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Diesel Emission Control Technologies in Review

Tim Johnson
August 5, 2008

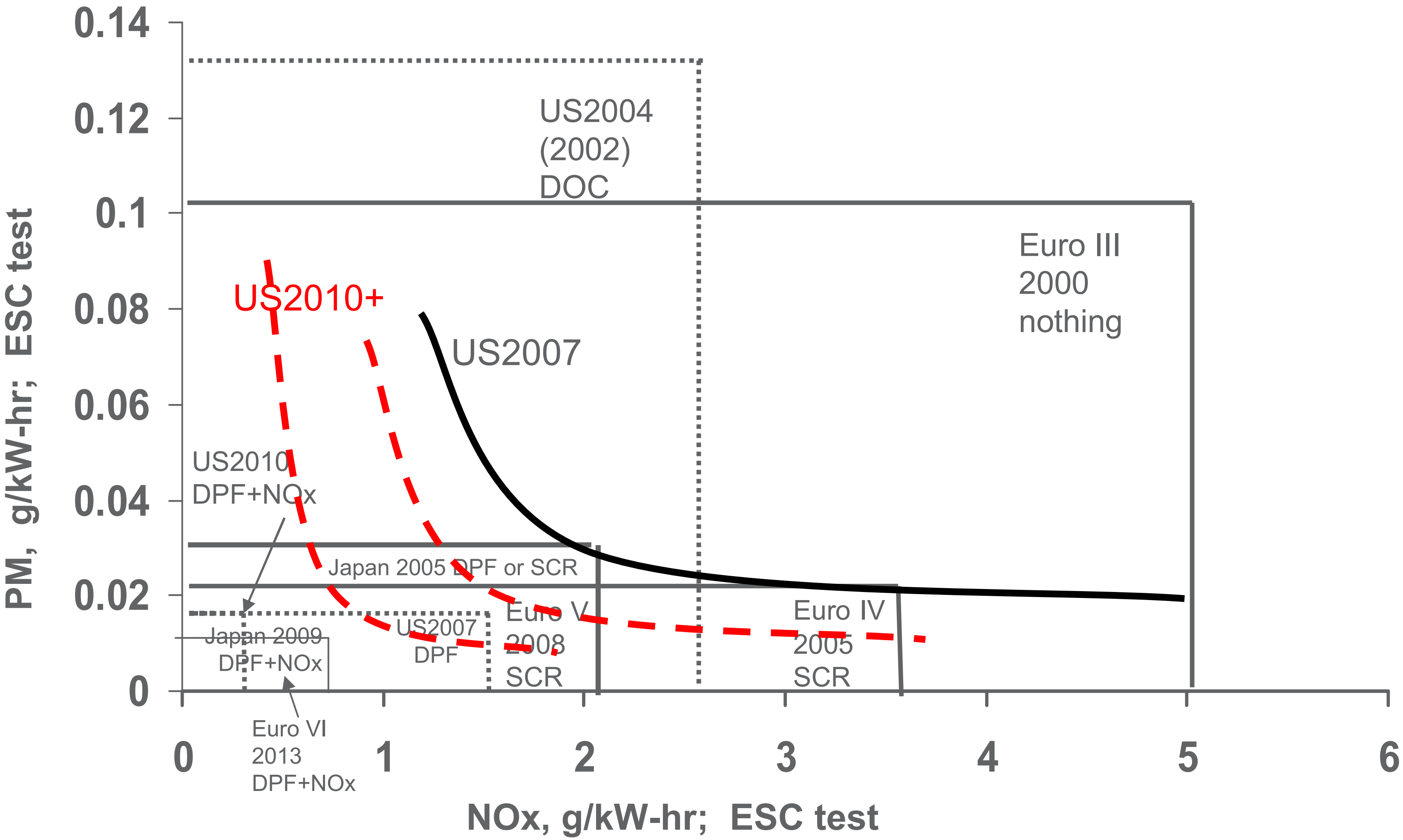
DEER Conference
Dearborn, MI

Summary

- Regulatory action: Euro VI HDD, CARB LEV3, CO_2
  - HD technology harmonization; SULEV fleet average?; challenging CO_2 regs
- Roadmaps for LD and HD are proposed. Significant opportunity for CO_2 and NOx reductions.
- SCR is advancing
  - DPF+SCR component; new catalysts/configurations; quantified durability;
- HC-deNOx developments show lots of advancement
  - New formulations (traditional and new families); new configurations; optimization
- DPF developments focusing on improved, more efficient regeneration
  - Oxide DPFs can save energy
  - Soot/catalyst interaction coming into the spotlight
  - Filtration “membrane” keeps soot out of wall for reduced Δp
  - OBD via modeling and sensors
- DOC fundamental improvement might be improtant for advanced combustion regimes

New Emissions Regulatory Developments

Regulatory and engine technology framework



Euro VI is very much in play

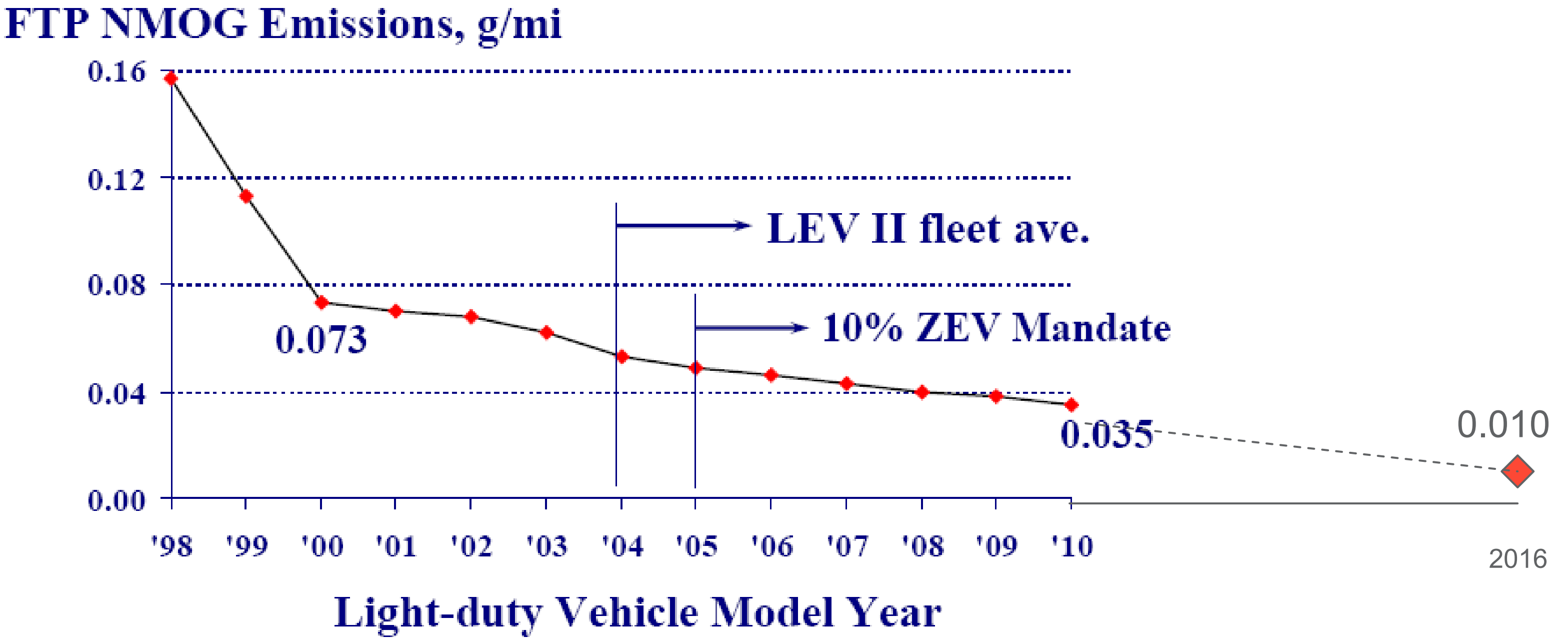
Version from the Parliament Environmental Committee

- 500 mg/kW-hr NOx vs. 260 mg/kW-hr for US2010
- 10 mg/kW-hr PM vs. 13 mg/kW-hr for US2010
  - P#-based regulation coming (limit values TBD)
- Timing tied to completion of technical protocols
  - January 2013 to January 2014, if protocol adheres to required timing
- Early tax incentives eliminated
- Strong support for ambitious and harmonized retrofits to Euro VI
- No NO_2 provisions; No tie of P# reg to DPF capability

Full Parliament vote in late September,
then goes to Council of Ministers

CARB is considering LEV3.

Fleet average SULEV on the table for 2016+

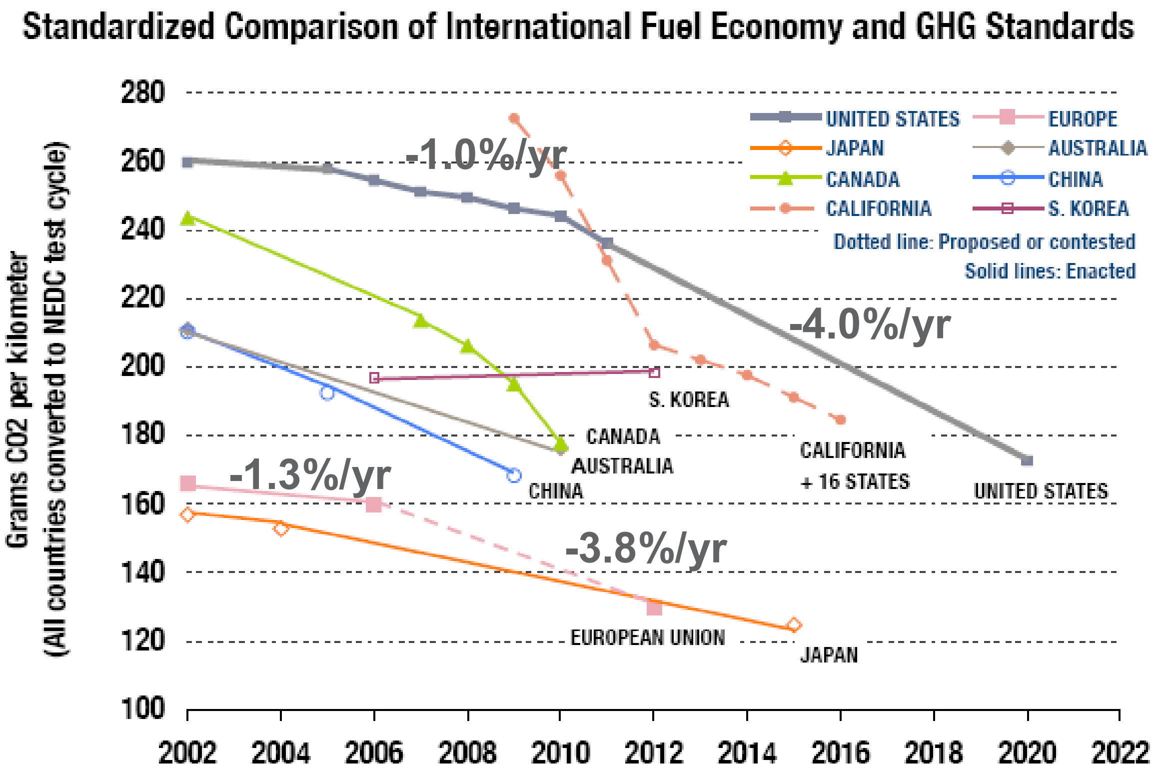


Implications:

- Can diesel hit it? Any vehicle above this limit means some will have to be ZEV. Will there be any in the market?

Comparison of CO$_2$ Regulations Across the World.

New regulations in Europe and US will challenge industry.



Source: *Passenger Vehicle Greenhouse Gas and Fuel Economy Standards: A Global Update*, International Council on Clean Transportation,

Regulated CO$_2$ emissions standards normalized to the NEDC test cycle.

European Commission recently pulled back to 5% biofuel mandates.
US is at ~20% by 2022.

ICCT, 7/07; TheICCT.org

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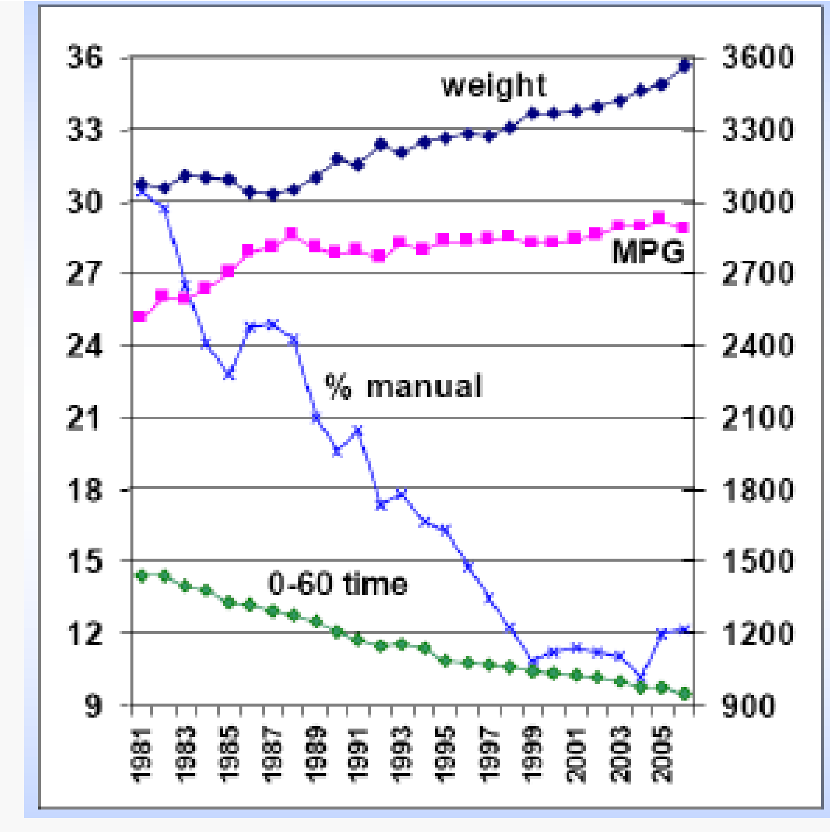
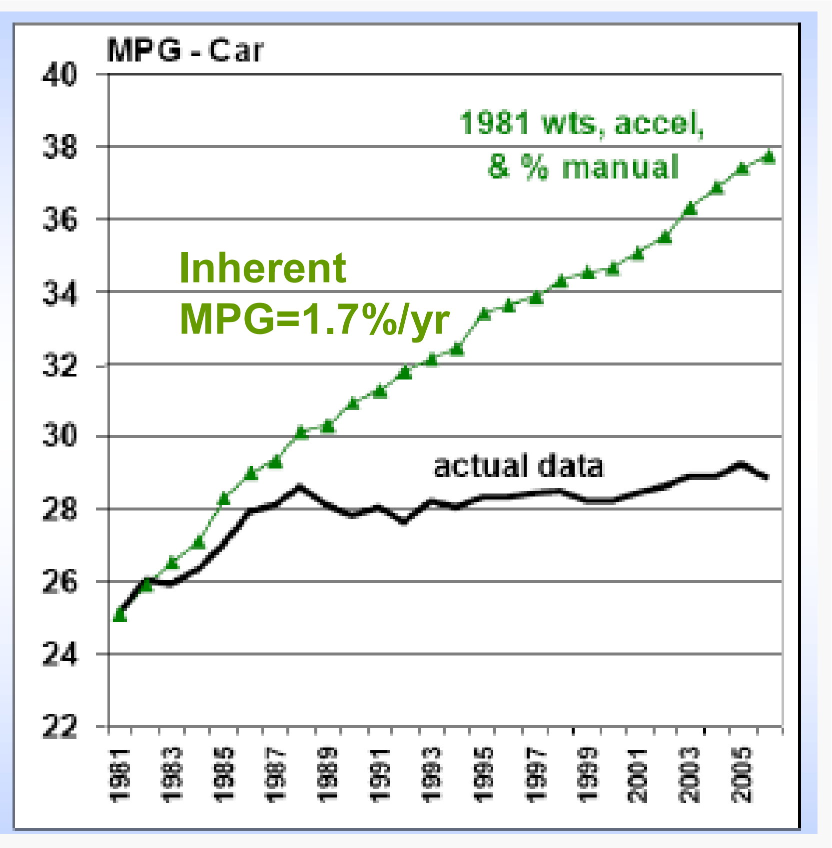
Fuel consumption opportunities

US cars would be at 38 MPG if we had the same performance attributes of 30 years ago.

