Removing nitrogen oxides from Diesel exhaust via promoted NOx decomposition to have **zero-pollution** cars

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PND should replace SCR.

[Ta-Jen Huang *et. al*, "Promoted Decomposition of NOx in Automotive Diesel-like Exhausts by Electro-Catalytic Honeycombs", Environmental Science & Technology, 49 (2015) 3711−3717.]

EUROFORUM

11th International CTI Conference

SCR Systems

Selective Catalytic Reduction

Europe's biggest and best SCR conference CTI - Car Training Institute Conference *7 to 9 July 2015, Stuttgart*

HIGHLIGHTS

(PND) (ECH)

INNOVATION: Promoted NOx Decomposition by Electro-Catalytic Honeycomb

DeNOx Control System for Future RDE Standards

VECTO Tool / PEMS Testing

Blue Sticker for Environmental Zone

Control and OBD-Monitoring of SCR Systems

Novel Titania / Vanadate SCR Catalyst-Powder

SCR on Filter Systems

Producing NH_3 via thermolysis

Different Approaches for Urea Quality Sensors

Optical Visualization for Efficient Catalyst Layout

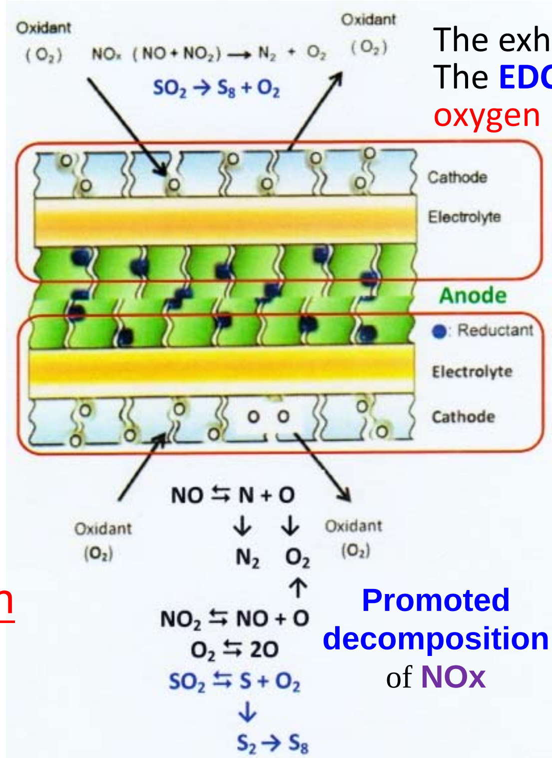
Electro-catalytic honeycomb (ECH)

De-NOx for Diesel cars but get away from the troubling SCR (selective catalytic reduction) system has been realized by Diesel de-NOx honeycomb catalyst, *i.e.* Electro-Catalytic Honeycomb (ECH) as described in the following paper on Promoted NOx Decomposition (**PND**). [Ta-Jen Huang *et. al*, "Promoted Decomposition of NOx in Automotive Diesel-like Exhausts by Electro-Catalytic Honeycombs", Environmental Science & Technology, 49 (2015) 3711−3717.]

The PND technology will certainly replace SCR. This is because the ECH for Diesel de-NOx is very much cheaper than the SCR system and free of operating cost, according to:
-- PND has much higher de-NOx rate (per treatment area) than SCR, *i.e.*, the catalytic honeycomb of PND, the ECH, is smaller than that of SCR.
-- PND does not need any reductant or other resource, being free of operating cost. Just like placing a TWC (three-way catalyst) converter, but the ECH is also free of engine AFR (air fuel ratio) control.
-- Higher NOx concentration leads to higher de-NOx rate (proven repeatedly and been according to Chemical Engineering principles).
-- PND is effective from 900°C down to 15°C (tested) and can be more effective at lower temperature (under 0°C) according to its principle.
-- PND can treat NOx to **zero** NOx emission (tested). Thus, **zero-pollution** cars become possible.
Thus, highly efficient engines can be designed without any constraint by environmental regulations.

The **PND** device for automotive usage is **Electro-Catalytic Honeycomb** (**ECH**), which is based on the novel electrochemical double-cell (**EDC**)

The electrochemical double-cell (**EDC**) is composed of two electrochemical cells that share the same anode (reducing environment). Thus, the cell volume is reduced considerably and a honeycomb-type PND device becomes possible.



The exhaust flows over the cathode. The **EDC** can deNO_x, needing facile oxygen desorption.

NO_x: NO & NO_2

$NO \leftrightarrows N + O$

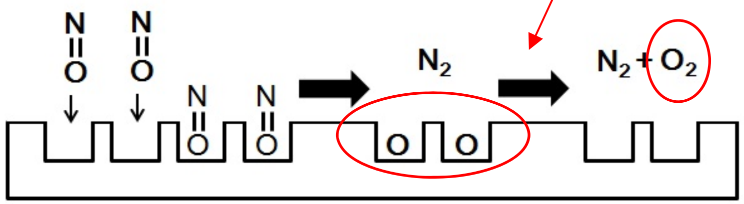
$\downarrow \quad \downarrow$

N_2 O_2 (needing facile oxygen desorption)

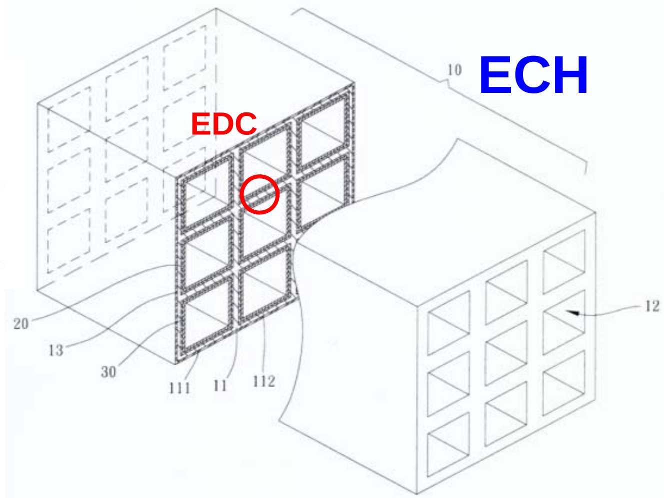
$\uparrow$

$NO_2 \leftrightarrows NO + O$

$O_2 \leftrightarrows 2O$



The **PND** device of **Electro-Catalytic Honeycomb** (**ECH**) has been granted EU, US, JP, TW, CA, KR, PRC patents.



10: Electro-catalytic honeycomb (**ECH**)
11: **Anode**, forming ECH structure
111 & 112: outer & inner surface of the anode structure
12: Exhaust flow channel
13: Shell, covering the outer surface of the anode structure
20: **Electrolyte** layer, coated on the inner surface of the anode structure
30: **Cathode** layer, facing the exhaust flow channel for exhaust treatment

Principle of facial oxygen desorption

The removal of the O species in NO_X had long been studied by direct decomposition of **NO_X** (**NO** plus **NO_2**): It is basically NO ⇆ N + O over catalyst with 2N → N_2 easily.

