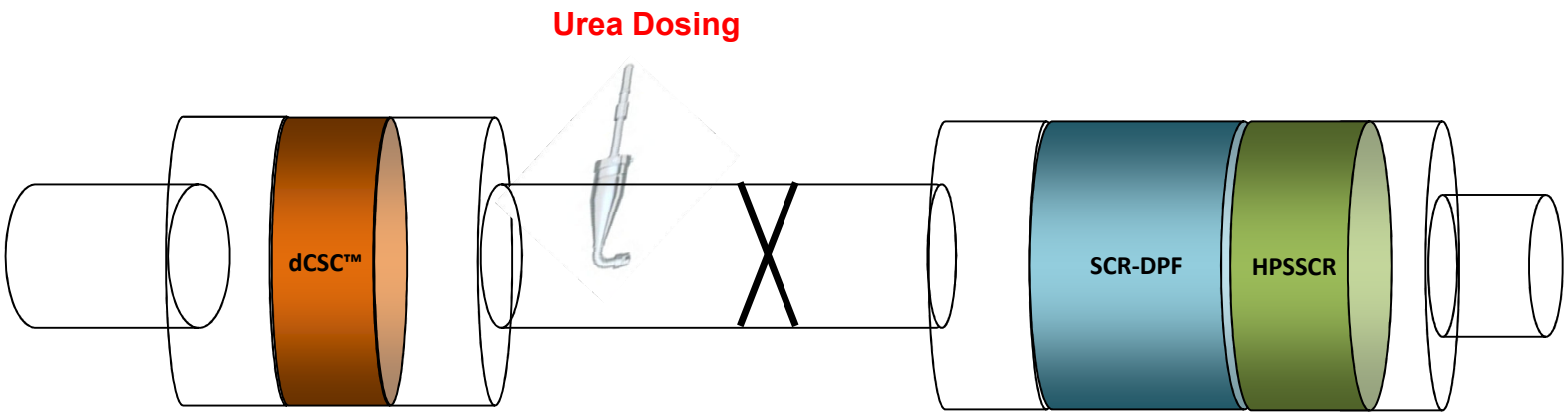
- **DOC**
  PGM loading: 115g/ft^3 4:1(Pt:Pd), total volume: 2.0 L
- **dCSC™**
  PGM loading: 152g/ft^3 8:13(Pt:Pd), total volume: 2.0 L

- **Aging**
  DOC/dCSC™ – hydrothermal 800°C for 16 hours
  SCRF® - hydrothermal 800°C for 16 hours