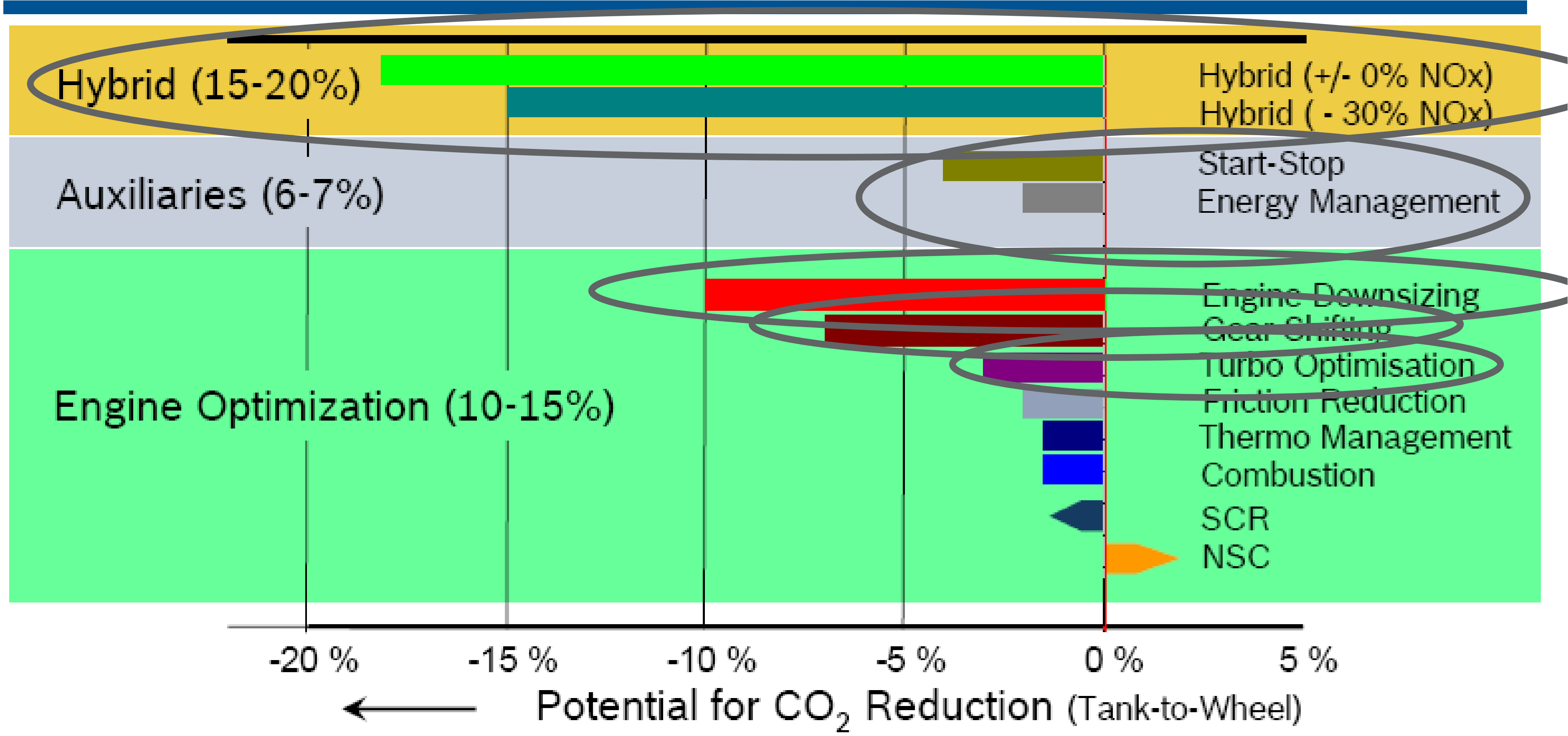




In the US, 1.7%/yr appears to be a natural evolution. 4%/yr, as required in the US and Europe (earlier slide) is a significant challenge.

Ford, 3-08

LDD has much potential for further CO_2 reductions.



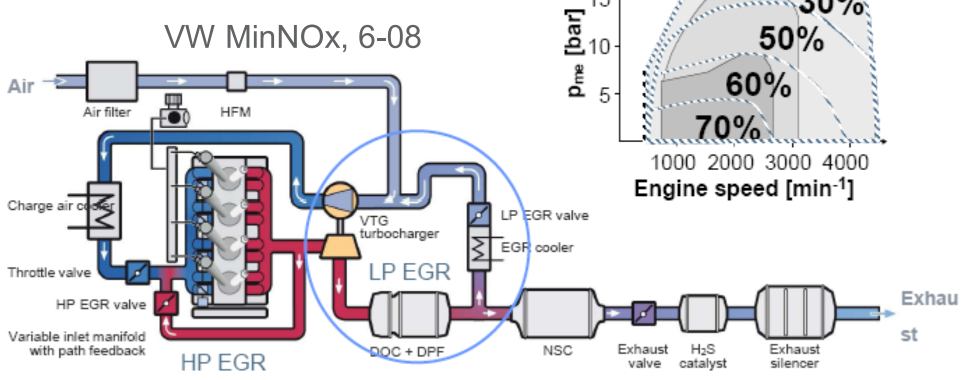
Baseline: 2.2 l, Euro4 with DPF

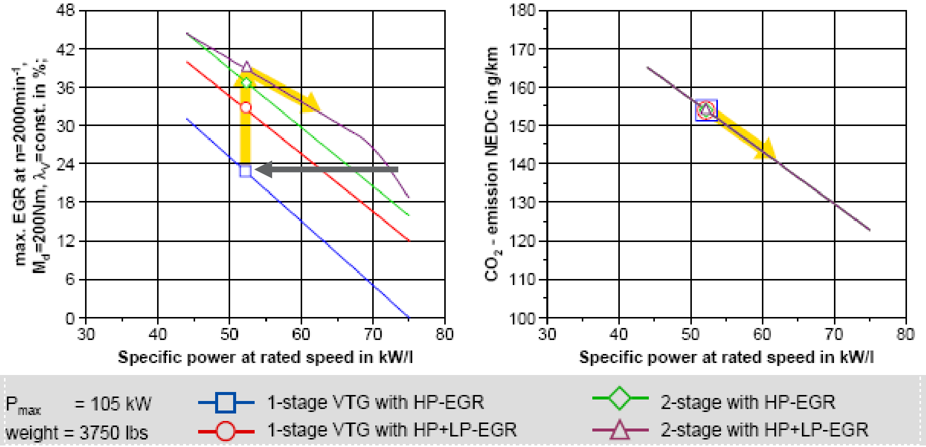
Bosch, Gov and Industry Mtg 5-08

Advanced air handling and hybrid EGR (LP+HP) provide reduced CO2 and emissions w/o performance sacrifice.

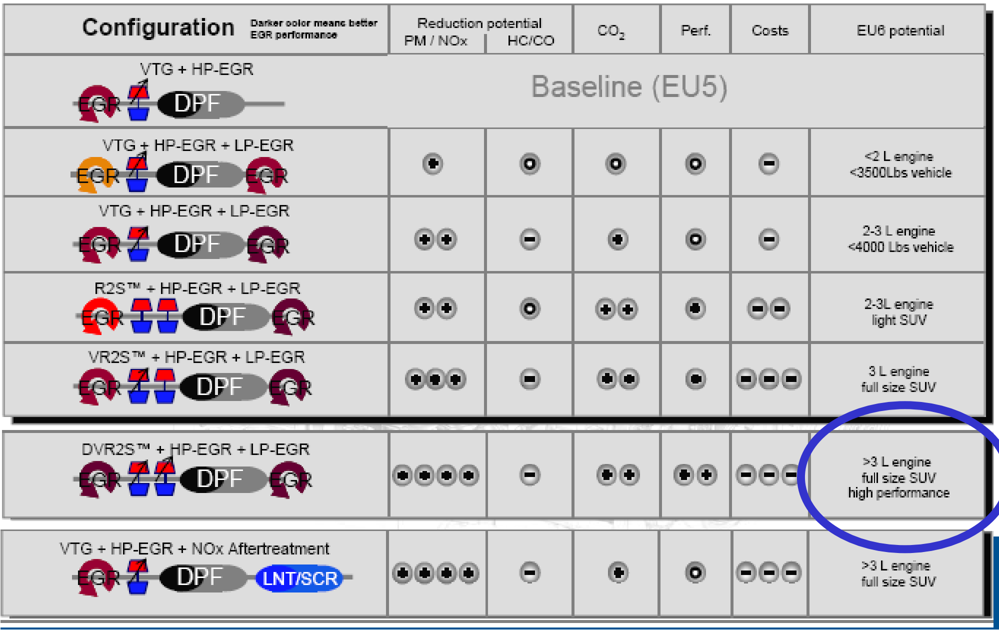
Euro 6 for large platforms w/o deNOx possible.

NOx reduction due to cooled LP EGR with non cooled HP EGR





Migrating from 1-stage turbo+ HP-EGR to 2-stage turbo+LP-EGR results in higher EGR (reduced NOx) without sacrificing fuel consumption. IAV MinNOx 6-08.

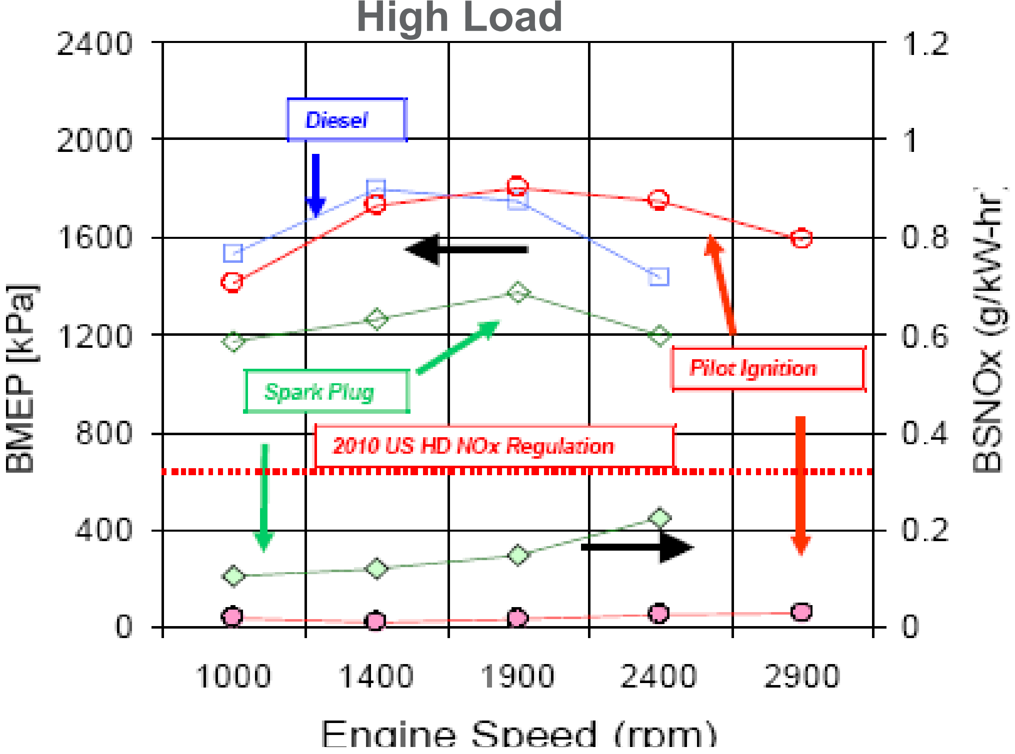


Configuration Darker color means better EGR performance	Reduction potential PM / NOx	Reduction potential HC/CO	CO$_2$	Perf.	Costs	EU6 potential
VTG + HP-EGR EGR DPF	Baseline (EU5)					
VTG + HP-EGR + LP-EGR EGR DPF EGR	⊕	⊙	⊙	⊙	⊖	<2 L engine <3500Lbs vehicle
VTG + HP-EGR + LP-EGR EGR DPF EGR	⊕⊕	⊖	⊕	⊙	⊖	2-3 L engine <4000 Lbs vehicle
R2S™ + HP-EGR + LP-EGR EGR DPF EGR	⊕⊕	⊙	⊕⊕	⊕	⊖⊖	2-3L engine light SUV
VR2S™ + HP-EGR + LP-EGR EGR DPF EGR	⊕⊕⊕	⊖	⊕⊕	⊕	⊖⊖⊖	3 L engine full size SUV
DVR2S™ + HP-EGR + LP-EGR EGR DPF EGR	⊕⊕⊕⊕	⊖	⊕⊕	⊕⊕	⊖⊖⊖	>3 L engine full size SUV high performance
VTG + HP-EGR + NOx Aftertreatment EGR DPF LNT/SCR	⊕⊕⊕⊕	⊖	⊕	⊙	⊖⊖⊖	>3 L engine full size SUV

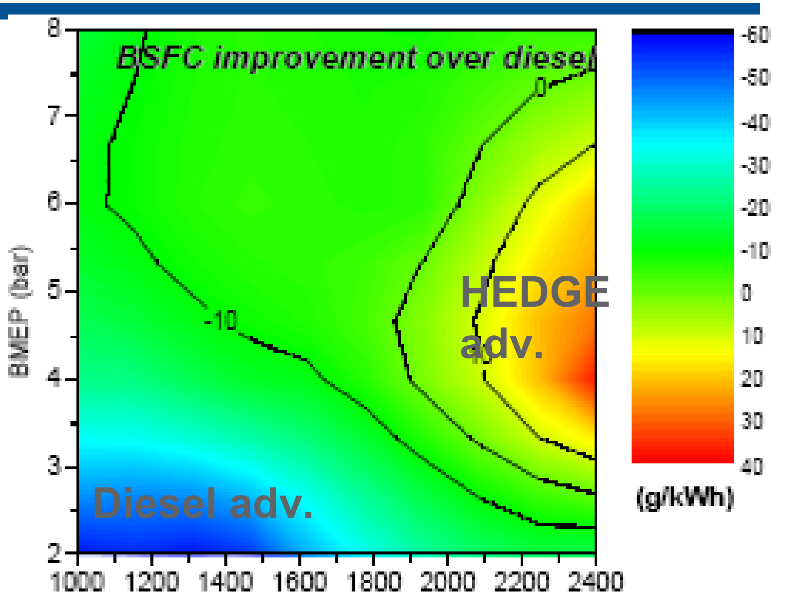
- 2-stage turbo w/ lots of hybrid EGR might hit Euro 6 for a 3 liter large SUV
- Flexibility of dual-EGR loop enables higher specific power at reduced emissions with better response over a wide range of conditions.
- Control and components described.

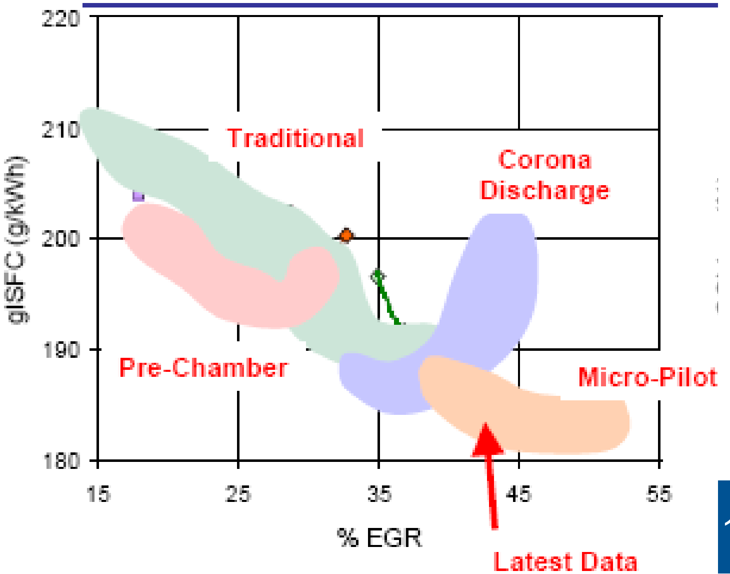
Borg Warner, MinNOx 6-08

Highly Efficient Dilute Gasoline Engine. Stoichiometric, MPI delivers diesel torque and CO_2 with low NOx. Needed: strong spark.

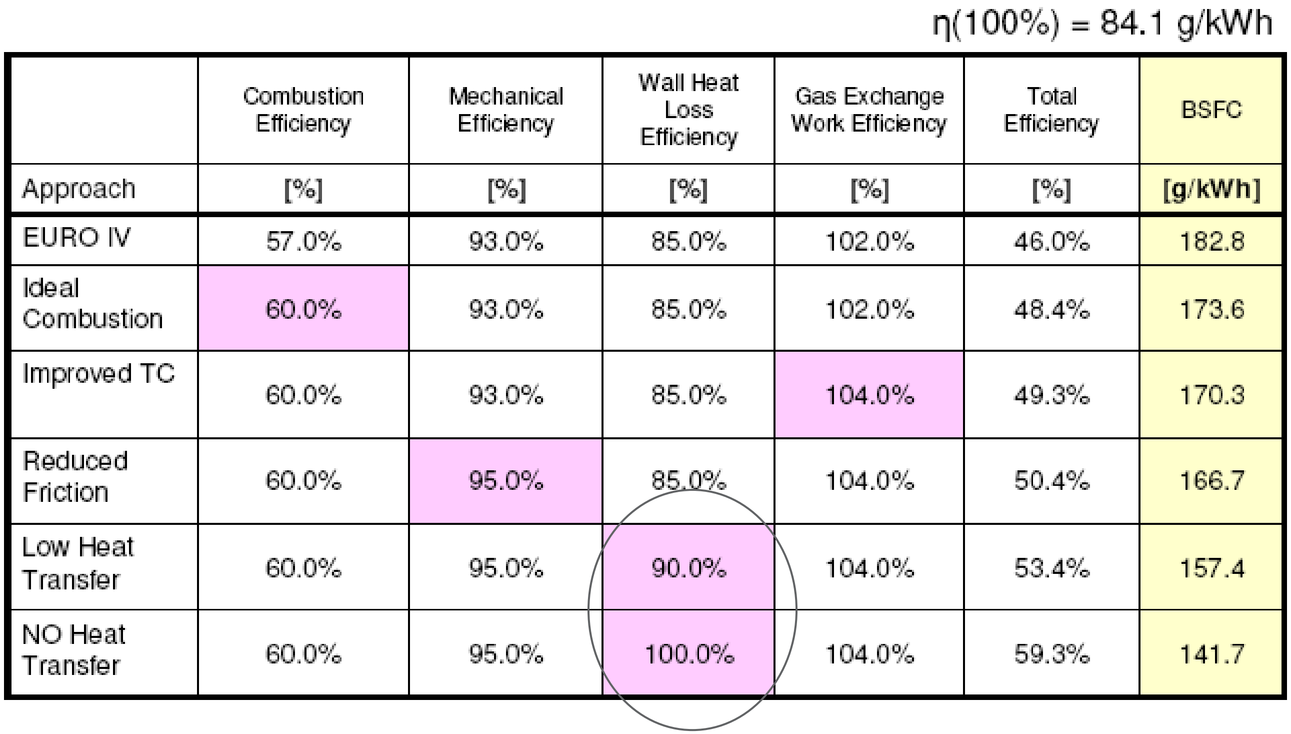


- ➢ *Highly dilute for knock and pumping loss reduction*
  - ➢ *Advanced ignition improves EGR tolerance*
- ➢ *Boosted / downsized for high specific power and efficiency*
- ➢ *High CR for high efficiency*
- ➢ *Stoichiometric for low tailpipe emissions*
- ➢ *High load operation at low speeds to maximize efficiency*





More emphasis will be placed on fuel consumption, even in HD



η(100%) = 84.1 g/kWh

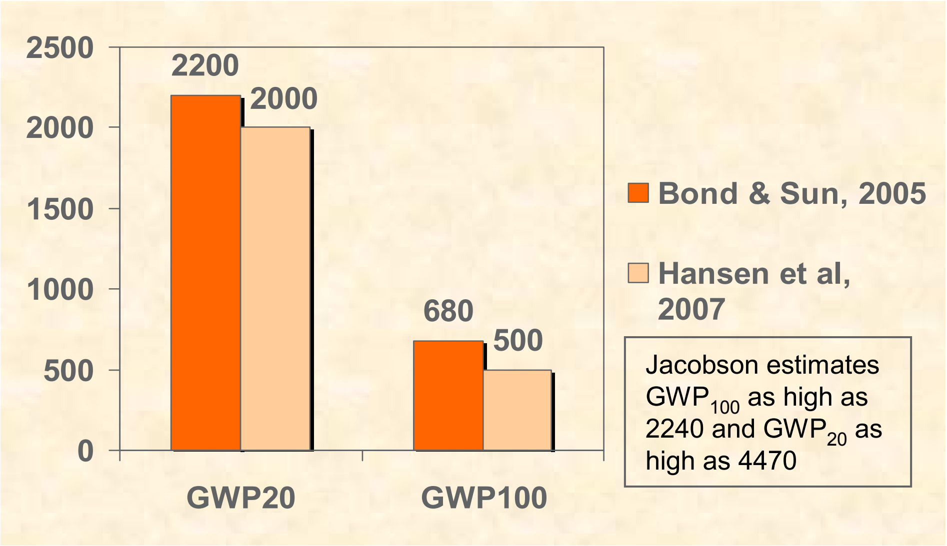
Approach	Combustion Efficiency [%]	Mechanical Efficiency [%]	Wall Heat Loss Efficiency [%]	Gas Exchange Work Efficiency [%]	Total Efficiency [%]	BSFC [g/kWh]
EURO IV	57.0%	93.0%	85.0%	102.0%	46.0%	182.8
Ideal Combustion	60.0%	93.0%	85.0%	102.0%	48.4%	173.6
Improved TC	60.0%	93.0%	85.0%	104.0%	49.3%	170.3
Reduced Friction	60.0%	95.0%	85.0%	104.0%	50.4%	166.7
Low Heat Transfer	60.0%	95.0%	90.0%	104.0%	53.4%	157.4
NO Heat Transfer	60.0%	95.0%	100.0%	104.0%	59.3%	141.7

Highlighted items show best potential.