Thus, 2NO → N_2 + 2O; NO_2 ⇆ NO + O [Note that there is no reducing agent involved]

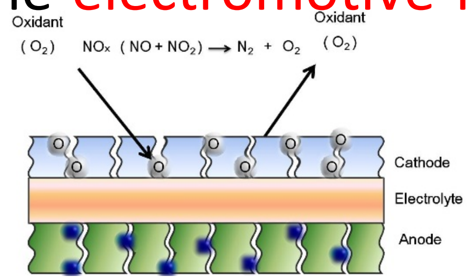
Fortunately, the overall reaction of decomposition of NO_X in automotive exhaust is exothermic; this is very important for $deNO_X$ at engine cold start.

However, the formed O species is strongly adsorbed on conventional catalysts and thus facile desorption of the O species as gaseous O_2 is key for NO_X decomposition. (facile oxygen desorption)

[Y. Teraoka et al., *J. Chem. Soc. Faraday Trans.* 94 (1998) 1887]

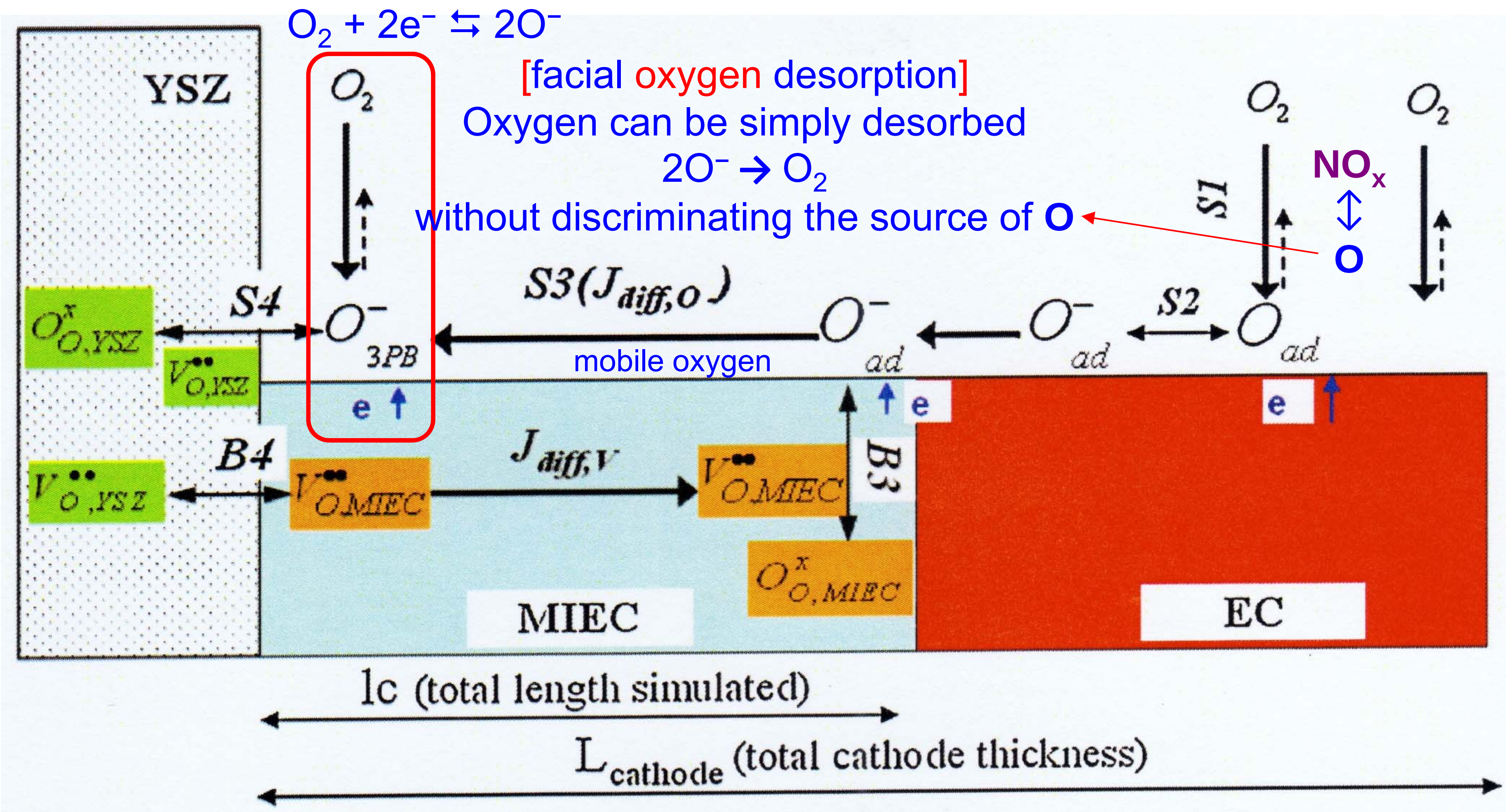
Since the presence of a voltage can weaken the chemisorptive bond strength of the O species [C.G. Vayenas, S. Bebelis, *Catal. Today* 51 (1999) 581], facile oxygen desorption is realized in an electrochemical cell, which can self-generate such a voltage. This voltage is called the open-circuit voltage in the field of fuel cells, and is generally called the electromotive force (*emf*).

Thus, **PND** is direct decomposition of NO_X with *emf*-promoted facile oxygen desorption, and can occur in any electrochemical cell.



an **electrochemical cell**
composing **Cathode**, **Electrolyte** & **Anode**

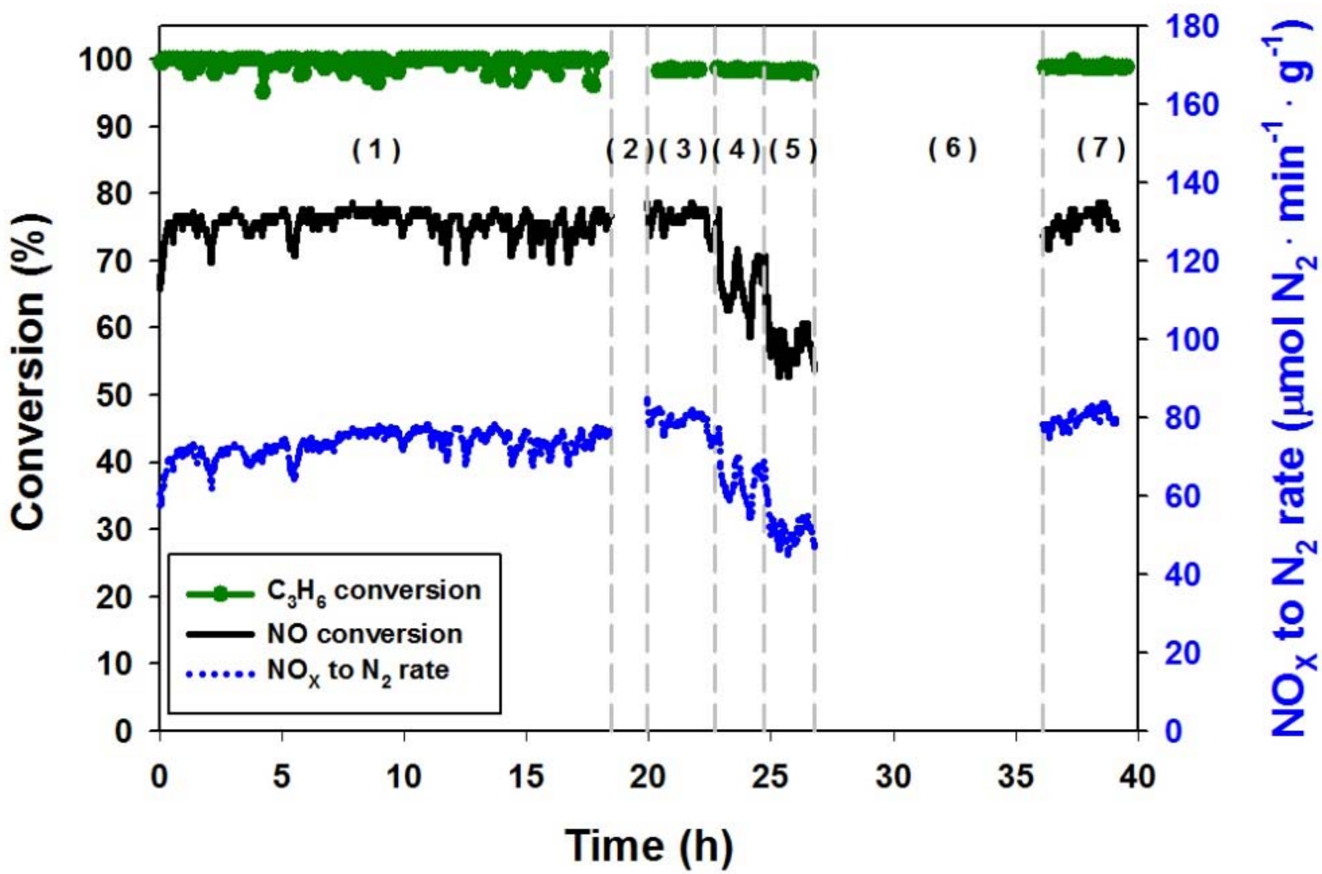
Principle of **promoted NO_x decomposition** (**PND**)