dCSC™ catalyst show excellent NOx storage and release properties



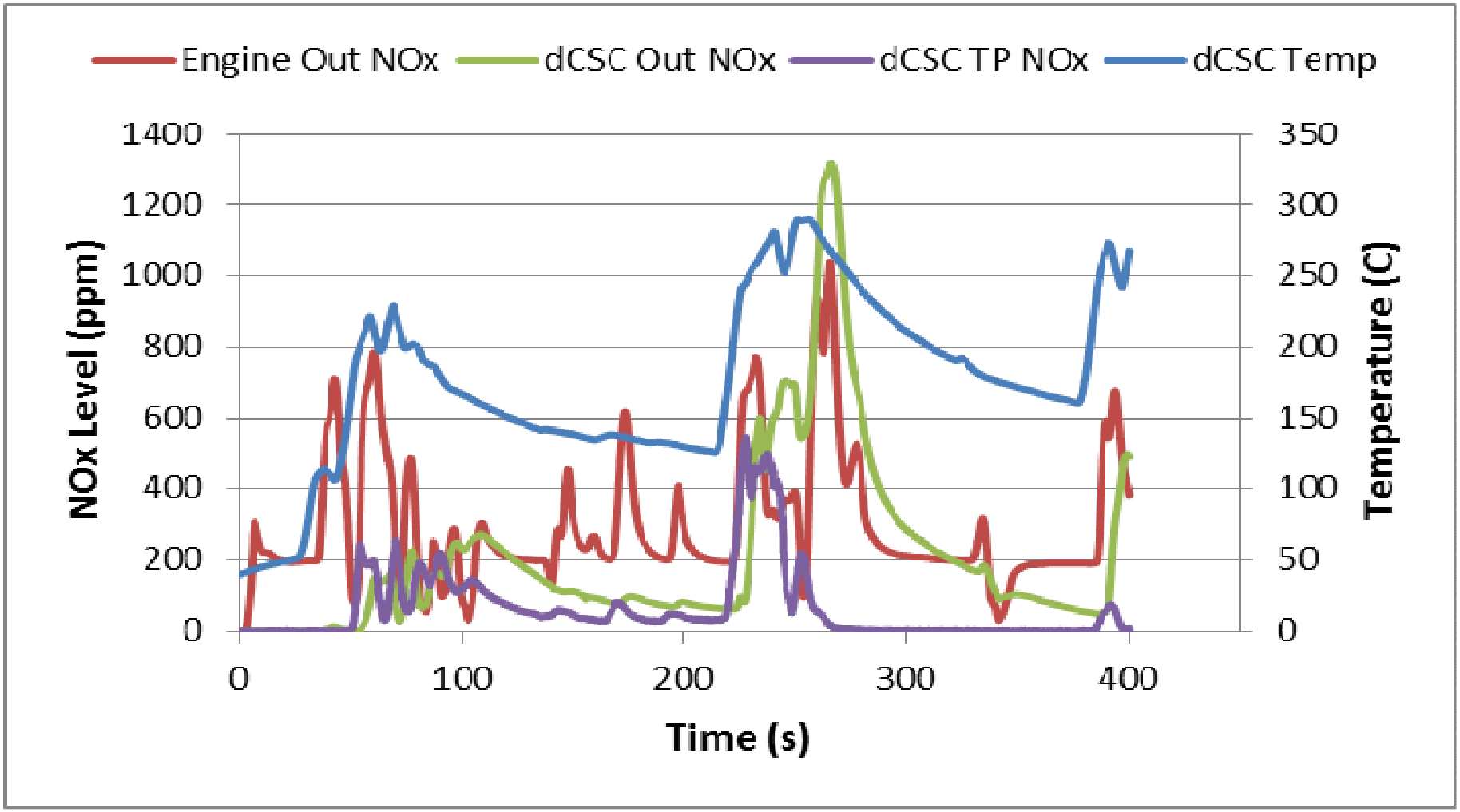
dCSC™ catalyst engine testing on a 8.9L engine HDD FTP transient test cycles



System	Fresh/Aged	Dimensions
Cold Start Concept catalyst	Aged at 650°C/100 hrs	10.5x6”
SCR-DPF	Aged at 650°C/100hrs	10.5x12”
SCR	Aged at 650°C/100hrs	HP substrate, 600 cpsi, 10.5x6”

M. Naseri, et al., SAE 2015-01-0992

Systems with dCSC™ catalyst + SCRF show promise for HDD low temperature NOx emission control