Iveco, CTI 6/07

Atmospheric components and global warming effects.

Global Warming Potential of Black Carbon



Jacobson estimates GWP_{100} as high as 2240 and GWP_{20} as high as 4470

Comment: Nominally 20-25% of CO_2 equivalent footprint (20 yr) of unfiltered diesel exhaust is in carbon soot.

CO_2 has a GWP=1

GWP20 means 20 years.

Base slide courtesy of Mike Walsh

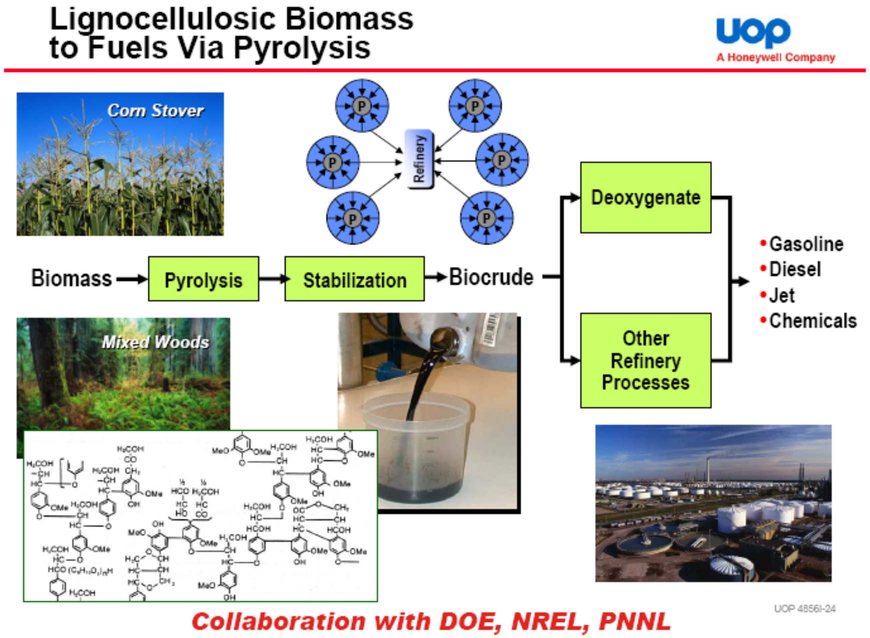
Hansen J, Sato M, Kharecha P, Russell G, Lea DW, Siddall M. 2007. Climate change and trace gases. Philosophical Transactions of the Royal Society A 365:1925-1954.

Jacobson MZ. 2007. Testimony for the Hearing on Black Carbon and Global Warming. House Committee on Oversight and Government Reform. 110th Congress, First Session. Washington, DC.

Bond TC, Sun H. 2005. Can Reducing Black Carbon Emissions Counteract Global Warming? Environ. Sci. Technol. 39(16):5921-5926.

Upgrading biomass to biocrude in the field appears more cost effective and efficient than cellulosic ethanol routes.

Biocrude becomes refinery feedstock.



Lignocellulosic Biomass to Fuels Via Pyrolysis

uop A Honeywell Company

- Gasoline
- Diesel
- Jet
- Chemicals

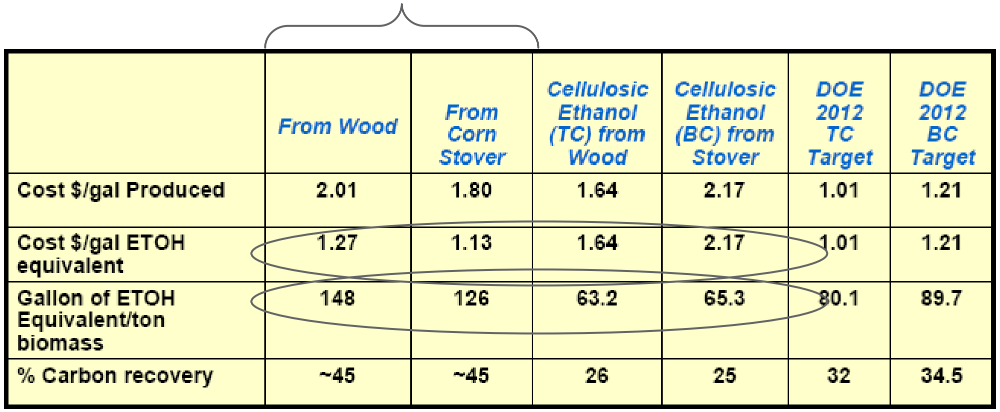
Collaboration with DOE, NREL, PNNL

UOP 4856I-24

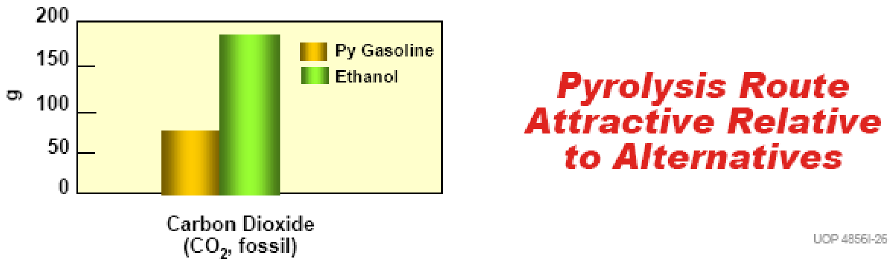
Pyrolysis route makes concentrated biocrude from biomass.

Significantly increases economical transportation distance for biomass.

Pyrolysis



	From Wood	From Corn Stover	Cellulosic Ethanol (TC) from Wood	Cellulosic Ethanol (BC) from Stover	DOE 2012 TC Target	DOE 2012 BC Target
Cost $/gal Produced	2.01	1.80	1.64	2.17	1.01	1.21
Cost $/gal ETOH equivalent	1.27	1.13	1.64	2.17	1.01	1.21
Gallon of ETOH Equivalent/ton biomass	148	126	63.2	65.3	80.1	89.7
% Carbon recovery	~45	~45	26	25	32	34.5



Pyrolysis Route Attractive Relative to Alternatives

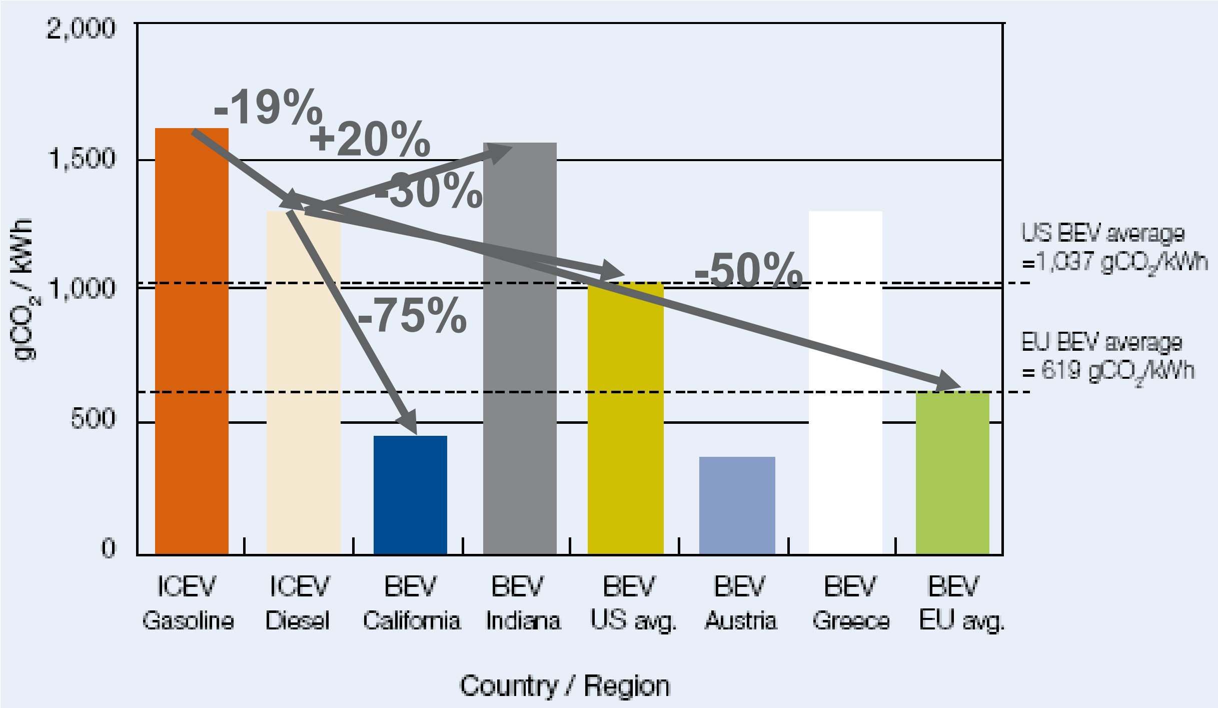
UOP 4856I-26

Pyrolysis route is 20-50% cheaper than cellulosic ethanol, has 2 – 2.3X more yield, and 60% less CO2.

UOP, EFI Conf. 2/08

CO_2 intensity of gasoline and diesel vehicles is compared to battery electric vehicles (BEVs) on several grids.

PHEVs drop CO2 ~25% in the US and ~40% in Europe vs. diesel.



- Diesel has 19% lower CO_2 than gasoline.
- Battery electric vehicles (BEVs) on average grids have -20% CO_2 vs. diesel in the US. Euro: -62% and -52% respectively.
- Grids vary widely in CO_2 intensity (3.4X in US).
- PHEVs might derive anywhere from 70 to 95% of fuel from grid, depending on configuration, saving 20 to 28% CO_2 vs. diesel in the US, and 34 to 48% in Europe.

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SCR

The first reports on an integrated SCR+DPF unit show good performance.

Durability and calibration issues need addressing.

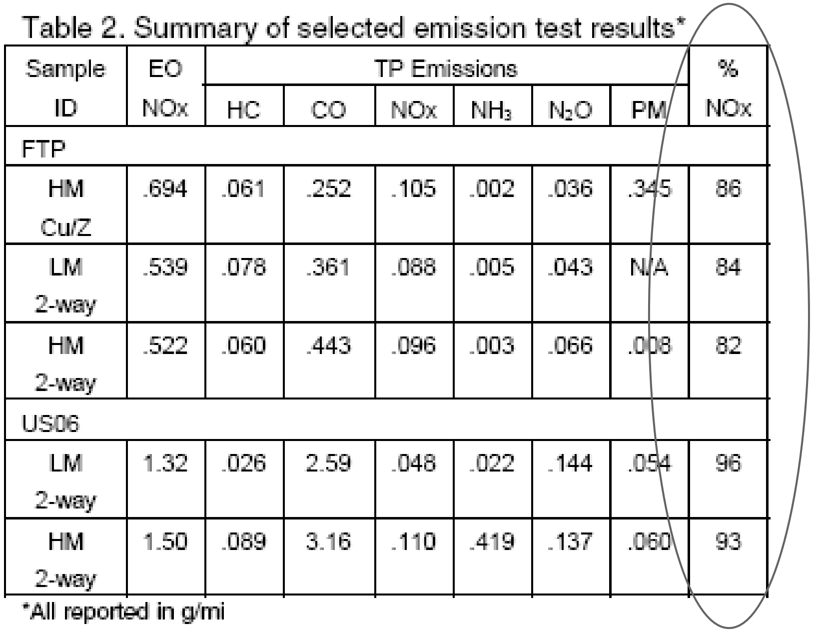


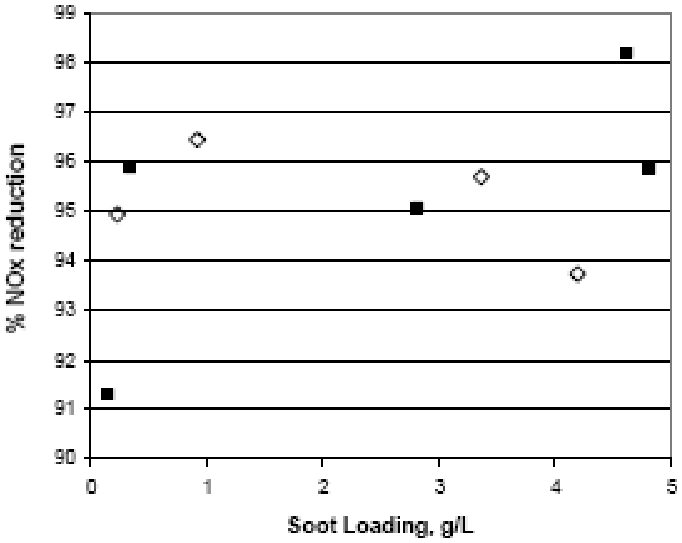
Table 2. Summary of selected emission test results*

Sample ID	EO NOx	TP Emissions HC	CO	NOx	NH_3	N_2O	PM	% NOx
FTP								
HM Cu/Z	.694	.061	.252	.105	.002	.036	.345	86
LM 2-way	.539	.078	.361	.088	.005	.043	N/A	84
HM 2-way	.522	.060	.443	.096	.003	.066	.008	82
US06								
LM 2-way	1.32	.026	2.59	.048	.022	.144	.054	96
HM 2-way	1.50	.089	3.16	.110	.419	.137	.060	93

*All reported in g/mi

Integrated deNOx efficiency similar to SCR-alone system. Incr in NH3 for US06 HM due to less oxidation. US06 HM hotter due to backpressure.

"HM" = high mileage; "LM"=low mileage; 4.9 liter V6 engine; SVR SCR = 1.7.

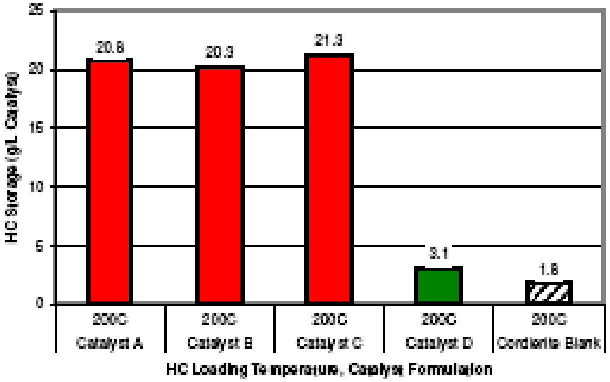


SCR eff. indep of soot loading. Phase 2 of FTP

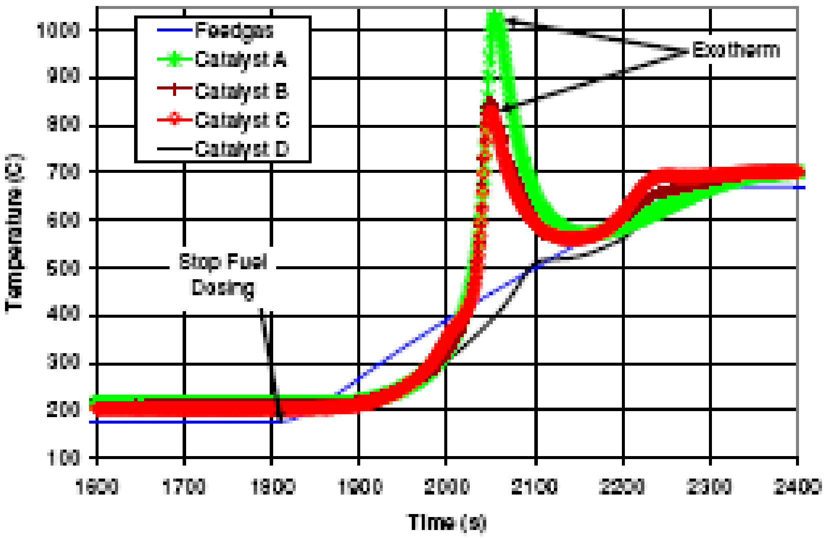
- NOx emissions high during DPF regen. Recalibration needed.
- Cu-zeolite needs more durability to withstand DPF regenerations.