Schematic description of bi-pathway dominated **oxygen reduction** on Solid Oxide Fuel Cell cathode

[M. Gong, R.S. Gemmen, X. Liu, ***J. Power Sources*** 201 (2012) 204]

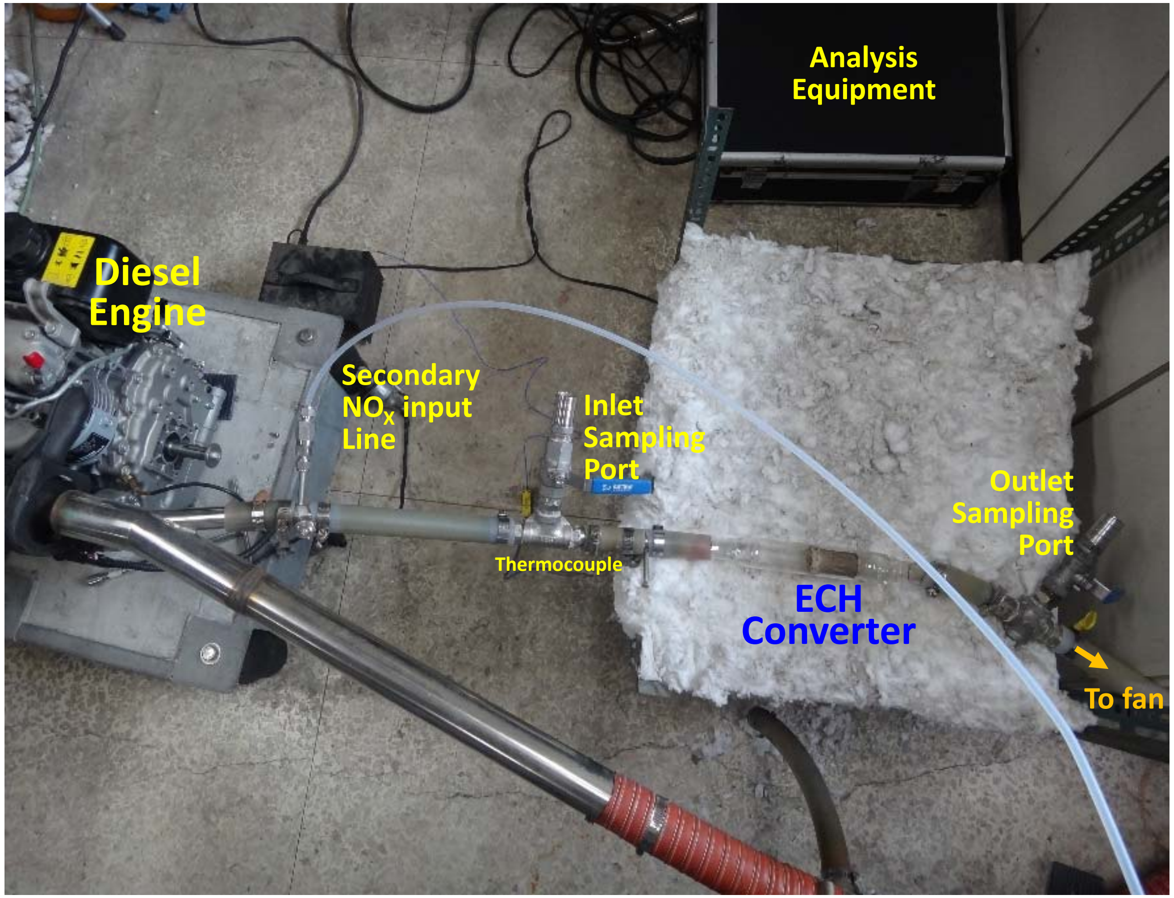
The mobile oxygen (O^-) over the cathode surface can promote the oxidation of hydrocarbons (HCs) to result in complete oxidation of HCs



[T.J. Huang et al., ***Applied Catalysis B*** 110 (2011) 164]

A real-world device of electro-catalytic honeycomb (**ECH**) has been invented for the novel technology of promoted NO_X decomposition (**PND**).

The **ECH**'s deNO_X (NO_X to N_2---**consuming nothing**) rate is higher than NH_3-**SCR**'s per treatment area.



No reagent or other resource was consumed in **ECH**-deNO_X, because the **ECH** converter is simply placed in the exhaust pipe—there is no supply of any reagent or other resource.