M. Naseri, et al., SAE 2015-01-0992

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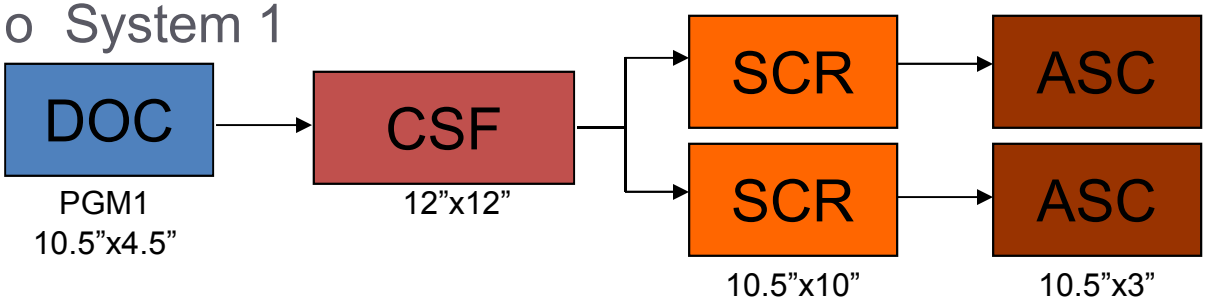
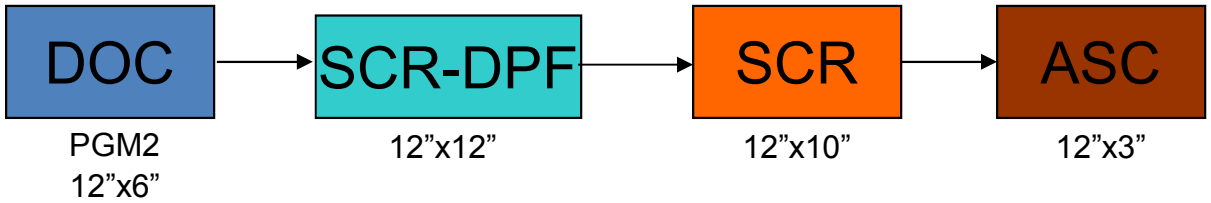
Modeling study has been carried out to compare various system configurations

- Different system configurations (simulated)
  - System 1

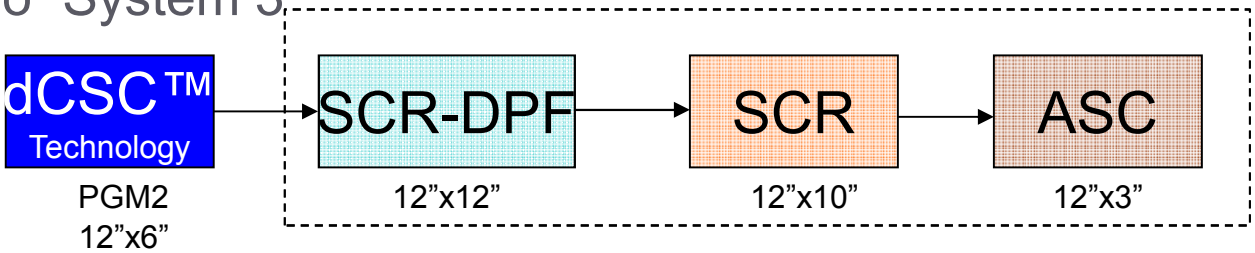


  - System 2



Max SV: 150k/hr 75k/hr 90k/hr 300k/hr

  - System 3

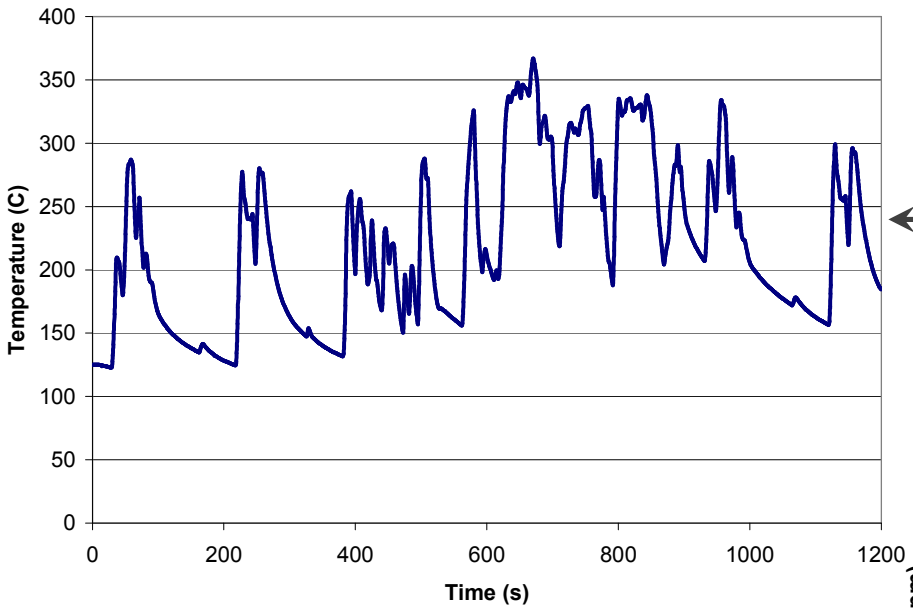


- **Focus**:
  - NOx reduction
  - NH_3 slip
  - N_2O formation (limited systems)
- **Design flow:**
  DOC
  SCR-DPF/CSF
  SCR
  ASC