GM, SAE 2008-01-0072

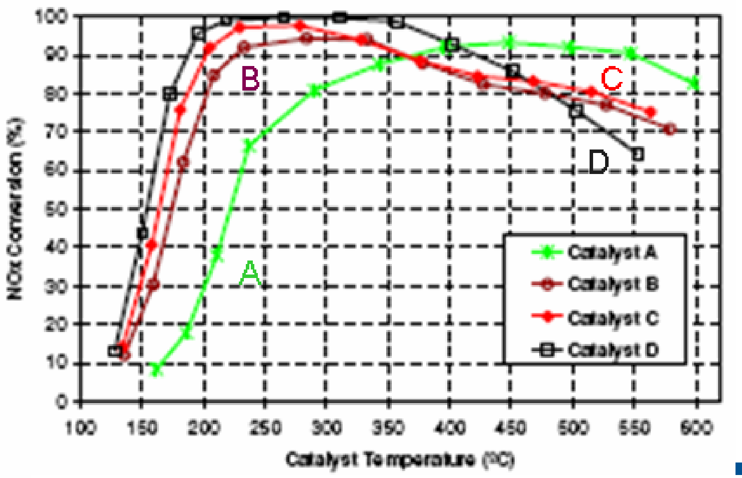
HC adsorption can age zeolite SCR catalysts from exotherm. New formulations help.



Different zeolites have different HC adsorption capacities.



HC oxidation exotherms can get high

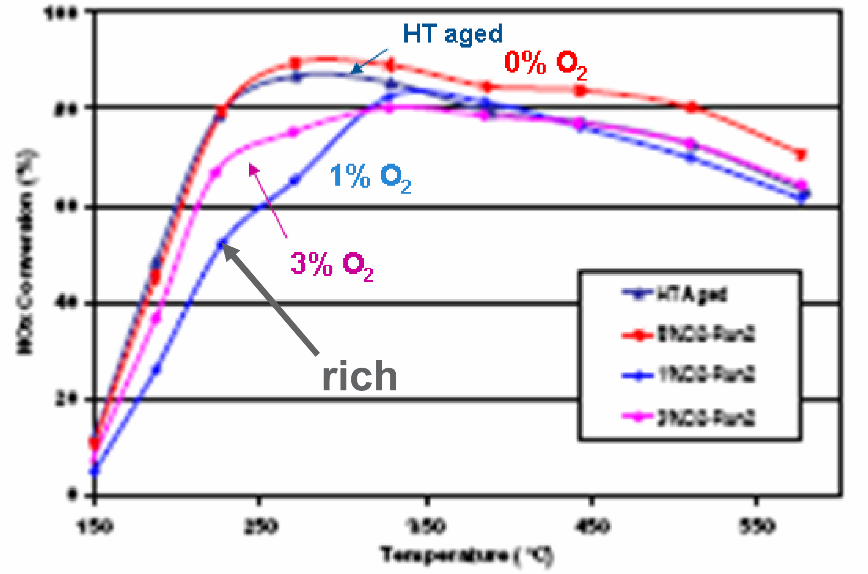


Aged 64 hr at 670C; SV=30,000/hr

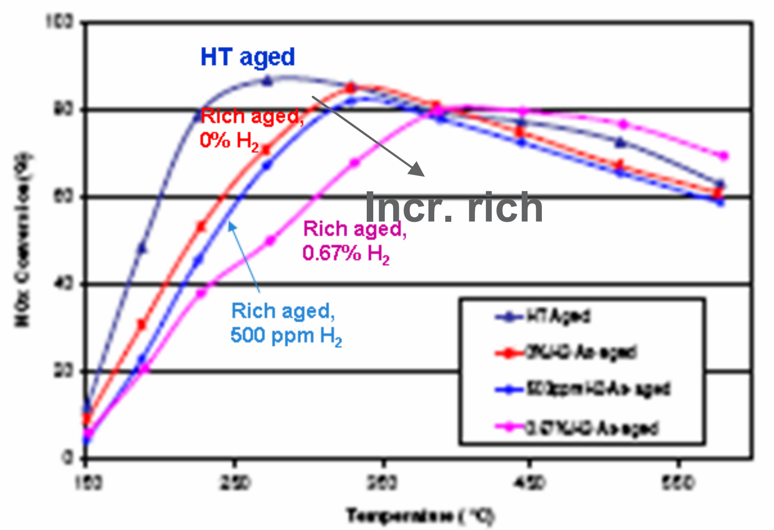
Ford, SAE 2008-01-0767

Cu-zeolite aging under reducing conditions is investigated. Cu^0 formation is main cause of deactivation.

Exposure to hot and rich conditions should be avoided.



Aging in model gas with 1000 ppm C_3H_6 and 2% CO for 16 hrs at 650C. 1% O_2 is rich; 3% O_2 is lean. Hot (exotherm) rich causes most deterioration of Cu-zeolite (Cu^0 formation).



Increased aging with increasingly rich gas using hydrogen. Very little aging under lean conditions.

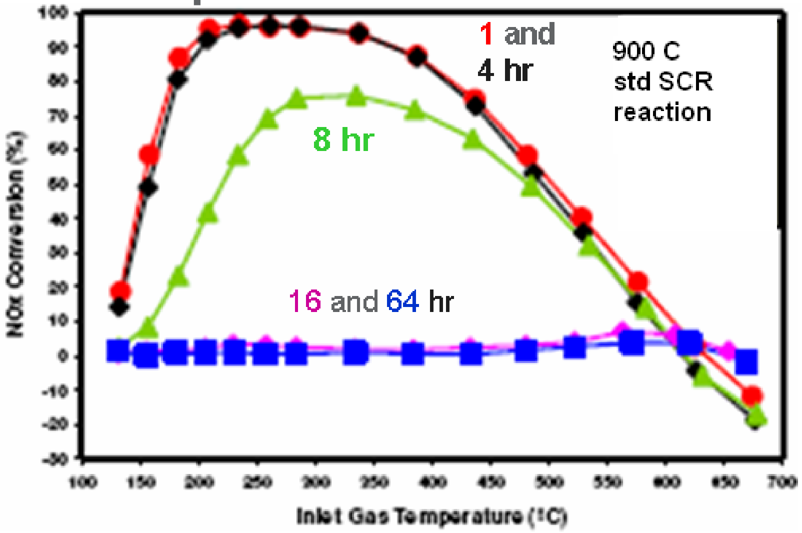
Aging in model gas with 1000 ppm C_3H_6 , 2% CO, and 1% O_2 for 16 hrs at 650C. λ=0.98.

Ford, SAE 2008-01-1021

Enhanced durability of Cu-zeolite catalysts is shown

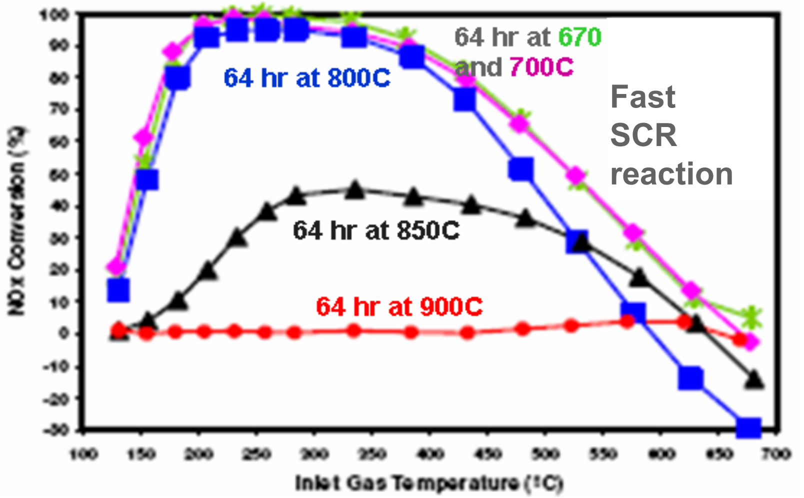
Ford, SAE 2008-01-1025

Exposure time at 900C



For the standard SCR reaction (NO only), exposure to 4 hr at 900C or 1 hr at 950C is maximum.

Exposure temperature for long times



For the fast SCR reaction (NO+NO_2), long term exposure to 700C and 1 hr exposure to 950Care maximum.

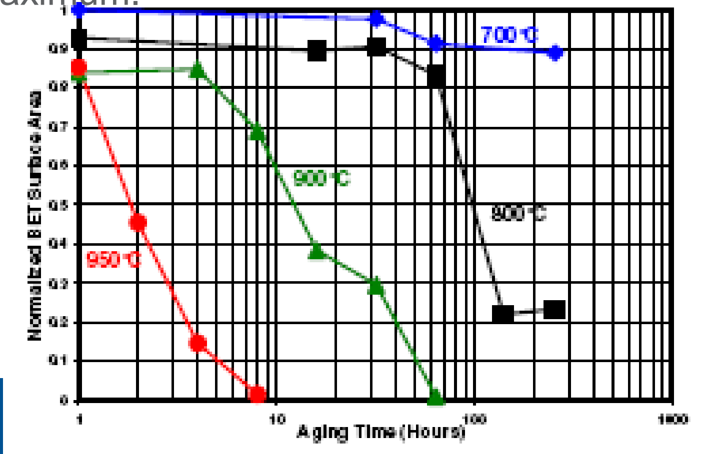
Maximum exposures

> 256 hours at 700°C.

64 hours at 800°C.

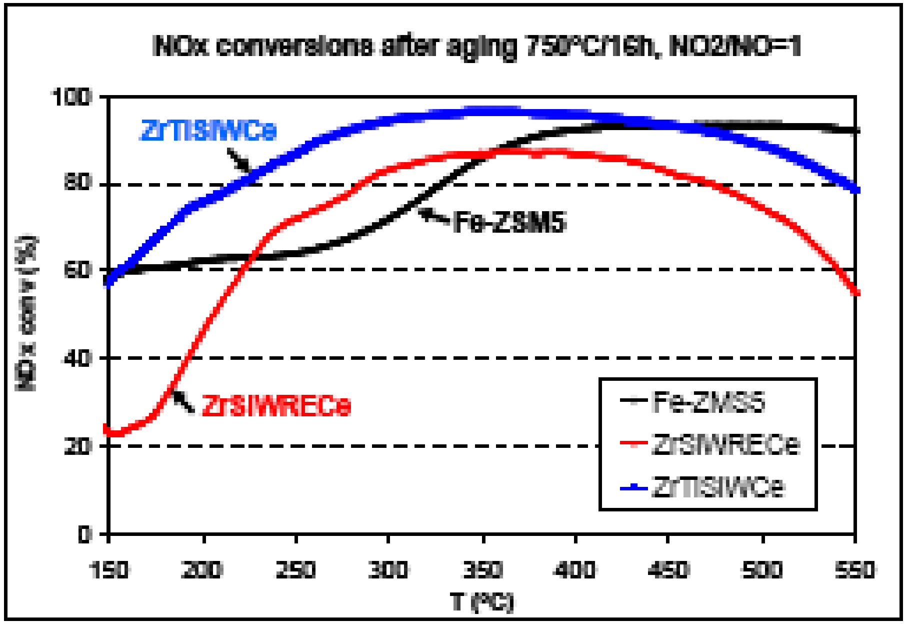
4 hours at 900°C.

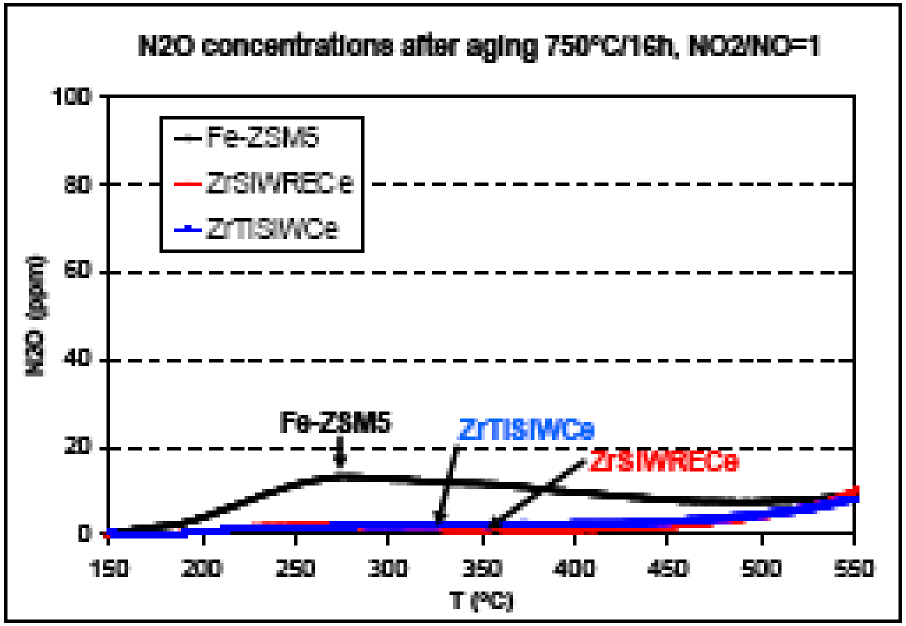
1 hour at 950°C.



Loss of surface area is cause for deterioration

A new family of SCR catalysts is derived from doped acidic zirconia.





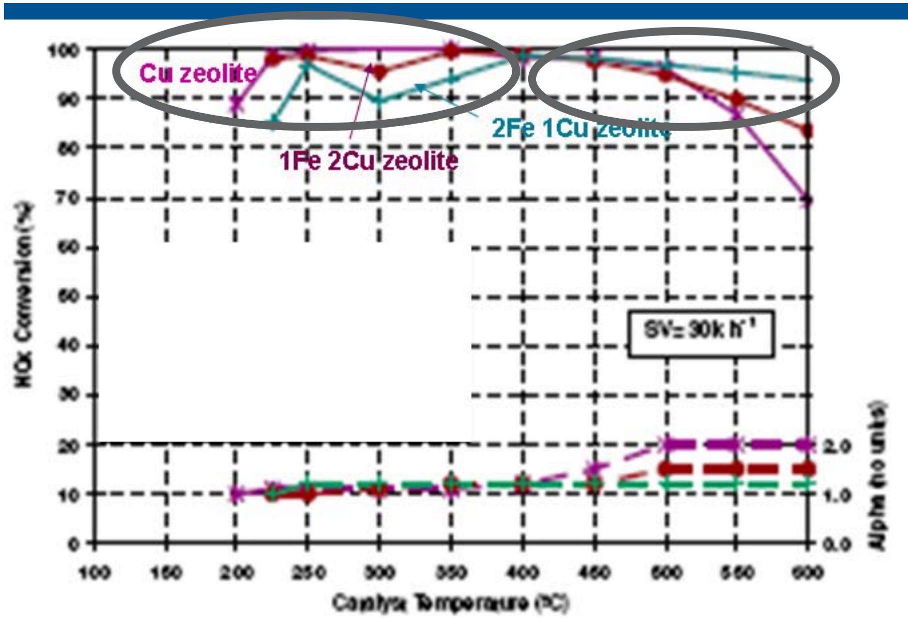
Acidic Zr formulation has better LT performance than Fe-zeolites, up to ~400C, while maintaining some HT efficiency at 550C.

Acidic Zr formulations have no N_2O emission in the presence of NO_2

Rhodia, SAE 2008-01-1022

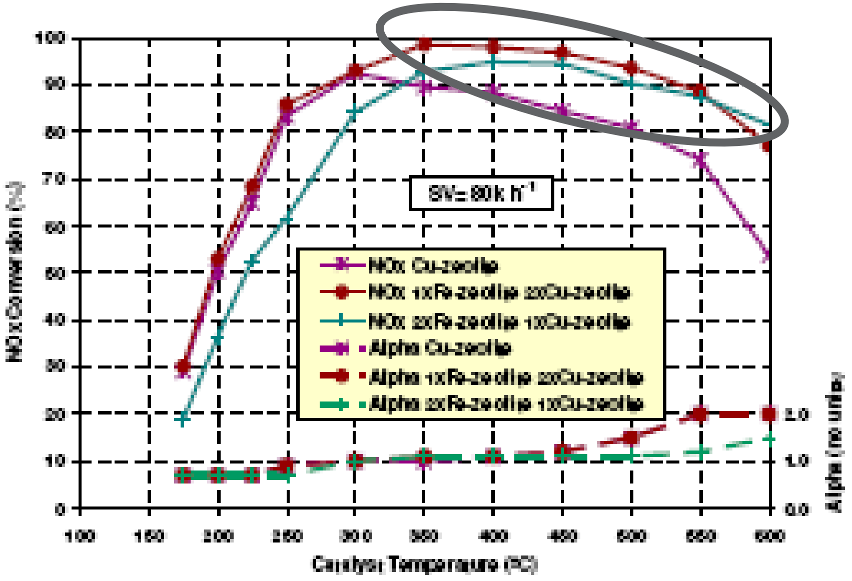
Cu and Fe zeolites can be combined to provide balanced LT and HT performance.

At high space velocity, hybrid catalyst shows benefit.

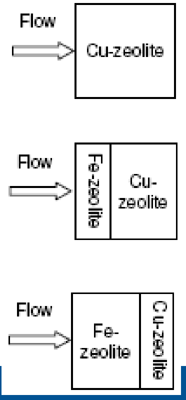


Fe-zeolites enhance the HT performance of Cu-zeolites. Dip at 300C caused by higher NH3 consumption of Fe-zeolite.