ECH converter

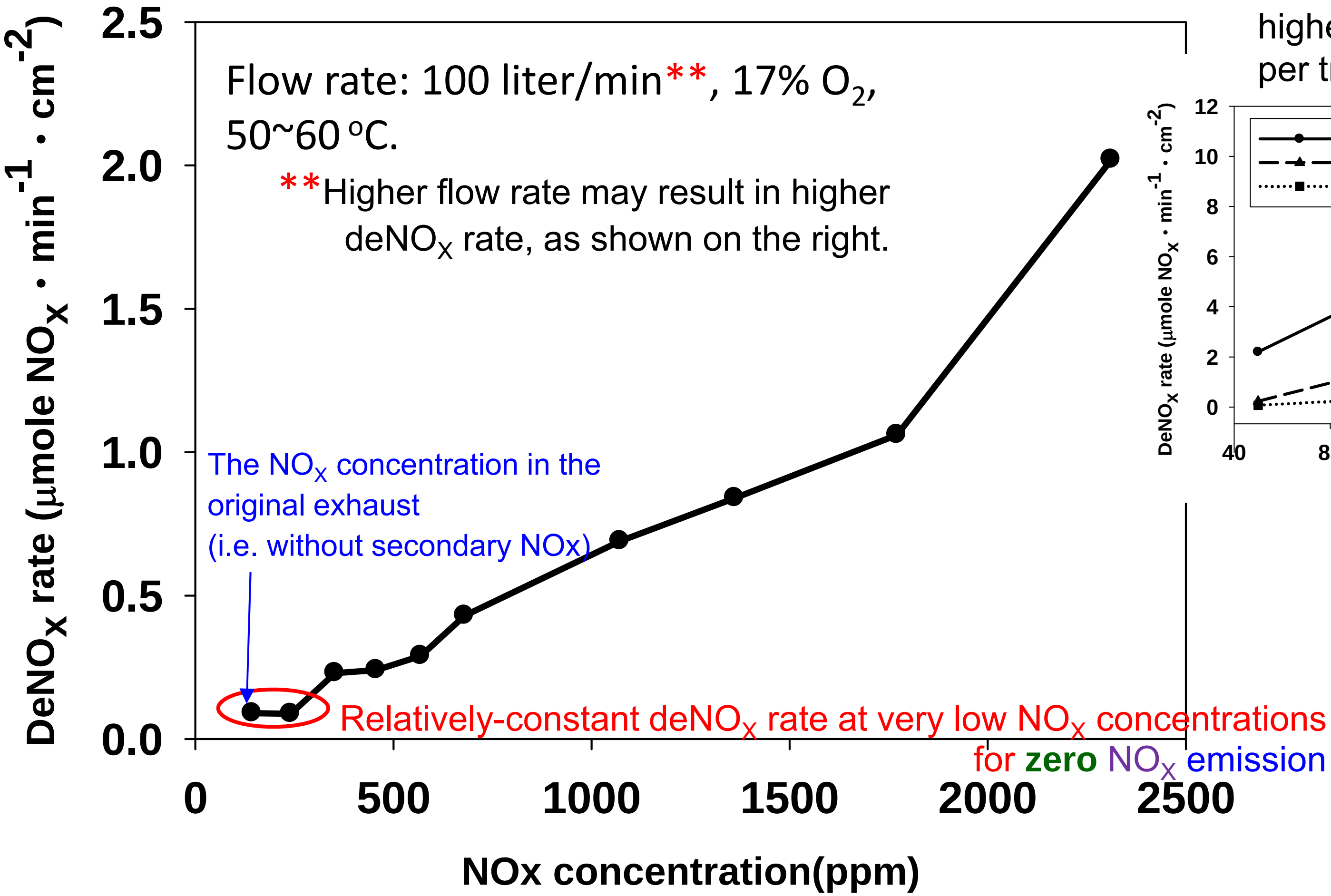
Experimental testing of **ECH**-deNO_X on Diesel exhaust:

The diesel engine: 0.219 liter, Yanmar L48N6-METMYI, made in Italy.

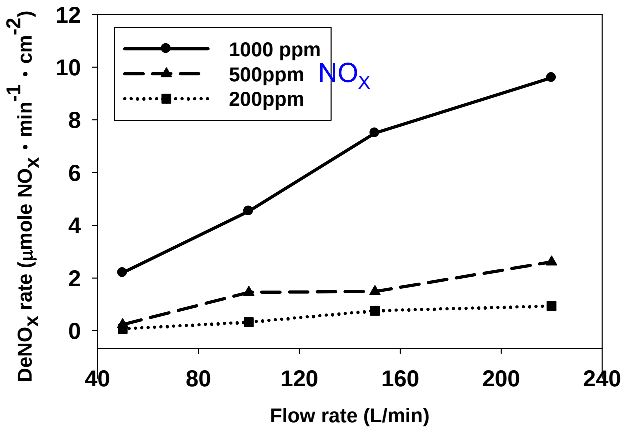
The analysis equipment: Flue gas analyzer, testo 350-XL, USA.

Further testing has been carried out with a diesel lifting car.

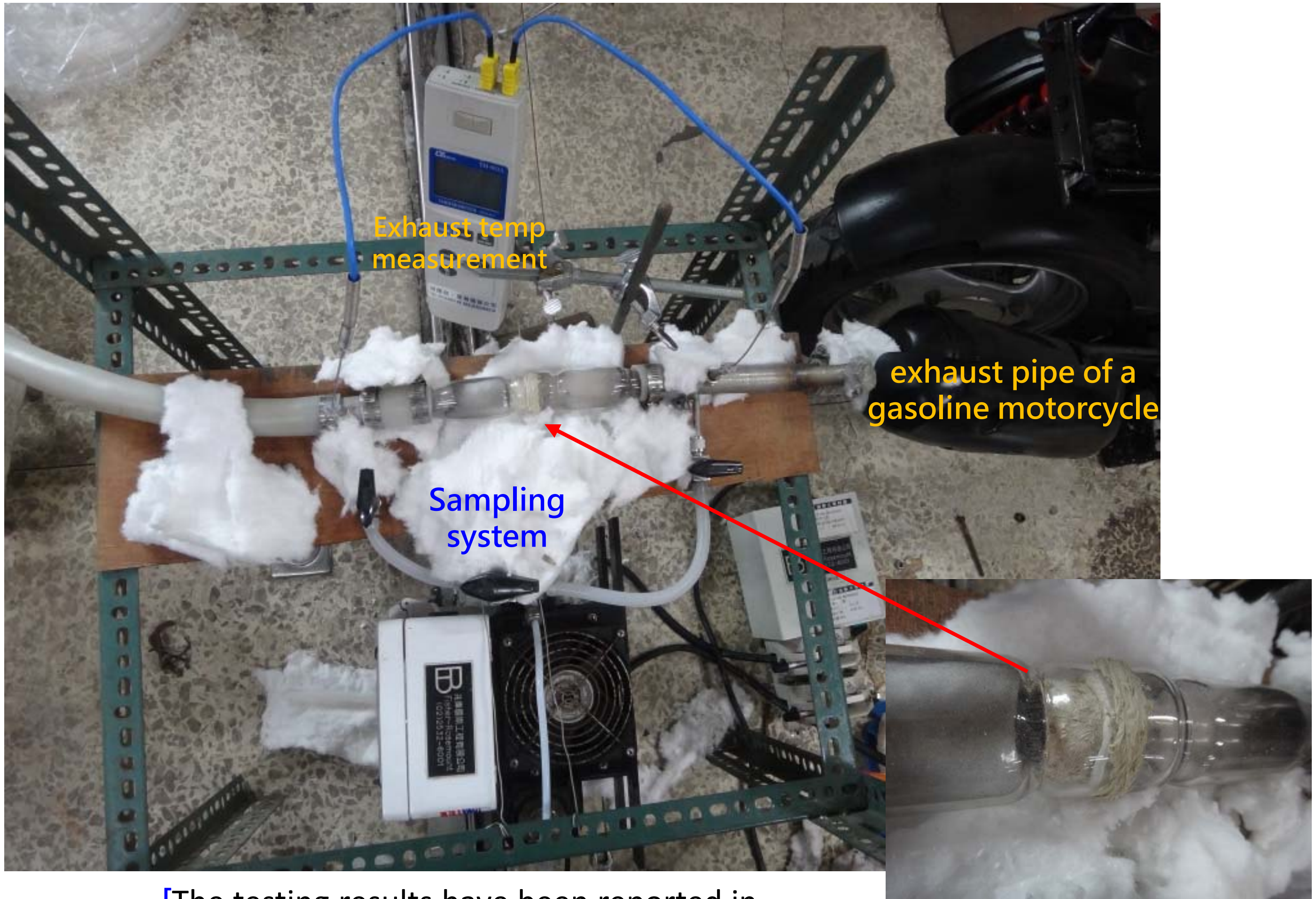
Typical testing results of **ECH**-deNO$_x$ on Diesel exhaust



Can be more than 10 times higher than SCR-deNO$_x$ per treatment area.