B. Sukumar, et al., 2014 CLEERS

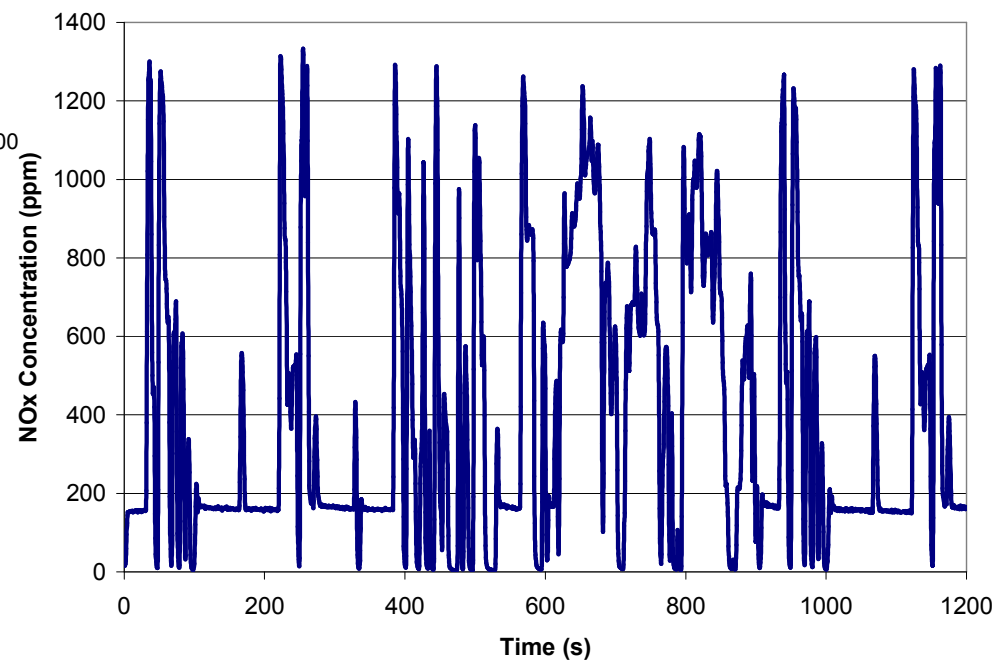
HD-FTP data used for simulation purpose

Engine out data



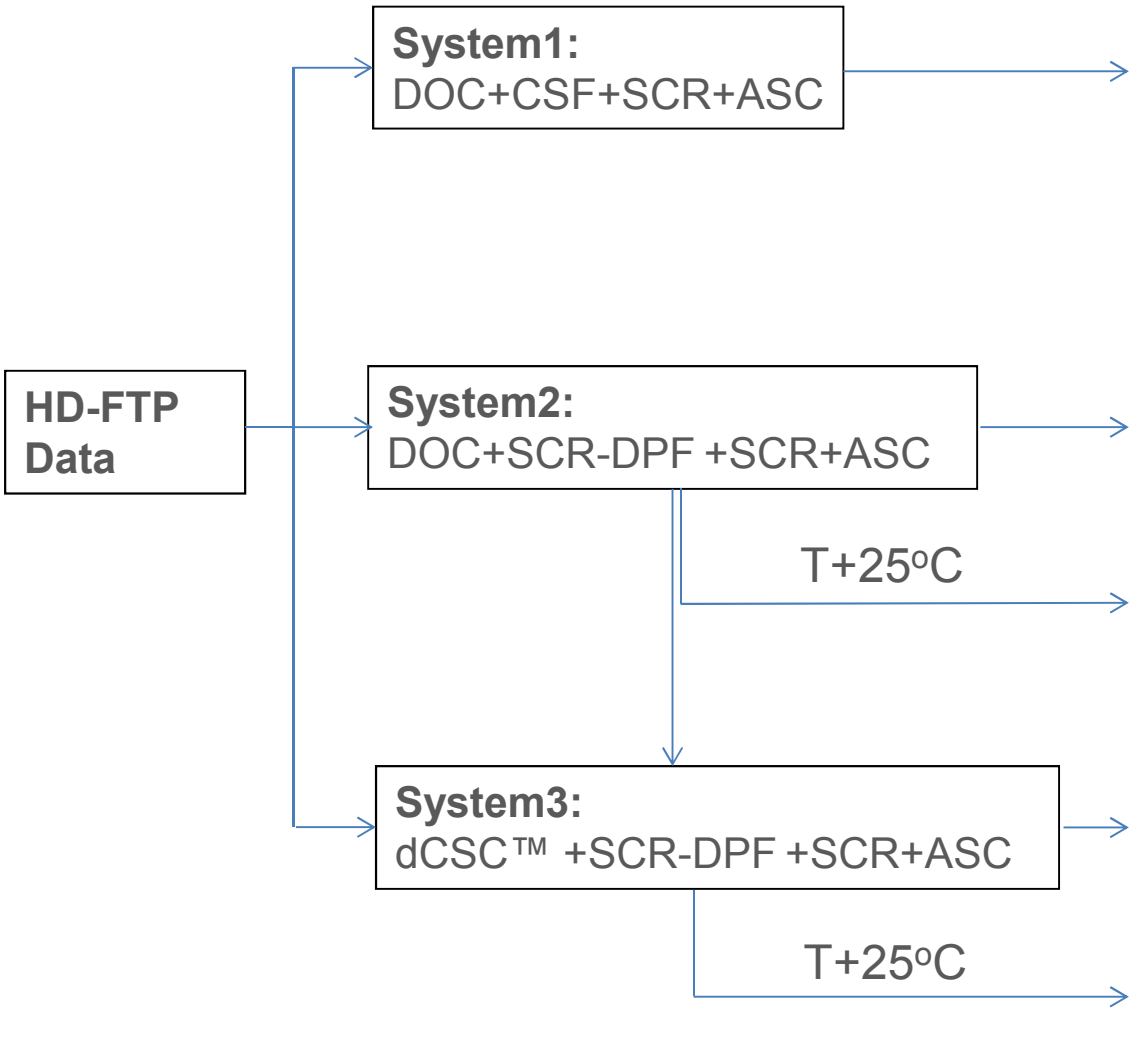
Average Temp: 219°C

NOx: 8.78 g/kwhr



B. Sukumar, et al., 2014 CLEERS

The system with the dCSC™ technology clearly shows advantages, mainly due to low temperature NOx reduction



	NOx (g/kwhr)	N_2O (g/kwhr)	NOx Conversion
System1: DOC+CSF+SCR+ASC	0.91	0.26	89.6%
System2: DOC+SCR-DPF +SCR+ASC	0.81	0.34	90.8%
System2: T+25°C	0.41	0.33	95.3%
System3: dCSC™ +SCR-DPF +SCR+ASC	0.40	Not modeled	95.4%
System3: T+25°C	**Very low NOx levels**	Not modeled	**>99%**

B. Sukumar, et al., 2014 CLEERS

Summary

- Low temperature emission control is a major challenge
  - Control of cold-start emissions is crucial to meet the future stringent emission regulations
  - Fuel economy and GHG legislation lead to lower exhaust temperatures
- Zeolite supported Pd catalysts exhibit high NOx/HC storage capacity with high trapping efficiency at low temperatures
  - Pd at the exchange sites can adsorb NO directly
  - Zeolite structures affect both the NO storage and release profiles
  - Catalysts show good tolerance to sulfur poisoning
- Fully formulated catalysts show promising results on vehicle testing
- Modeling study is instrumental in system design