Ford SAE 2008-01-1185



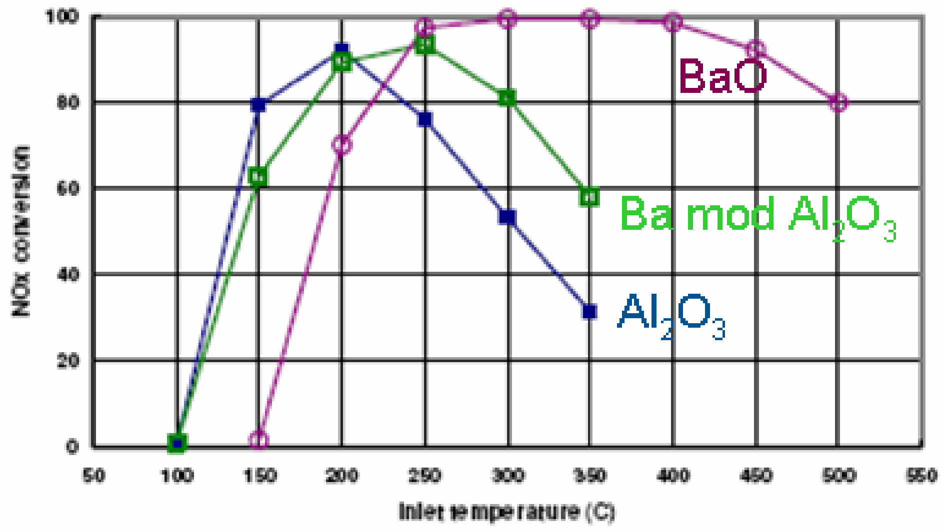
At higher SV, 1Fe 2Cu zeolite has best LT and HT performance balance.



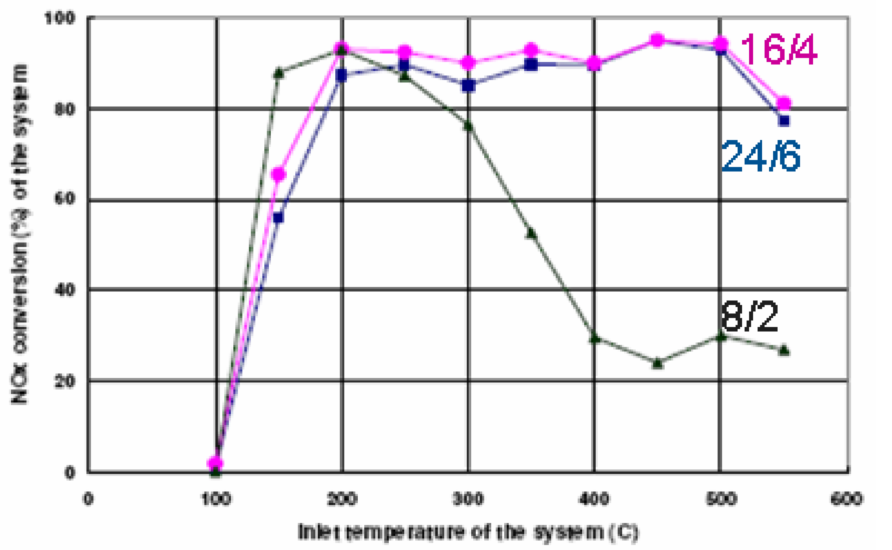
- T<300C: Transient response of mixed zeolite not as good as for Cu-zeolite probably due to NH3 storage by Fe-zeolite.

HC-deNOx

Alumina based LNTs show good LT performance, and can be used in series to give good results. Low desulfation temperatures needed.



Ion exchanged Ba (2-3%) in Al_2O_3 adds some HT deNOx to Al_2O_3

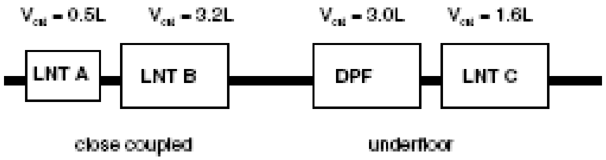


DeNOx eff. of two-stage alumina LNT system (simulates DPF in between). ΔT is 150C. Rich/lean cycles shown. During desulf, SO2 passed through 2nd LNT.

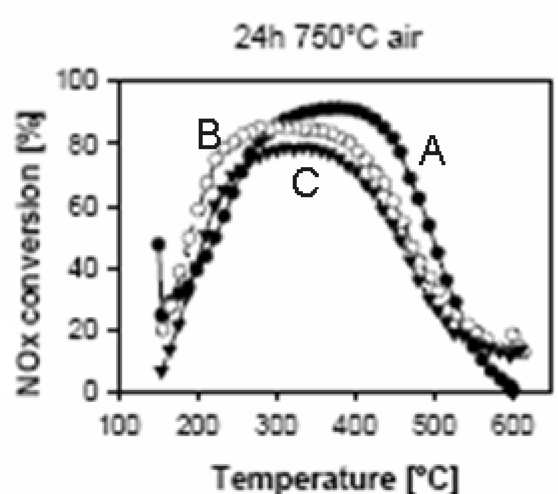
Desulfation of all formulations occurs at 500-650C for only 1-2 minutes in slightly rich conditions (λ=0.987).

Ford SAE 2008-01-0451

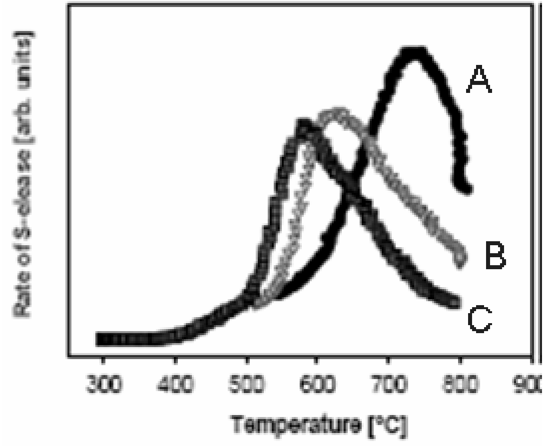
Three LNT formulations are combined in a system to optimize performance.



Best layout for system SVR=1.7

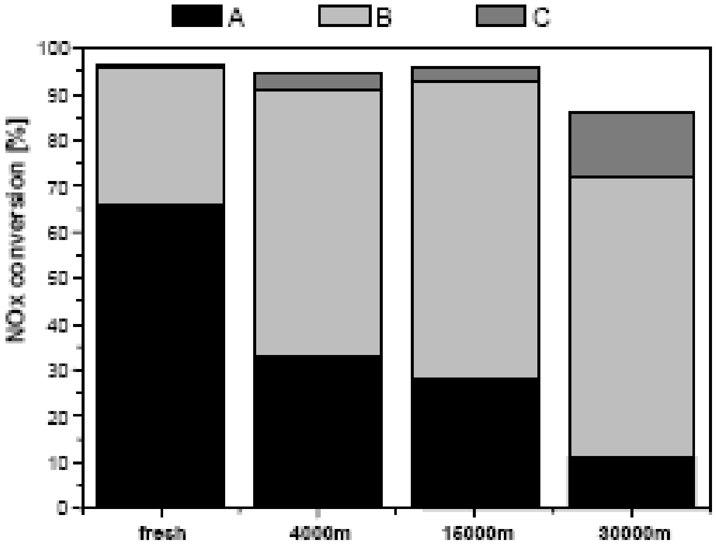


“A” has best thermal durability.
“B” has best LT performance.



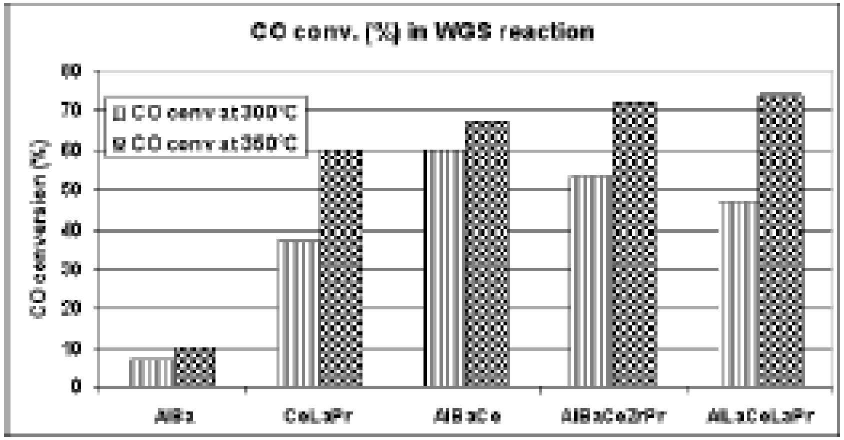
“C” shows the easiest desulfation.

Due to different aging characteristics and layout, deNOx shifts to back LNTs upon aging.



Umicore, SAE 2008-01-0766

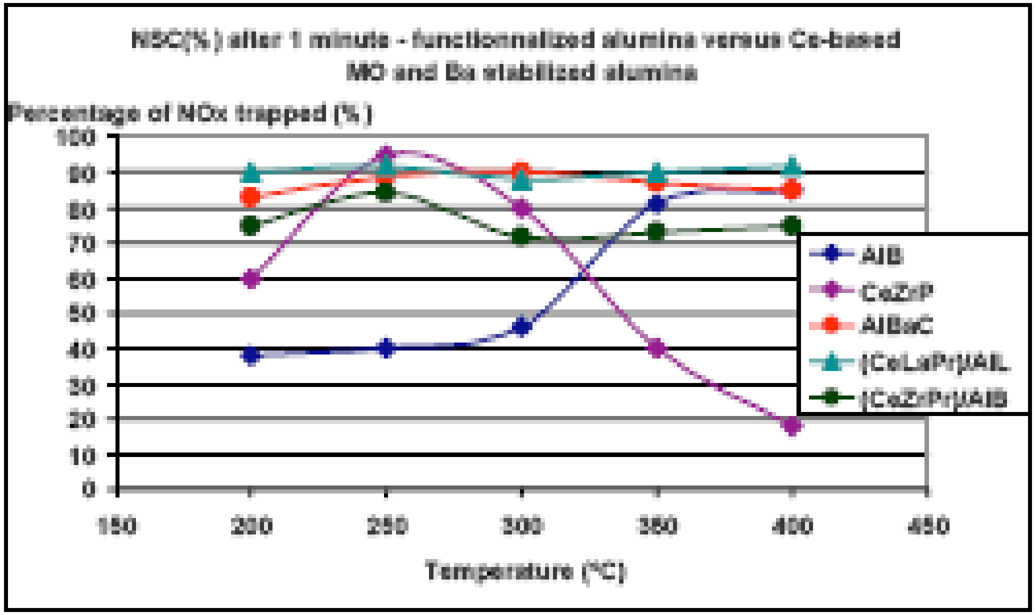
New ceria and alumina rare earth LNT formulations show good NOx storage, desulfation and WGS reaction characteristics



Water gas shift reaction is critical for hydrogen formation to promote NH3 for subsequent SCR catalysts.

CePr w/o Al showed 100% desulf at 600C

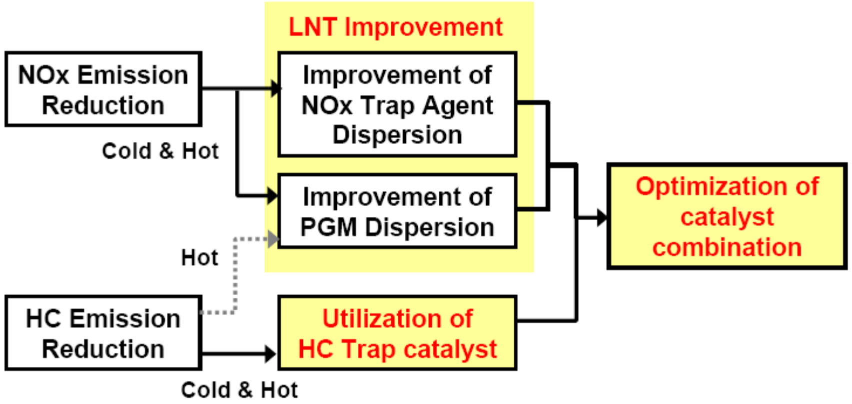
Rhodia SAE 2008-01-0450

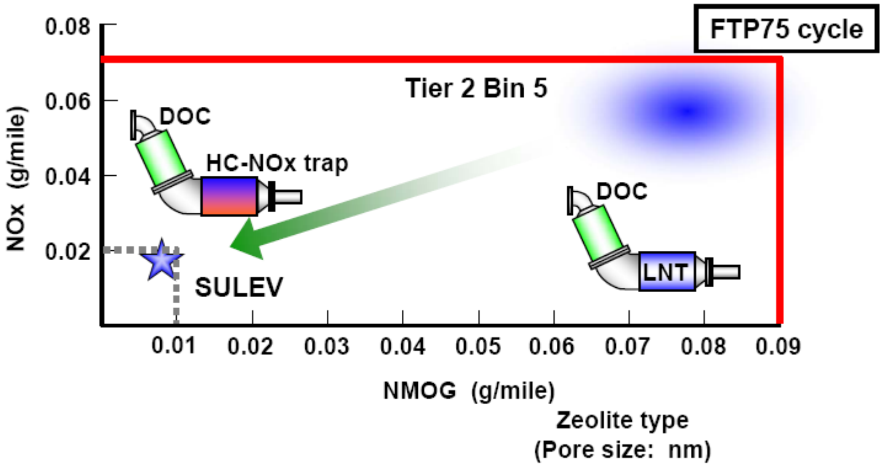


* Ce-based mixed oxides show high NSC at low temperature (250°C), CeLaPr and CeZrPr samples being the most efficient. A 2 minutes running test shows a strong decrease of the NSC at high temperature.

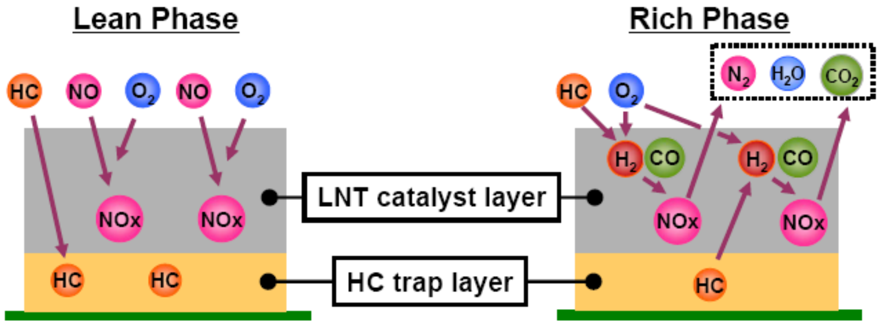
* Functionalized alumina show the highest NSC on the whole temperature range AlBaCe and AlLaCeLaPr being the preferred carriers.

By integrating HC control into an LNT, synergies are realized and useful to achieving SULEV (Bin 2) NOx.





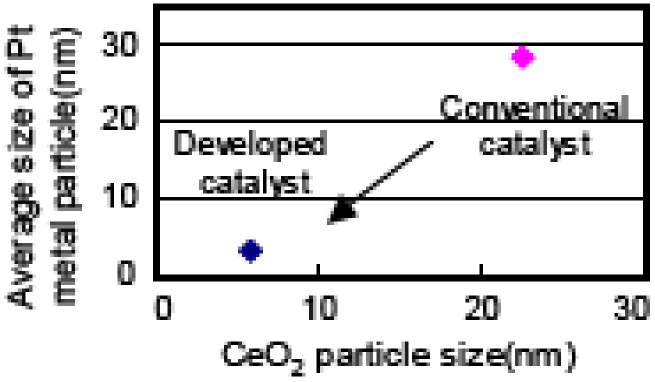
By incorporating HCT layer in the LNT catalyst, H_2 and CO is generated effectively by HC in gas phase and HC trap layer.



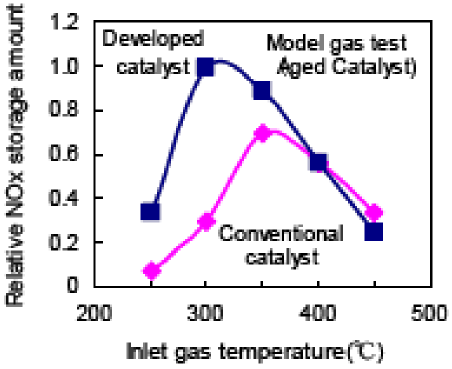
Nissan SAE 2008-01-0449

The DPNR is updated.

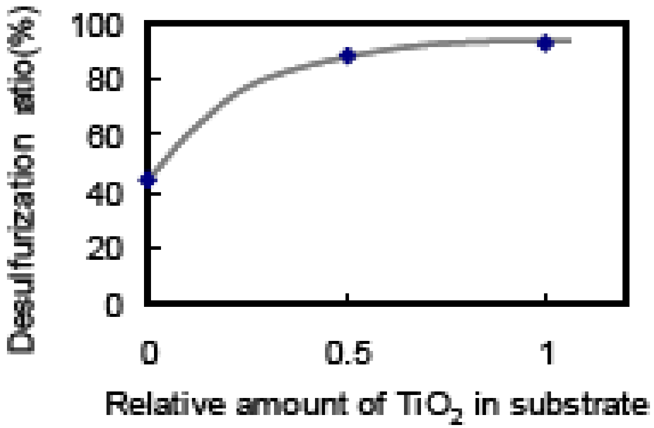
Various improvements increase de-NOx from 40% to 70+%



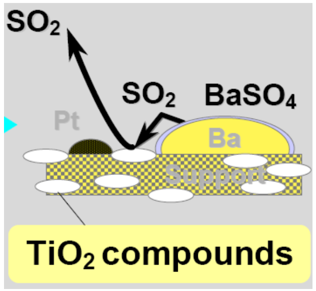
New ceria additive pins Pt grain to inhibit growth. Pt growth also depends on ceria grain size.

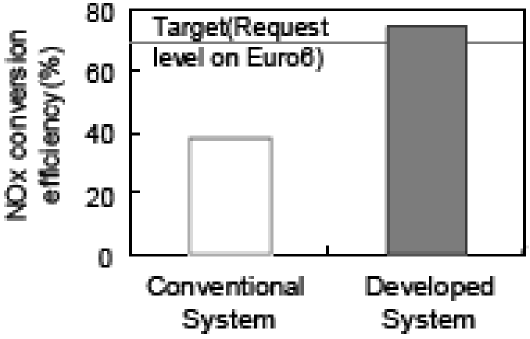


New formulation increases NOx storage capacity through better NO2 formation. More OSC slightly inhibits HT storage.