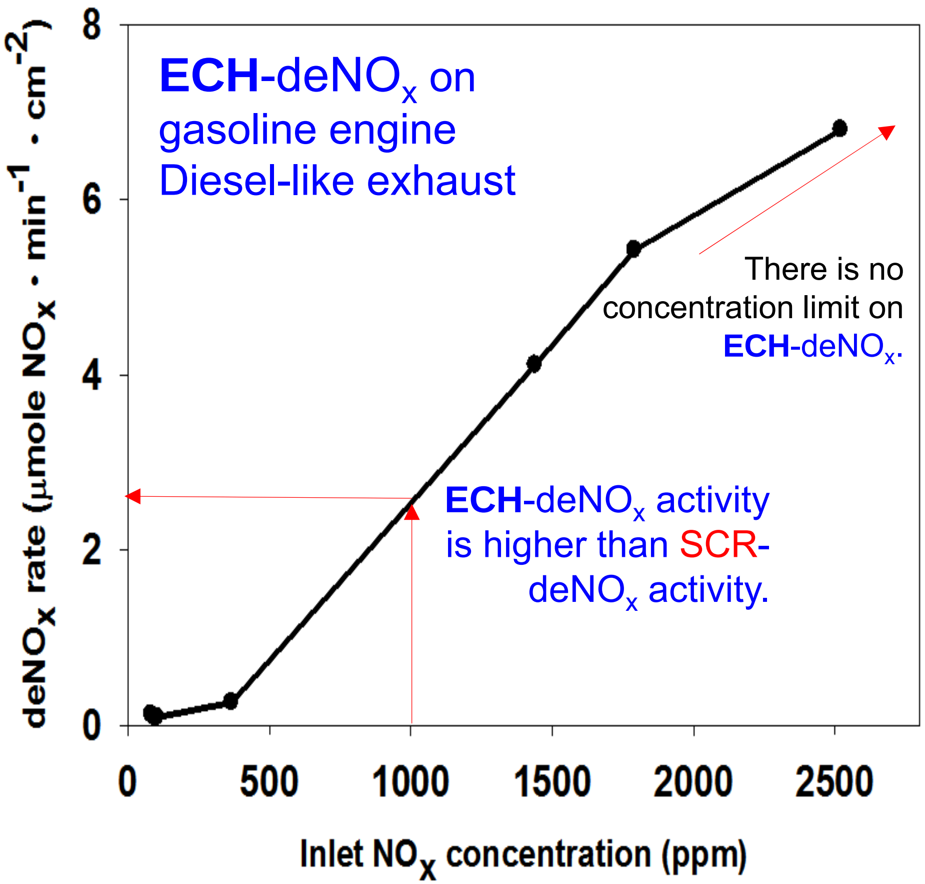
Experimental testing of **ECH**-deNO$_X$ on lean-burn (Diesel-like) gasoline exhaust



[The testing results have been reported in
T.J. Huang et al., ***Environ. Sci. Technol.*** 49 (2015) 3711]

Experimental evidences for

Higher NO concentration can lead to higher $deNO_x$ rate, without consuming any resource



[T.J. Huang et al., ***Environ. Sci. Technol.*** 49 (2015) 3711]

Comparisons with SCR

(1) For SCR-deNO$_x$ onboard of heavy-duty Diesel vehicles with commercial $V_2O_5/WO_3–TiO_2$ catalyst on standard metal substrates with a cell density (~honeycomb) of 400 cpsi, the highest activity for 1000 ppm **NO** at 52,000 h^{-1} & 400 °C is 1.24 μmole NO·min^{-1}·cm^{-2}.

[O. Krocher, M. Elsener, ***Appl. Catal. B: Environ.*** 75 (2008) 215]

(2) SCR-deNO$_x$ activity of 0.024 μmole NO·min^{-1}·cm^{-2} was reported for treating 250 ppm **NO** at 200 °C with catalyst plate.

[X. Fan et al., ***Catal. Commun.*** 12 (2011) 1298]

A comparison of **ECH** and **SCR**

	ECH	SCR
Reductant	No need, noting that PND is pure decomposition	Need ammonia from thermolysis of urea solution
Operation temperature	No limit (from ambient temperature up)	Needing ~200°C or higher operation temperature
During cold start	High deNOx efficiency	Ineffective
N_2O	Does not produce	Will produce
deNOx efficiency	Relatively high	lower
Complete deNOx for zero NOx emission	Can be realized	Not probable without ammonia slip
EGR (exhaust gas recirculation)	Not required	Required to reduce the consumption of urea solution
Controlling system and analyzers	Not required	Required for real-time NOx treatment, e.g. controlling the injection of proper amount of urea solution
Other	With the combustion temperature being no longer limited, soot can be reduced to very low level so that DPF may not be required or at least there can be no need to regenerate the CDPF	Needing DPF (diesel particulate filter) or CDPF (catalytic diesel particulate filter)

Typical characteristics observed from testing both Diesel and gasoline exhausts for Promoted NO_X Decomposition

- Higher NO concentration can lead to higher deNO_X rate, without consuming any resource.
  Thus, the combustion temperature is no longer limited by **NO_X** formation (EGR is no longer needed) and the fuel efficiency (thermal efficiency) can be highly increased.
- Higher O_2 concentration can lead to higher deNO_X rate.
  Thus, high enough O_2 concentration in association with high enough combustion temperature can result in complete combustion of all combustible constituents in the fuel for their zero pollution. PM can be combusted or at least be less toxic.
- No temperature window and effective deNO_X from engine cold start.
  Thus, there is no deNO_X treatment delay or period of non-treatment.
  This is because the overall reaction of automotive NO_X decomposition is exothermic, and lower temperature can result in higher *emf*, *i.e.* higher promoting force for PND.
- Relatively-constant deNO_X rate at very low NO_X concentrations for zero NO_X emission.

These characteristics show that NO_X is no longer an issue.

Publications supporting
the described typical characteristics of **PND**

underlined is the inventor of the **ECH**, Professor Ta-Jen Huang

- Ta-Jen Huang, C.L. Chou, ***Electrochem. Comm.***, 11 (2009) 477–480.
- Ta-Jen Huang, C.L. Chou, ***J. Power Sources***, 193 (2009) 580–584.
- Ta-Jen Huang, C.L. Chou, ***J. Electrochemical Society***, 157 (2010) P28–P34.
- Ta-Jen Huang, C.L. Chou, ***Chem. Eng. J.***, 160 (2010) 79–84.
- Ta-Jen Huang, C.L. Chou, ***Chem. Eng. J.***, 162 (2010) 515–520.
- Ta-Jen Huang, I.C. Hsiao, ***Chem. Eng. J.***, 165 (2010) 234–239.
- Ta-Jen Huang, C.Y. Wu, Y.H. Lin, ***Environmental Science Technology***, 45 (2011) 5683–5688.
- Ta-Jen Huang, C.Y. Wu and C.C. Wu, ***Chem. Eng. J.***, 168 (2011) 672–677.
- Ta-Jen Huang, C.Y. Wu, C.C. Wu, ***Electrochem. Comm.***, 13 (2011) 755–758.
- Ta-Jen Huang, C.Y. Wu, C.C. Wu, ***Chem. Eng. J.***, 172 (2011) 665–670.
- Ta-Jen Huang, C.Y. Wu, S.H. Hsu, C.C. Wu, ***Energy Environmental Science***, 4 (2011) 4061–4067.
- Ta-Jen Huang, C.H. Wang, ***Chem. Eng. J.***, 173 (2011) 530–535.
- Ta-Jen Huang, C.Y. Wu, S.H. Hsu, C.C. Wu, ***Appl. Catal. B: Environmental***, 110 (2011) 164–170.
- Ta-Jen Huang, C.Y. Wu, ***Chem. Eng. J.***, 178 (2011) 225–231.
- Ta-Jen Huang, C.H. Wang, ***J. Electrochemical Society***, 158 (2011) B1515–B1522.
- Ta-Jen Huang, S.H. Hsu, C.Y. Wu, ***Environmental Science Technology***, 46 (2012) 2324–2329.
- Ta-Jen Huang, C.Y. Wu, D.Y. Chiang, C.C. Yu, ***Chem. Eng. J.***, 203 (2012) 193–200.
- Ta-Jen Huang, C.Y. Wu, D.Y. Chiang, C.C. Yu, ***Appl. Catal. A: Gen.***, 445–446 (2012) 153–158.
- Ta-Jen Huang, C.Y. Wu, D.Y. Chiang, ***J. Ind. Eng. Chem.***, 19 (2013) 1024–1030.
- Ta-Jen Huang, D.Y. Chiang, C. Shih, C.C. Lee, C.W. Mao, B.C. Wang, ***Environmental Science Technology***, 49 (2015) 3711−3717.
- Ta-Jen Huang, C.W. Mao, C.C. Lee, D.Y. Chiang, C.S., B.C. Wang, S.Y. Lee, D.S.H. Wong, ***Chem. Eng. J.***, 284 (2016) 431−437.
- Ta-Jen Huang, B.C. Wang, C.C. Lee, C.W. Mao, ***Electrochimica Acta***, 187 (2016) 442−450.

Further testing results of ECH-deNO$_x$ on Diesel exhaust using ITRI/ACS ECH converter

ITRI/ACS ECH	NO$_X$ In ppm	NO In ppm	NO$_2$ In ppm	NO$_X$ Out ppm	NO Out ppm	NO$_2$ Out ppm	Inlet Exhaust Temp °C	NO$_X$ Conversion %	NO$_X$-to-N$_2$ Rate μmol $N_2 \cdot min^{-1} \cdot cm^{-2}$
NO. 1	243	170	74	225	156	69	60	7.46	0.94
NO. 2	243	169	74	210	145	66	61	13.4	1.67
NO. 3	252	179	73	191	116	74	61	24.47	2.52 200 times that of SCR
NO. 4	242	168	73	206	141	65	60	14.63	1.83
NO. 5	246	173	73	224	156	67	60	8.94	1.13

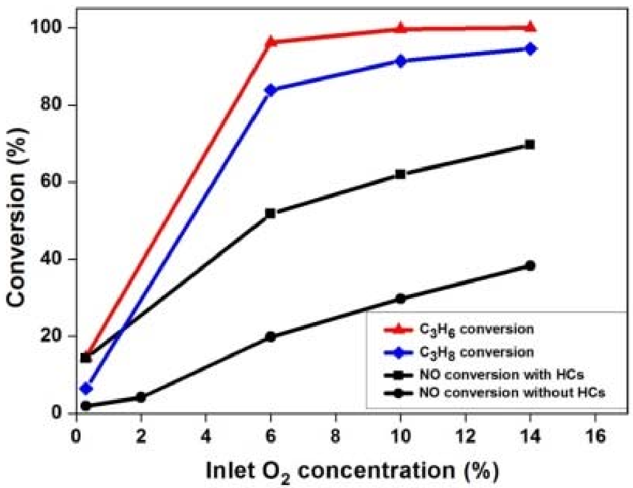
Note: The flow rate was kept at 110 liter/min. The oxygen concentration was about 18%.

It is seen that the **ECH's** NO$_X$-to-N$_2$ rate can be 200 times that of SCR-deNO$_X$, at 0.012 μmole $N_2 \cdot min^{-1} \cdot cm^{-2}$ as reported* for treating 250 ppm **NO** (with 10 ppm ammonia slip) at ~200 °C.

*[X. Fan et al., ***Catal. Commun.*** 12 (2011) 1298]

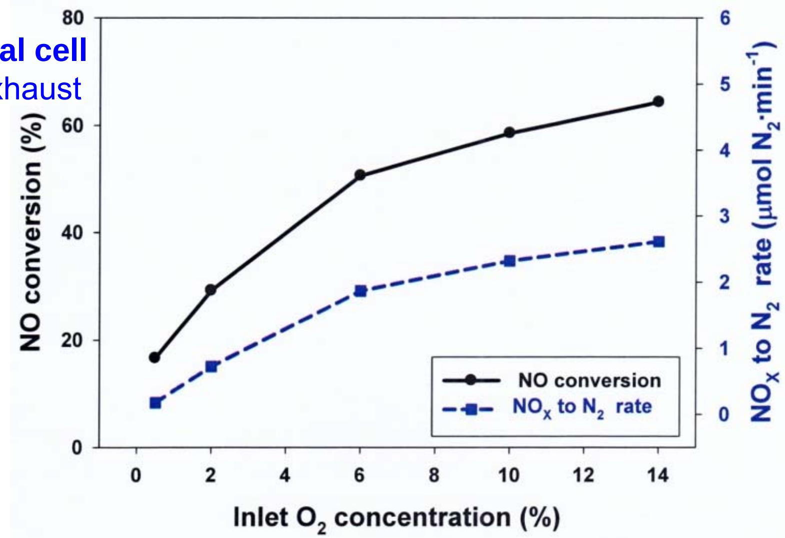
Higher O_2 concentration in the exhaust (over cathode) can lead to higher deNO_x rate

This **PND** characteristic can be attributed the Nernst equation for the generation of the *emf*, or called open-circuit voltage (OCV): *emf* (OCV)= (RT/4F)·ln ($P_{O2|cathode}$ / $P_{O2|anode}$)
Thus, higher O_2 concentration can lead to higher *emf* so to have higher promotion.