Titania increases desulfation rate.





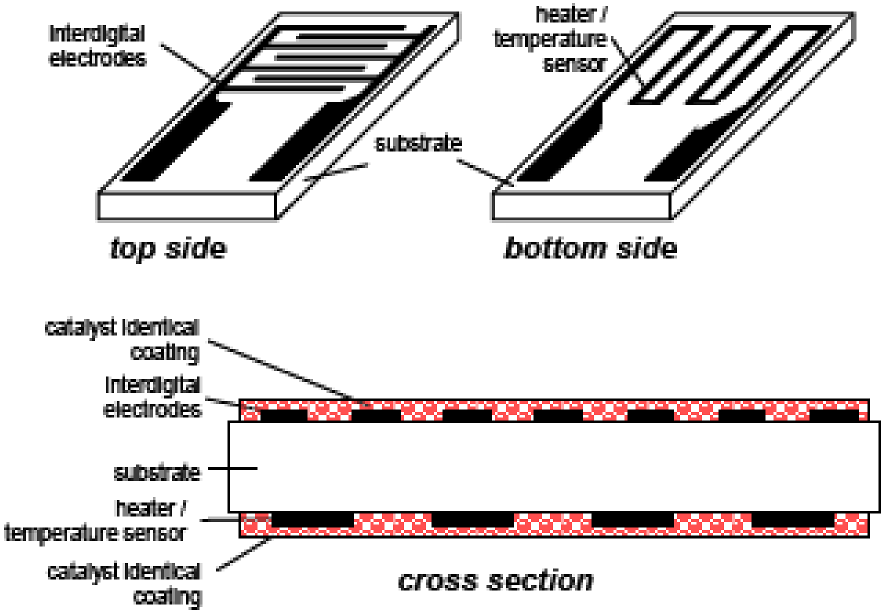
New DPNR is delivering 70+% deNOx

To regenerate LNT, rich combustion is preferred to standard exhaust port injection at lower load. If oxygen is removed for EPI, it is similar to rich combustion, but more robust. EPI preferred at higher loads.

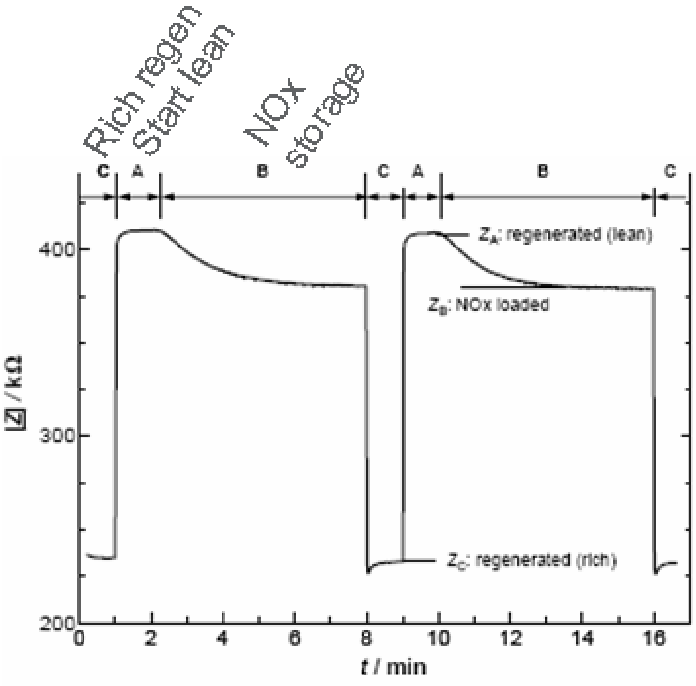
Future direction: Greatly reduced PGM and a sulfur trap.

Toyota, SAE 2008-01-0065, MinNOx 6-08

New LNT sensor directly measures state of NOx storage. Can show state of regeneration, sulfation, and NOx storage.



Sensor uses LNT material and measures changes in conductivity.

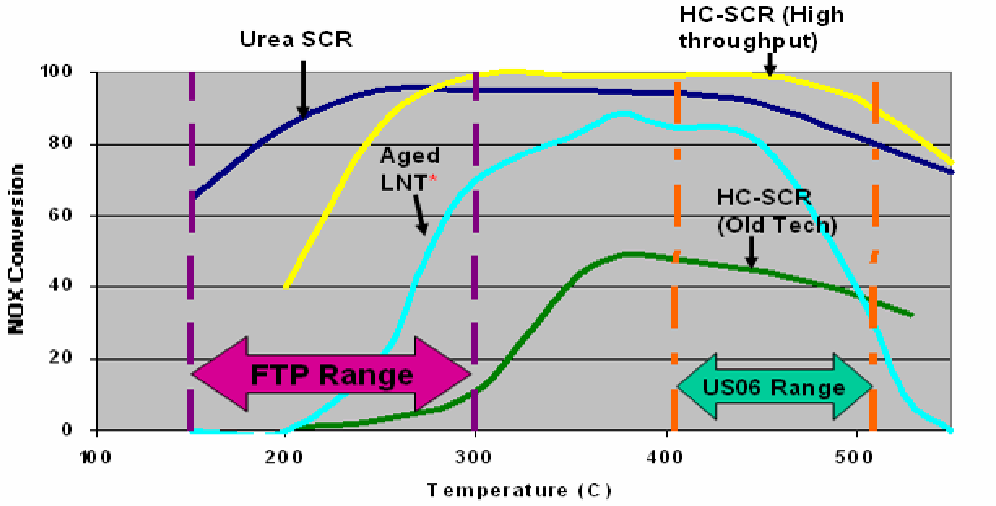


LNT catalyst impedance shows state of NOx loading

Univ Bayreuth, Daimler SAE 2008-01-0447

DOE experimental program is developing effective LNC compositions

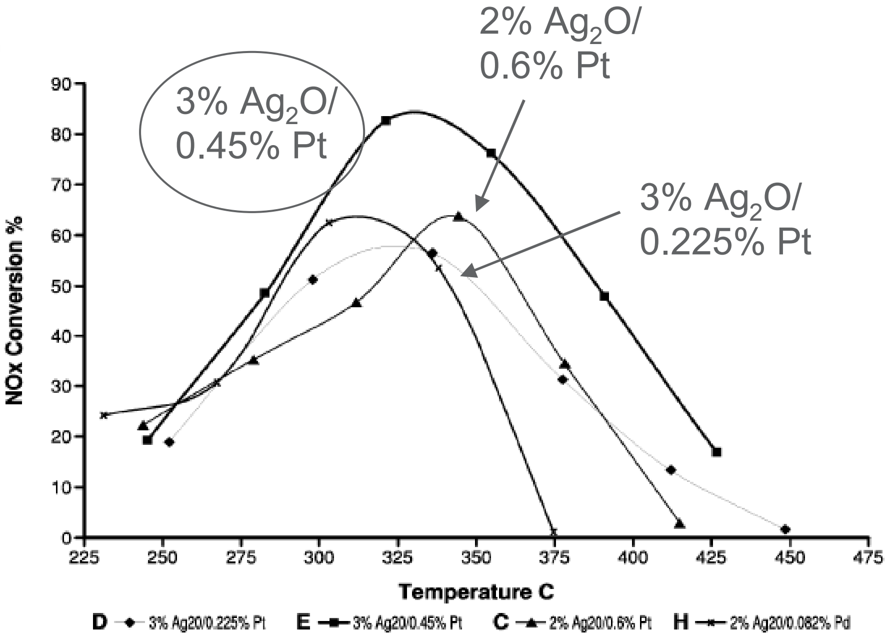
Bench Reactor Results



*Engine evaluation on aged LNT catalyst (4.9 L 5250 lbs weight class)

- Reactor conditions (water, CO_2, 25 ppm NO, 250 ppm H_2, 10% O_2, 80 ppm simdiesel or ammonia)
- Reactor samples hydrothermally aged for 16 hours at 650 °C

GM, CLEERS Workshop 5/07



The best composition has ~0.7 g/liter Pt.

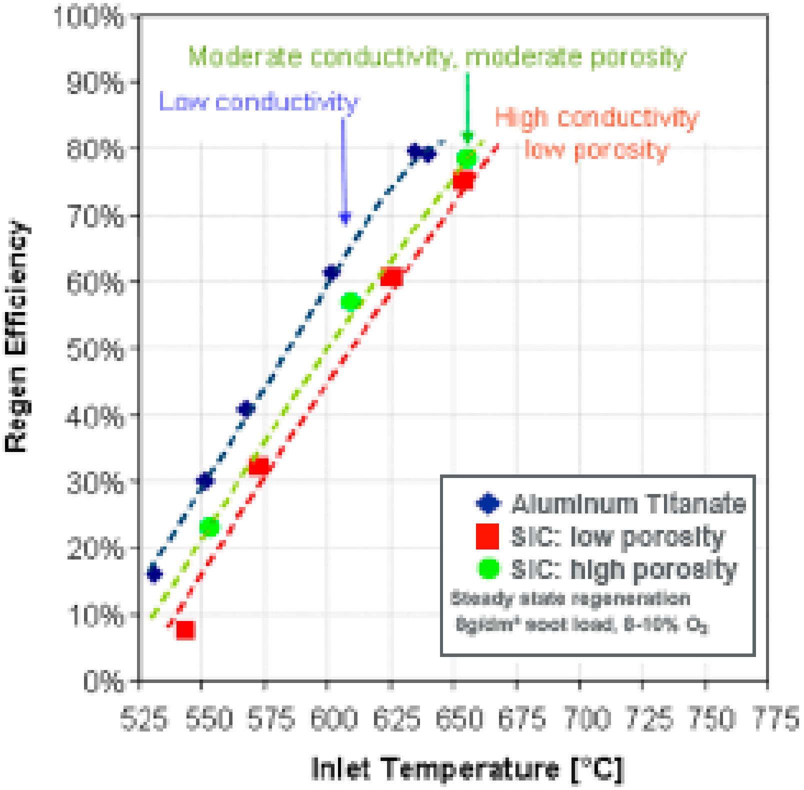
US Patent 2008/0070778 A1

CORNING

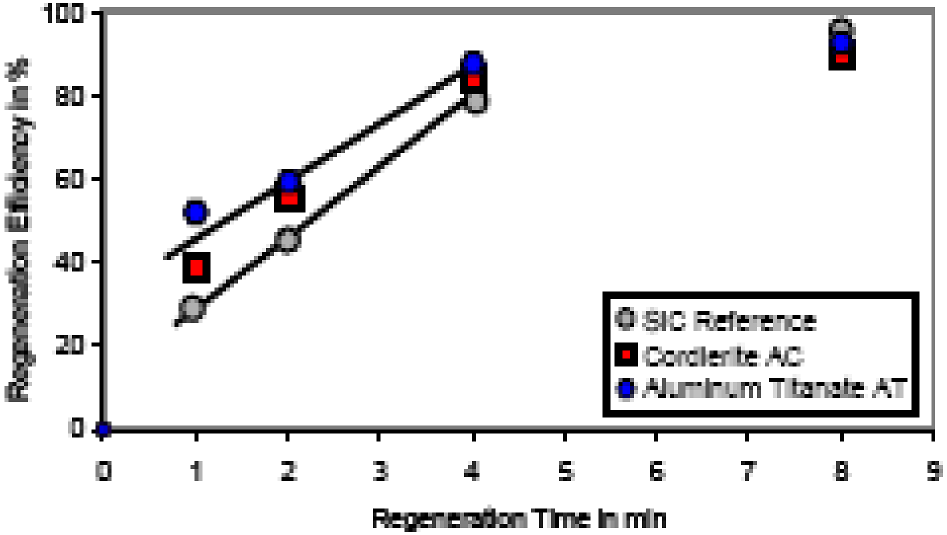
DPF

Oxide filters can reduce DPF regeneration fuel penalty.

~10% more efficiency vs. inlet temperature; less time to regenerate in transient conditions.



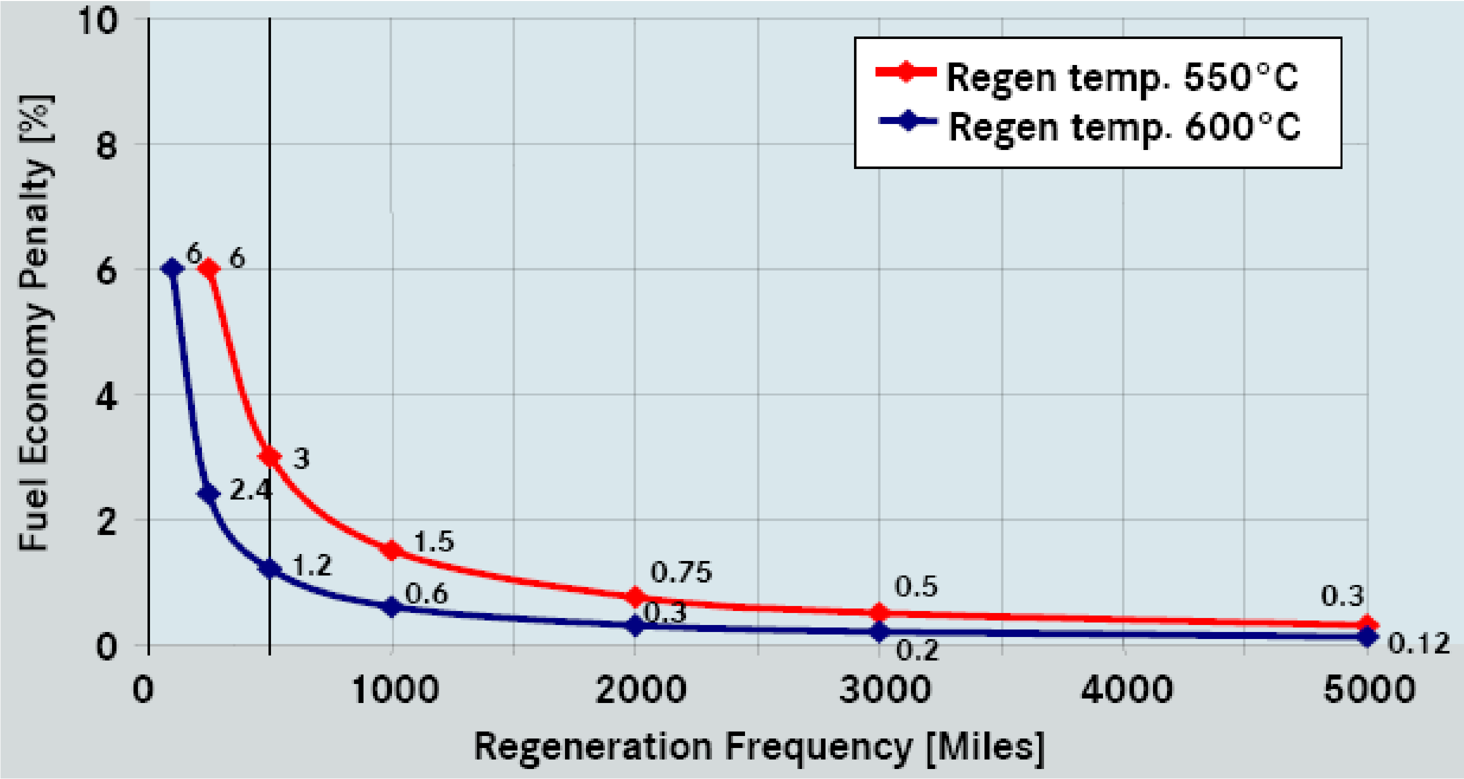
Oxide DPFs regenerate more completely at any given inlet temperature. Lower inlet temperatures are preferred. Both save fuel.



Oxide DPFs regenerate more completely in transient conditions.

Corning, SAE 2008-01-0328

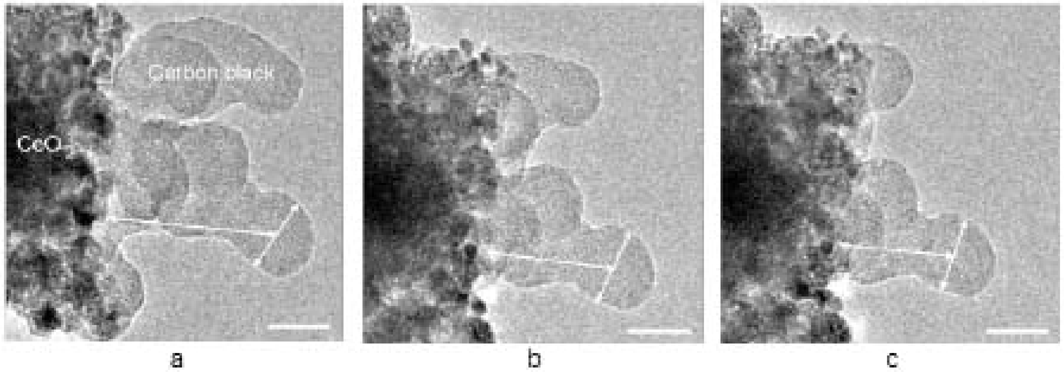
HDD fuel penalties are shown as a function of active regeneration frequency



Daimler, CTI Forum 1-08

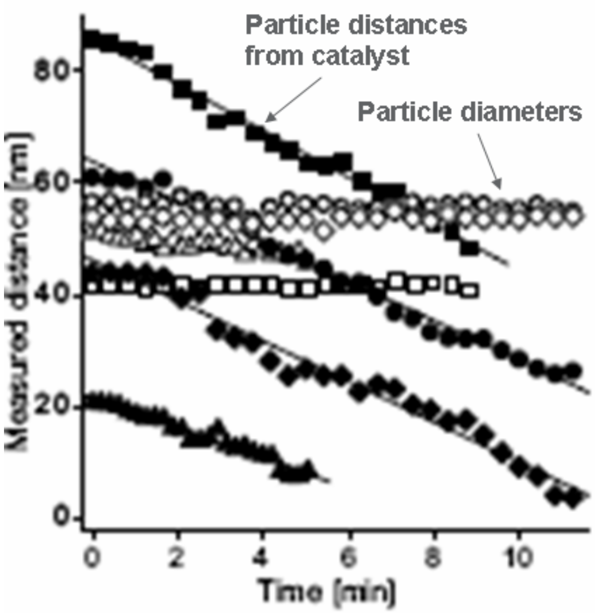
Direct observation of soot oxidation shows soot oxidation at ceria-soot interface and continuous movement of soot to interface.