[T.J. Huang et al., ***Appl. Catal. B*** 110 (2011) 164]

Electrochemical cell
on simulated exhaust



2020 ppm NO_x at 23 °C
[T.J. Huang et al., ***Appl. Catal. A*** 445–446 (2012) 153]

Inlet NO_x concentration (ppm)	Inlet O_2 concentration (%)	Inlet Temperature (°C)	Space velocity [a] (10^5 h^{-1})	deNO_x rate (μmole NO_x·min^{-1}·cm^{-2})
277	8 [b]	187	8.02	0.27
2320 [c]	3.5	107	4.64	1.95
2807 [c]	6 [b]	112	4.79	5.07

[T.J. Huang et al., ***Environ. Sci. Technol.*** 49 (2015) 3711]

[a] Defined as (volumetric flow rate)/(honeycomb volume).

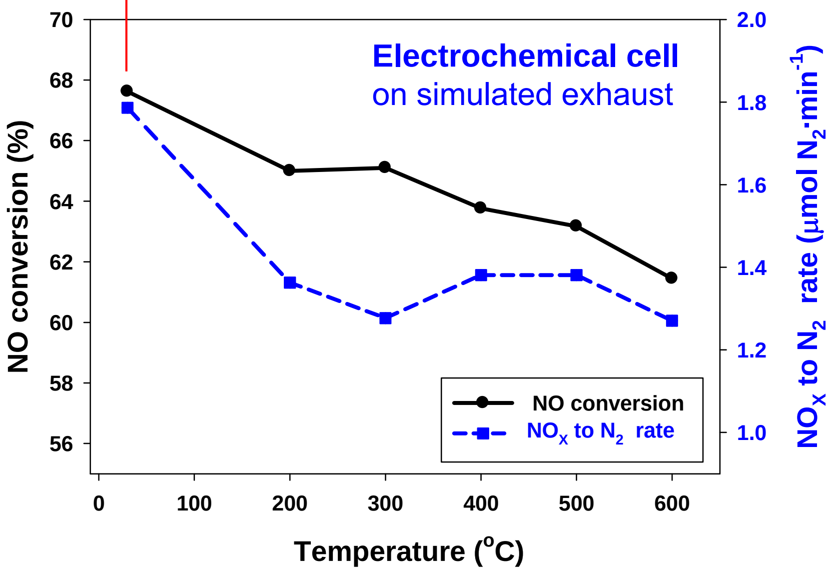
[b] Secondary O_2 was added.

[c] Secondary NO_x was added. For these operations, part of the engine exhaust flow was diverted and thus the space velocity through the ECH was lowered for convenience of adding secondary NO_x.

ECH-deNO_x on
gasoline engine exhaust

No temperature window and effective $deNO_X$ from engine cold start

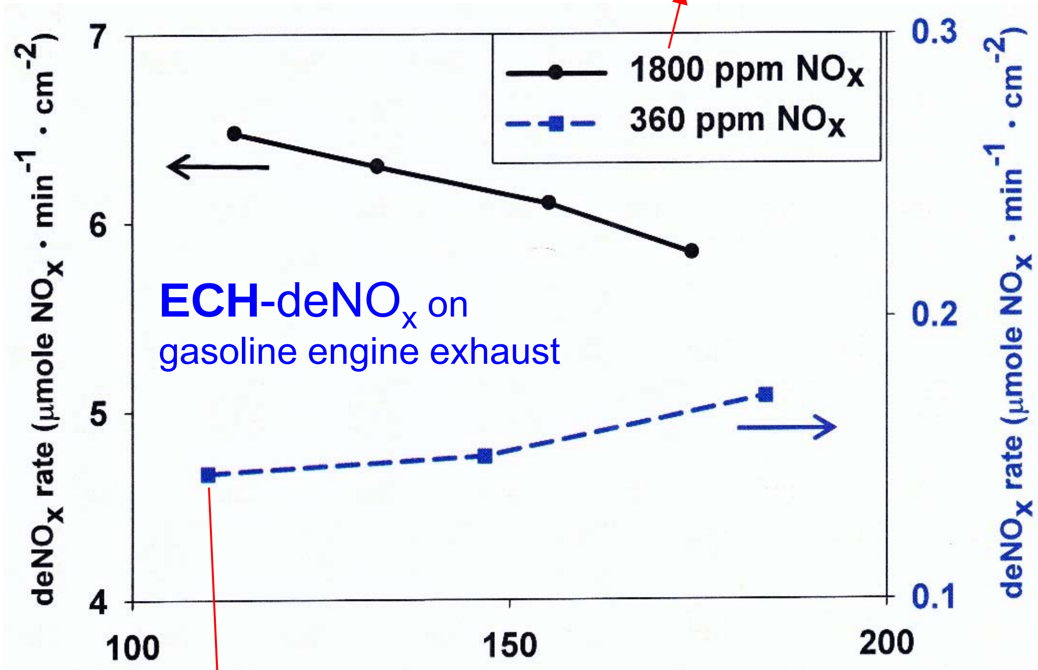
Room temperature



Inlet 2020 ppm NO_X

[T.J. Huang et al., ***Appl. Catal. A*** 445–446 (2012) 153]

Secondary NO_X added



[T.J. Huang et al., ***Environ. Sci. Technol.*** 49 (2015) 3711]

This lowest-temperature exhaust was that during engine cold-start.

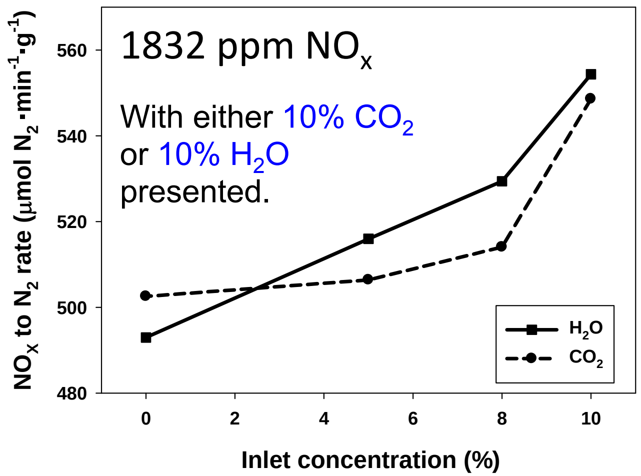
It has been observed that:

Lower temperature can result in higher $deNO_X$ rate with NO_X in the high concentration region. This is due to that lower temperature can result in higher *emf*.

Higher temperature can result in higher $deNO_X$ rate with NO_X in the low concentration region. This is due to that the surface-diffusion rate can increase with temperature.

Additional notes on ECH-deNO$_X$

- Presence of H_2O and CO_2 beneficial by helping the reaction kinetics with surface-diffusion controlling.

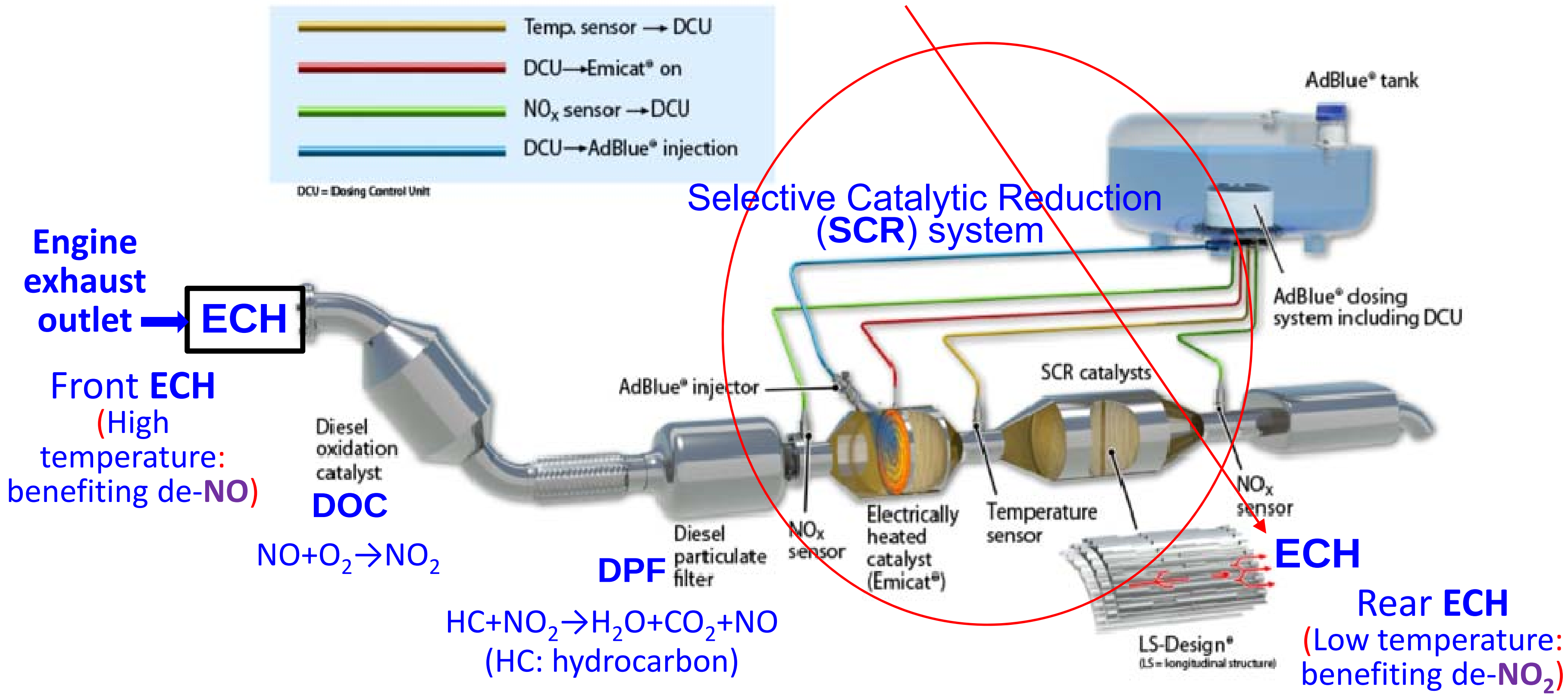


[T.J. Huang et al., ***J. Ind. Eng. Chem.*** 19 (2013) 1024]

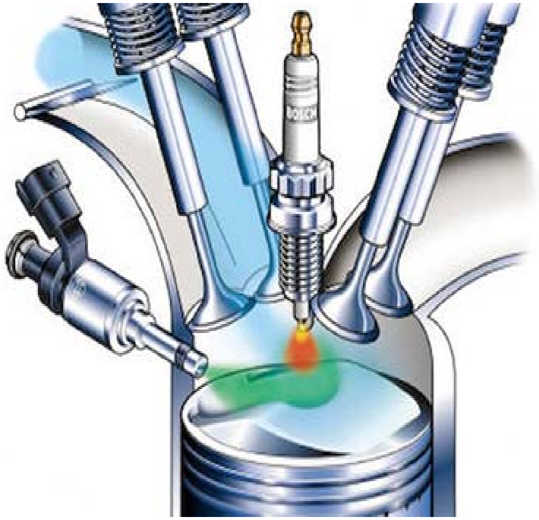
- SO_2 OK [ECH-deSO_2 has been confirmed from 70 °C up].
- No N_2O formation since N_2O formation from NO involves a reductant, such as NH_3 [Koebel et al., ***Catalysis Today*** 59 (2000) 335] or H_2 [Clayton et al., ***Appl. Catal. B-Environ.*** 81 (2008) 161].
- ECH is completely ceramic and does not need to use any precious metal.

Ways of applying ECH to have fuel-efficient and zero-pollution cars

Diesel way: A setup of ECH for replacing SCR system & for cold start & cold weather---Replacing the SCR system by ECH & adding ECH before the DOC

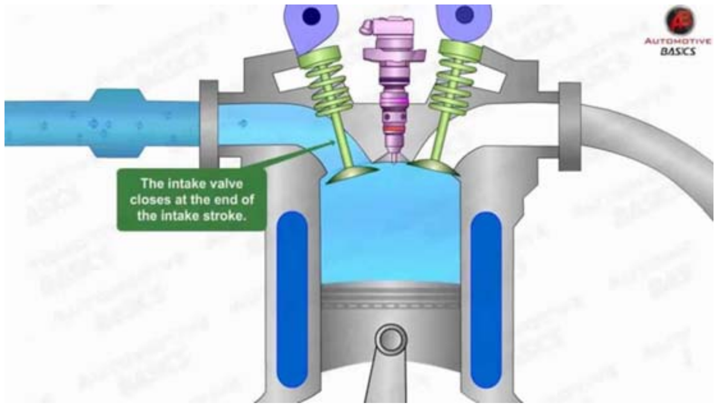


Gasoline way: for cars with Gasoline Direct-injection Compression Ignition (GDCI) engine --- Gasoline-powered Diesel-like engine



GDi engine

GDCI 1.8L Multi-cylinder Engine by Delphi Powertrain (Delphi Automotive, Delphi Corp.) Since 2013



Diesel engine

It is seen that the GDi engine is very much similar to the Diesel engine. In fact, the Gasoline-powered Diesel-like engine, the GDCI engine, can be considered as a simplified version of the GDi engine, i.e. removing the spark plug.

How to achieve **zero pollution** of CO & HCs without PM?

[in association with the GDCI engine]

This can be achieved by using gasoline* of un-branched open-chain alkane molecules for GDCI engine.

*Gasoline that can ignite very easily under compression, that is, having high cetane number. [future clean gasoline]

Note: Fuels with higher cetane number have shorter ignition delay, so to have more complete combustion to result in higher combustion temperature. Thus, there can be no HCs & CO in the engine exhaust so to result in **zero pollution**.

[Higher combustion temperature means higher NOx concentration in the engine exhaust. This is favored by PND with **ECH**.]

In addition, shorter ignition delay means less engine knock so to have more smooth and quiet engine.

Concluding Remarks

INNOVATION: Promoted NO_X Decomposition (PND) by Electro-Catalytic Honeycomb (ECH)

Typical characteristics of **PND:**

- Higher NO concentration can lead to higher $deNO_X$ rate, without consuming any resource.
- Higher O_2 concentration can lead to higher $deNO_X$ rate.
- No temperature window and effective $deNO_X$ from engine cold start.
- Relatively-constant $deNO_X$ rate at very low NO_X concentrations for **zero** NO_X emission.

With complete combustion in the engine without any constraint, **ECH**-$deNO_x$ can result in very high fuel efficiency with **zero pollution** of automobiles to help Creating Healthy, Livable Cities.