Confirms that soot/catalyst contact is vital to soot oxidation by oxygen.



Environmental TEM photos show soot shrinking into ceria washcoat during oxidation.

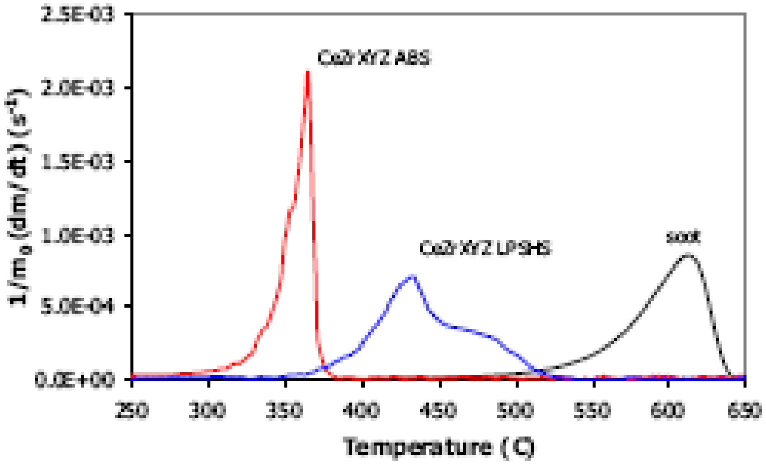
- Alumina did not show this behavior up to 600C (max T tested).
- Soot-ceria interface re-established itself. Interface might be mobile, or oxygen surface diffuses. More likely van der Waal forces re-established the interface.



Particle diameter (open symbols) remains fixed, but distance of center from catalyst decreases with oxidation.

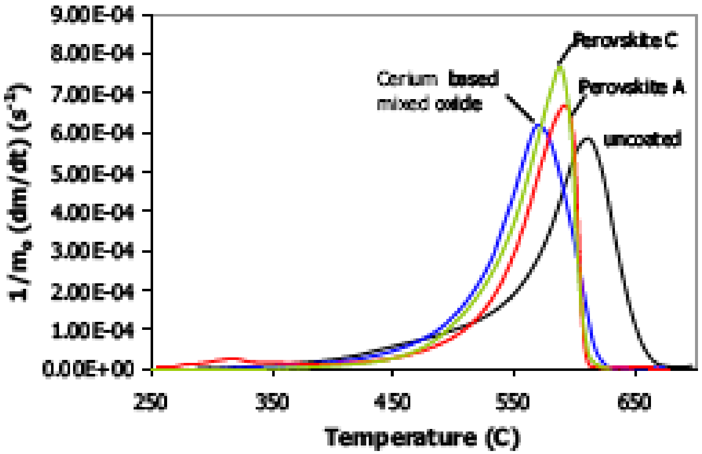
Haldor Topsoe, SAE 2008-01-0418

New cerium-based mixed oxide catalyst and coating method described. Soot/catalyst contact key to performance.

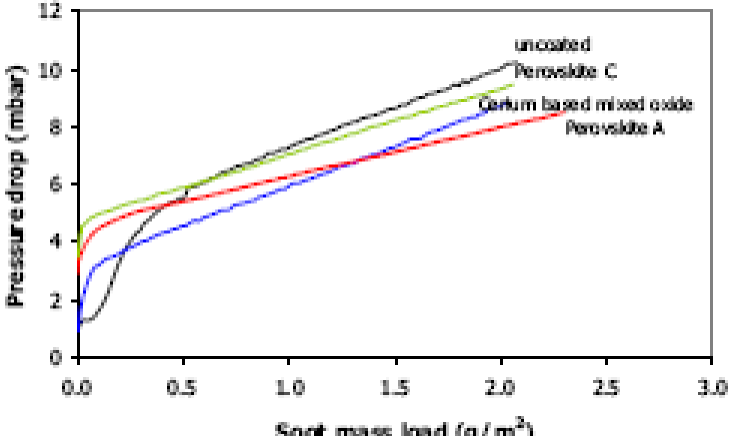


TGA experiments with good soot-catalyst contact. Catalyst processing method can impact oxidation temperature. “ABS” aerosol based deposition. “ LPSHS” is liquid phase self-propagating high temperature synthesis.

A&PT Lab, CERTH/CPERI
SAE 2008-01-0417



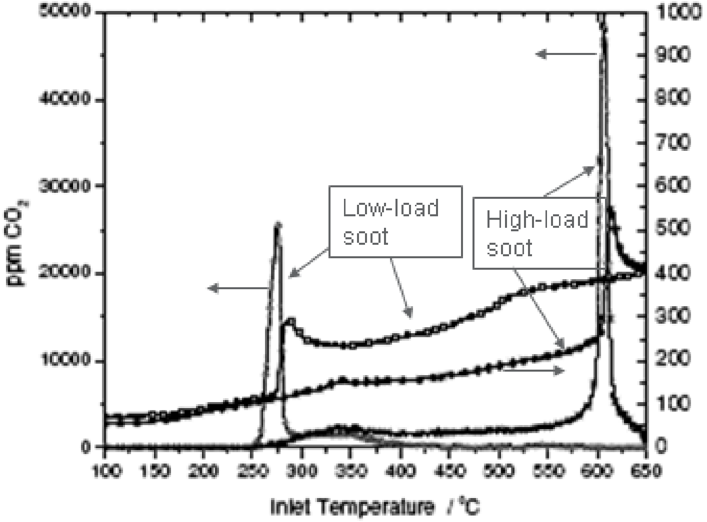
Monolith experiments not as differentiating as DTA, due to less soot-catalyst contact.



All catalysts have lower Δp vs. uncoated parts. Soot kept out of wall by catalyst.

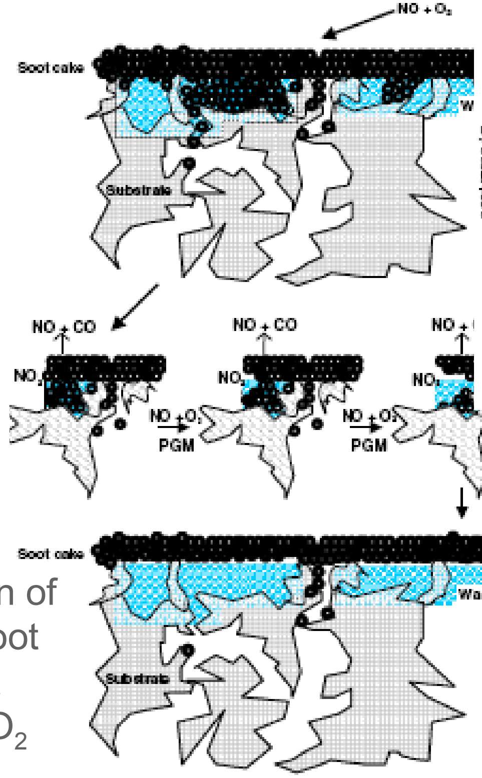
New evidence suggests LT direct oxidation of soot by oxygen when in good contact with advanced catalyst.

Model shows competition with NO_2 oxidation mechanism.

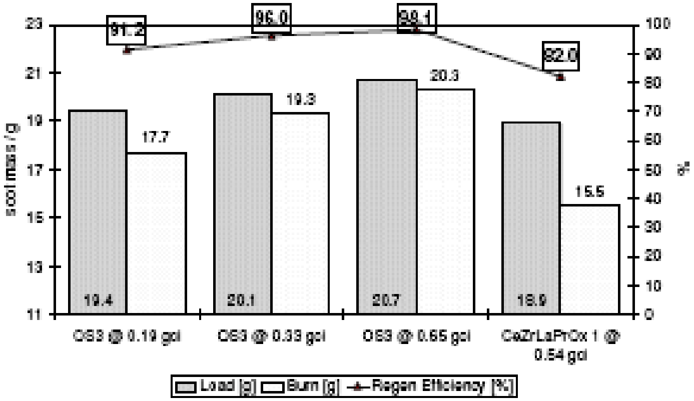


Initial screening studies showed LT oxidation of soot by oxygen depended significantly on soot characteristics. First evidence of direct soot oxidation at v. low temperatures. <5 ppm NO_2

Adding NOx scavenger (LNT) to DPF catalyst enhanced LT regeneration possibly due to minimizing NO2 oxidation of soot.



NO_2 oxidation deteriorates direct soot/catalyst contact. Competition for direct LT oxidation of soot.

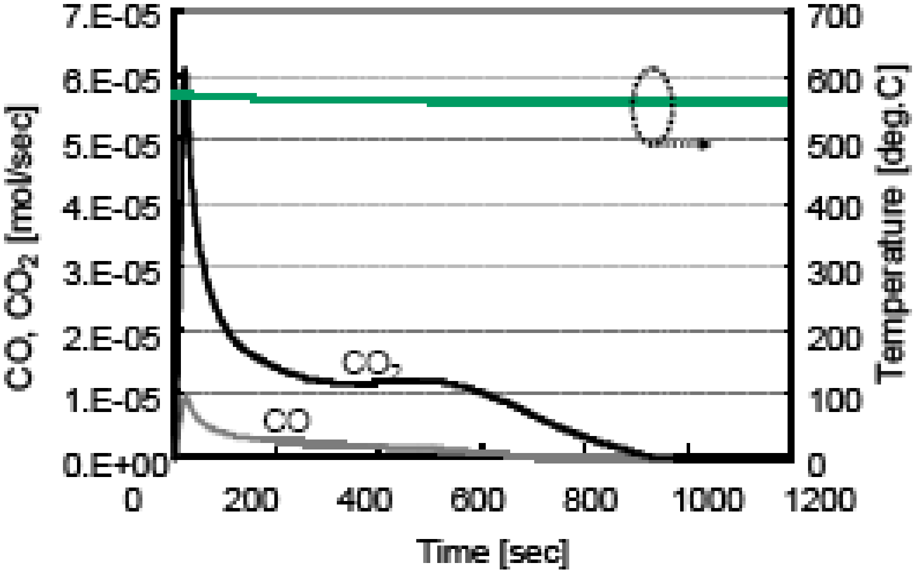


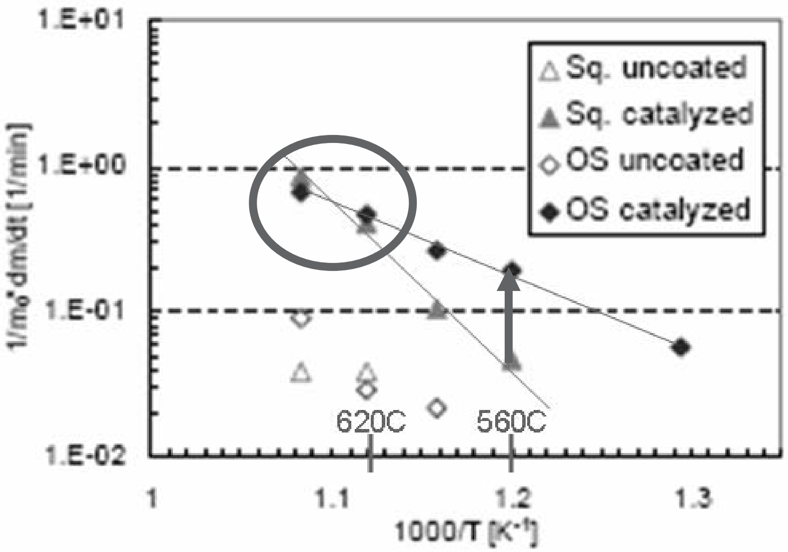
New advanced catalyst (“OS3”; no PGM on DPF) compared to OEM catalyst shows more regeneration at 580C inlet. Importance of contact evident by dependence of regeneration efficiency on loading.

Umicore, SAE 2008-01-0481

DPFs with higher GSA (geometric surface area) and catalyst layer coating perform better.

Soot-catalyst contact enhanced. Soot can't enter wall for low Δp.





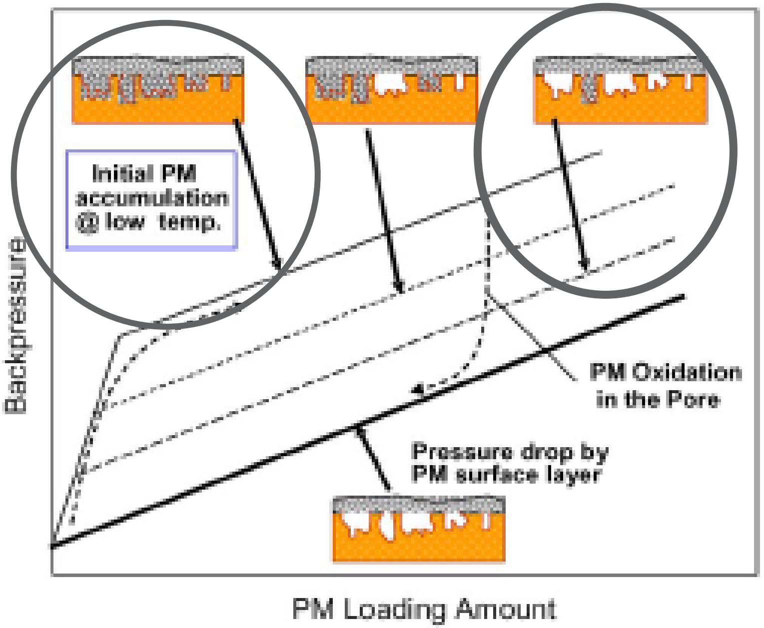
Ceria-based catalyst (no PGM) at 560C shows good soot oxidation selectivity to CO_2 (80%). 10X more oxidation than w/o catalyst.

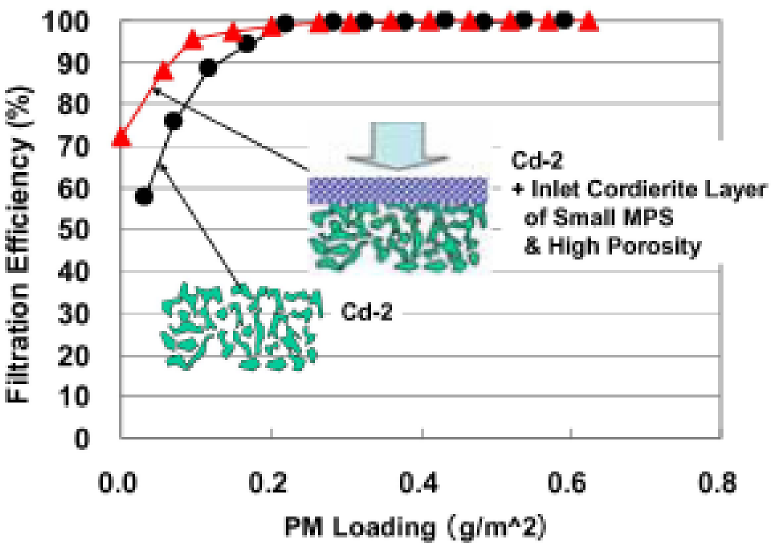
There is not much difference in oxidation rate for higher GSA DPF ("OS") above 620C. Soot-catalyst contact less important.

- Catalyst coating prevented soot from entering wall, so Δp was lower than for uncatalyzed DPF.
- Initial P# efficiency >95% with catalyst.

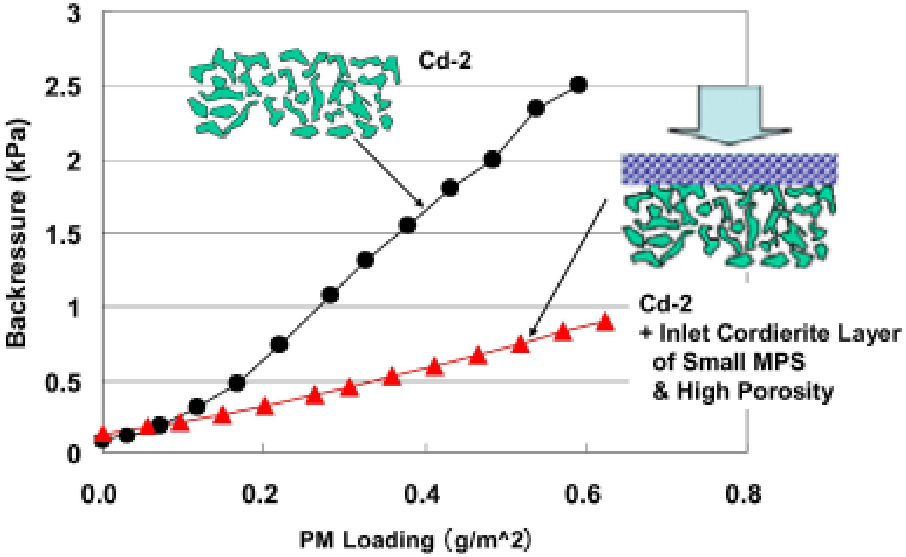
Ibiden, SAE 2008-01-0621

Adding a small-pored filter layer to the inlet walls of a DPF reduces back pressure and increases efficiency.





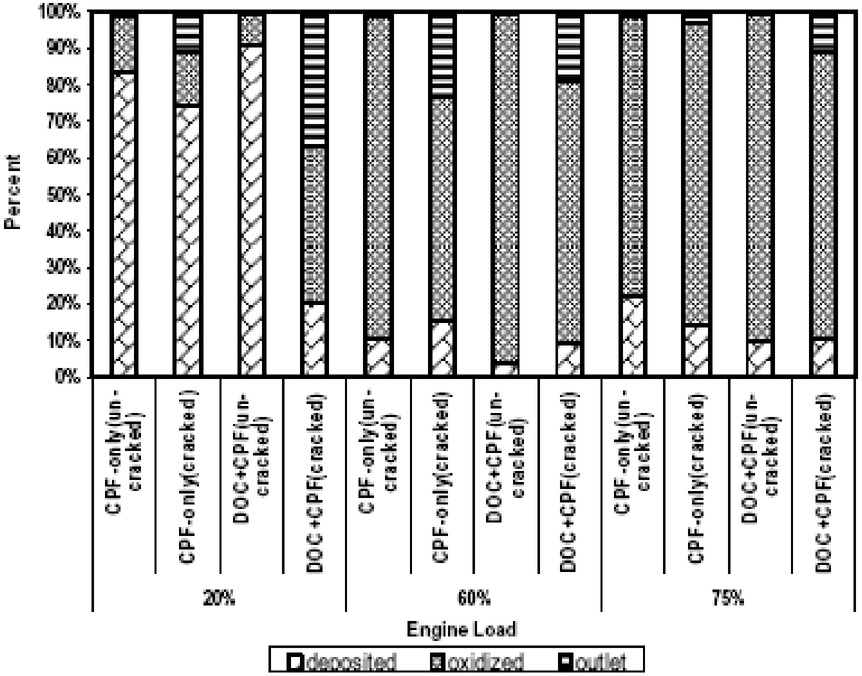
DPF backpressure is high when soot penetrates into the wall, blocking more pores. This inside soot can oxidize earlier than the full surface soot layer, giving backpressure hysteresis. Concept is to put a layer on the inlet wall to prevent soot penetration into wall.



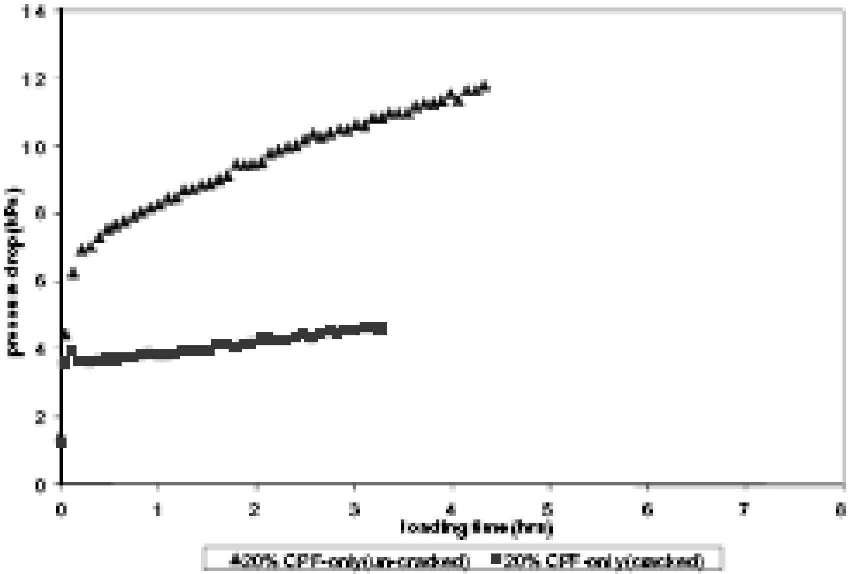
NGK SAE 2008-01-0618

A comprehensive model of soot mass is shown.

Preliminary results show it might be used for OBD.



Significant differences in oxidized soot between cracked and good filters

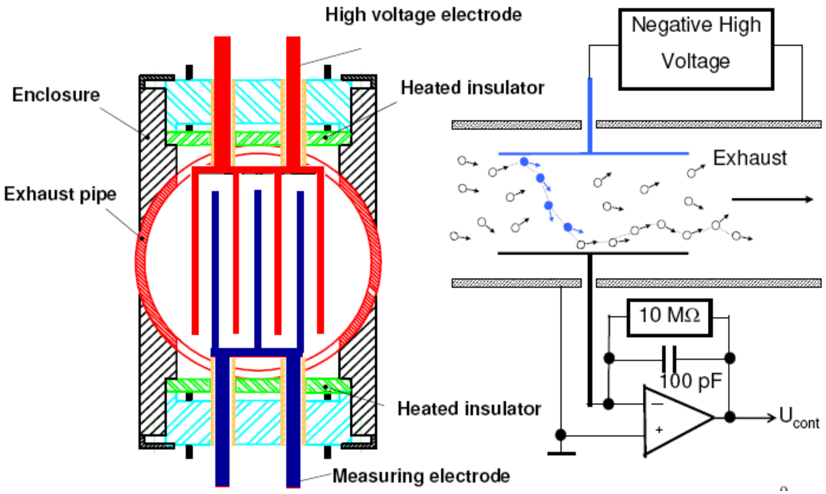


Aft complete regen, cracked DPF has much diff Δp behavior all load points. 20% load at rated speed shown here

Lower Δp for cracked filter yields negative soot mass in improved soot mass model. Loaded wall permeability is a key factor in the model. More work is needed to calibrate engine conditions to soot layer permeability and loading, especially in transient conditions.

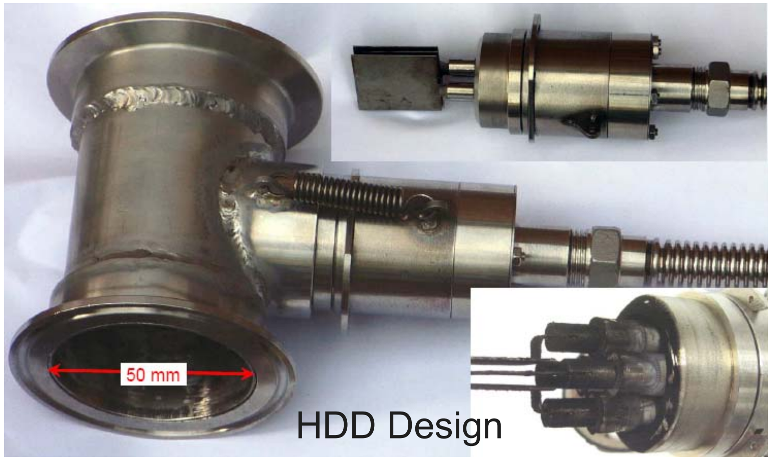
MTU, SAE 2008-01-0764

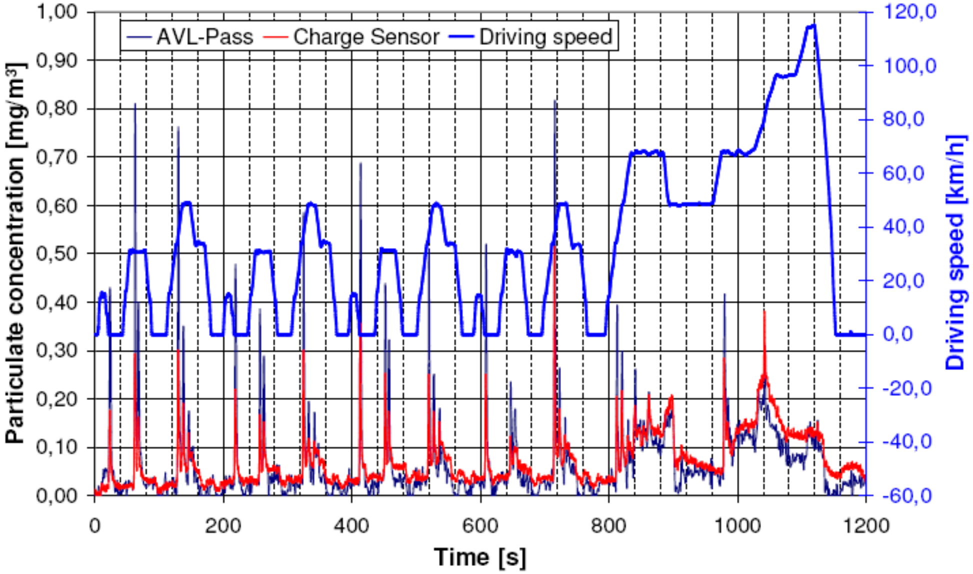
Soot charging sensor shows promise for post-DPF soot sensing for OBD.



Soot charging sensor measures post-DPF soot (0.05 mg/m^3) by looking at charge transfer to electrodes from soot. Soot picks up charge from top plate, is then repelled by same polarity to measuring plate.

EAST Solutions, CTI DPF Forum 7-07

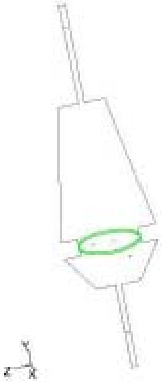


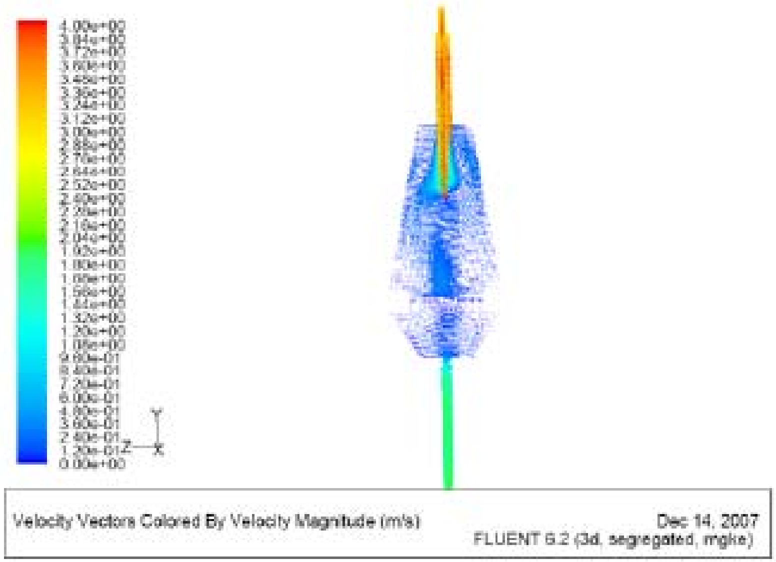


Charge sensor signal follows instrument signal very well in transient testing with a partially damaged DPF.

A new lab-scale DPF test method is developed.

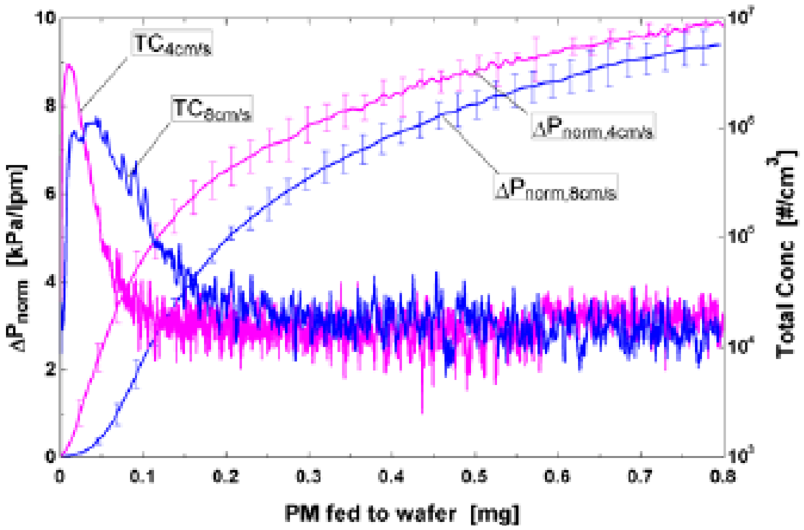
Allows easier fundamental study on substrate and catalyst effects.



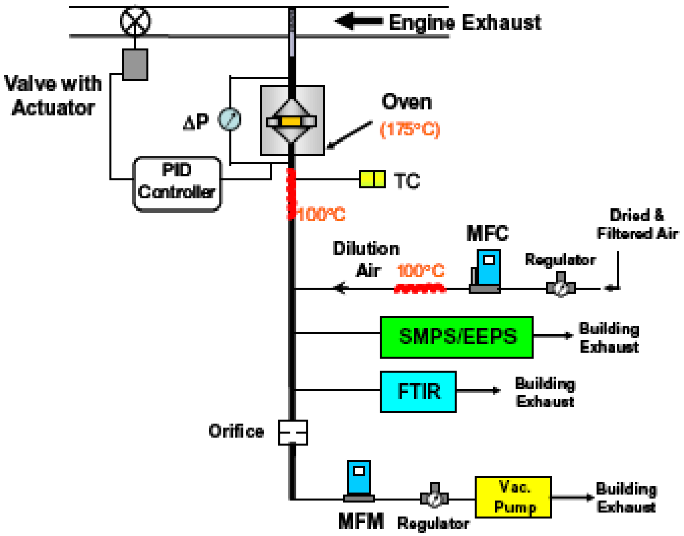


Velocity Vectors Colored By Velocity Magnitude (m/s)

Dec 14, 2007
FLUENT 6.2 (3d, segregated, rngke)



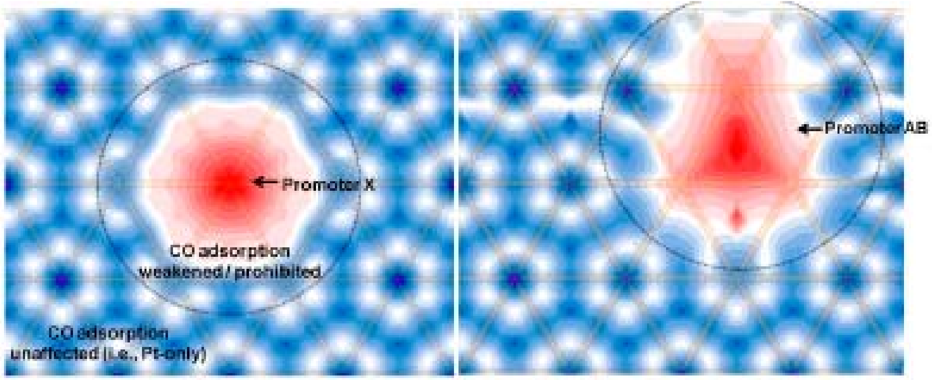
Results show similar behavior to full-sized filters



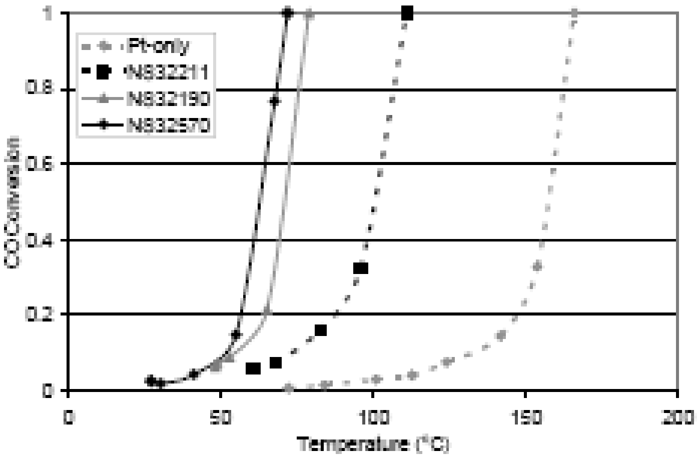
DOCs

Chemically promoted DOCs enhance performance.

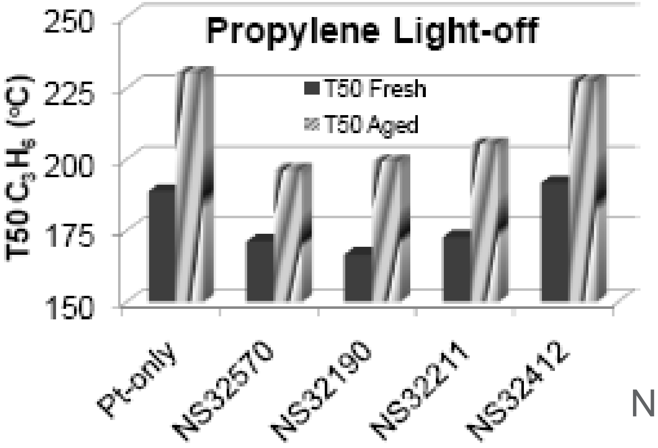
Works by increasing CO desorption tendency, allowing O to adsorb and react.



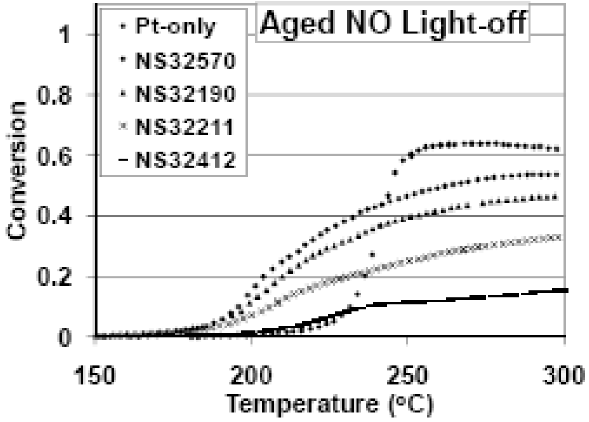
Catalysts saturate w/ CO at LT, leaving no room for oxygen. Promoters create CO-exclusion zones around adsorbed CO molecule to allow some O adsorption to get reaction moving.



CO T50 is decreased 100C using promoters.



Nanostellar, SAE 2008-01-0070



T50 for propylene decreased 40C for aged catalyst with promoter.

NO_2 formation can also be “tuned”

Summary

- Regulatory action: Euro VI HDD, CARB LEV3, CO_2
  - HD technology harmonization; SULEV fleet average?; challenging CO_2 regs
- Roadmaps for LD and HD are proposed. Significant opportunity for CO_2 and NOx reductions.
- SCR is advancing
  - DPF+SCR component; new catalysts/configurations; quantified durability;
- HC-deNOx developments show lots of advancement
  - New formulations (traditional and new families); new configurations; optimization
- DPF developments focusing on improved, more efficient regeneration
  - Oxide DPFs can save energy
  - Soot/catalyst interaction coming into the spotlight
  - Filtration “membrane” keeps soot out of wall for reduced Δp
  - OBD via modeling and sensors
- DOC fundamental improvement might be improtant for advanced combustion regimes