Critical Materials in Catalysis: Precious vs Base Metals in Automotive Catalyst Systems

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Outline

• Overview of modern automotive catalysts
• Why Base Metals are not effective TWCs
• Where Base Metals do work
• Example of a Cu/zeolite catalyst system
• Other Base Metal catalyst research
• Summary
What are Automotive Catalysts?

Catalysts are used to reduce the amount of regulated pollutants from gasoline and diesel vehicles:

- hydrocarbons (HC)
- carbon monoxide (CO)
- nitrogen oxides \( (\text{NOx} = \text{NO} + \text{NO}_2) \)
- particulate matter (PM)

\[ \downarrow \]

\[ \text{N}_2, \text{CO}_2 \text{ and } \text{H}_2\text{O} \]

Automotive Three-Way Catalyst

“Staying in the Window”

Catalytic converter:

Typical operating conditions:
- 350 – 650 °C (extremes: ambient to 1050 °C)
- near-stoichiometric exhaust gas
- 60 – 300 ms contact time

<1% oxygen at stoichiometry

Shelef and McCabe

Heck and Farrauto
Modern Automotive TWC

Electron microprobe view of washcoat (2000):

Typical catalyst composition (2000):

- **cordierite**: 70 wt%
- $\gamma$-**Al$_2$O$_3$**: 13
- **CeO$_2$**: 6
- **ZrO$_2$**: 4
- **La$_2$O$_3$/Nd$_2$O$_3$**: 3
- **BaO/SrO**: 2
- **NiO**: 1.5
- **Pt/Pd/Rh**: 0.5

Gandhi 2004
What Are Precious Metals vs Base Metals?

**Base metals** are non-precious, i.e., oxidize or corrode easily.

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**Platinum Group Metals (PGM)**
Technologies Deployed to Meet Increasing Stringent Emission Standards

- Base metals, Ag & Au: low activity and/or durability
- Ru, Ir, and Os: form volatile oxides
- Pt and Pd: suitable for oxidation catalysts

- Layers & metal segregation
- Stabilized cerium oxides

- More effective PGM use
- Sealed Fuel Vapor System
- Zone-coat TWC
- High cell density TWC
- NOx Trap
- PTEC Controller

- Ru, Rh, Pd
- Ag & Au: low activity and/or durability
- Os, Ir, Os: form volatile oxides
- Pt and Pd: suitable for oxidation catalysts

- Oxygen storage components added (Ce)
- Stabilized alumina (Ba, La)

Gandhi 2003/2004

PCV System
Spark Control, PVS, etc.
EGR valves
Thermactor

Oxidation Catalysts, some electronics, some feedback carb (EEC I & EEC II)

More Electronics (S/D) More F/B (EE III & V)
Pt/Rh TWC

Port Injection (S/D)
EEC IV
High-tech TWC

Mass Air (EEC V)

Pd/Rh TWC

More F/B
EEC III & V

Pt/Rh TWC

Throttle Body Injection

Pd-only TWC

EEC II Adapt. fuel
Misfire Detection

Adapt. fuel

EEC I & EEC II

PTEC Controller

Sealed Fuel Vapor System

Zone-coat TWC

High cell density TWC

NOx Trap

PTEC Controller

Supply Chain for Automotive Catalysts

- Raw Material Suppliers
- Catalytic Promoter Suppliers
- Substrate Manufacturers ➔ Catalyst Coaters ➔ Canners ➔ Automotive Assemblers ➔ Customers

- PGM mining ➔ PGM Refining ➔ PGM Market ➔ PGM Recycling

- Industrial Catalysts ➔ PGM Recycling

- Jewelry ➔ Electrical

- “open loop” recycled PGM

Partially derived from Platinum 2011
Main use for Rh is autocatalysts
Pt & Pd are also used in jewelry, industrial catalysts, and investment
Recently the demand for Pt and Pd is higher than the supply
Recycled PGM can help offset this deficit
PGM Price Volatility
Pt, Pd, and Rh prices since 1992

- Catalyst design with PGM is made more difficult by price volatility
- Metal type is kept varied to offer several TWC design options, i.e., Pt/Rh vs Pd/Rh vs Pd only
- Base metals such as copper are far less expensive

www.kitco.com
Base Metal TWC Research
(1980 Assessment)

1) PGM less affected by sulfur <500°C

2) PGMs have higher specific activity

3) PGM is more thermally resistant to loss of low temperature activity

Kummer, 1980
Base Metal TWC Performance
Example of Cu TWC on Modern Gas Engine

- Cu and Cu/Cr tested in lab and on engine
- 4wt%Cu/2wt%Cr provided highest net NOx conversion
- A rich bias was required, lowering fuel economy
- Copper catalysts must be close-coupled to the engine (hotter location) to avoid sulfur poisoning and increase activity

Theis, SAE 922251
Summary of 30+ Years of TWC

• Base metals, Ag & Au not active or durable enough
• Ru, Ir, and Os all form volatile oxides
• Pt and Pd were left for the oxidation catalysts
• Rh added for NOx control
• Oxygen storage components added (Ce); later stabilized with Zr
• Stabilized alumina with Ba, La
• Pd/Rh and Pd-only options enabled by Pb-free fuel
• Cu and Cu/Cr retested on modern gas engine; found rich bias required and sulfur still an issue
Diesel Fraction of New U.S. Vehicle Sales

Trucks
Class 3: 10,001-14,000 lbs
Class 2b: 8,501-10,000 lbs

Trucks
Class 1: < 6,000 lbs
Class 2: 6,001-10,000 lbs

Cars

Wallington et al., in review
A Brief History of U.S. Diesel Aftertreatment

Evolution of emissions standards for NOx and PM.

- mid-1990s: Diesel oxidation catalysts (DOCs) with ceria and alumina for PM oxidation
- 2007:
  - ultra-low sulfur diesel,
  - particulate filters for PM control
  - high precious metal DOCs
  - lean NOx control (NOx traps)
- 2010:
  - lean NOx control (urea SCR)

Wallington et al., in review
An Example of U.S. Diesel Aftertreatment
2011 MY Ford Diesel Super Duty

Aqueous urea tank
(refilled at oil change)

Pd-rich
HC + O₂ → CO₂
CO + O₂ → CO₂

Cu/zeolite
NH₃ + NOx → N₂

Pt/Pd
C + O₂ → CO₂
Exhaust Gas Temperatures

Chassis FTP-75 Cycle

Temperature (°C) vs. Test Time (s)

Ford 2011MY Diesel (9500 lbs)
Ford 3.5L GTDI (5250 lbs)

Vehicle speed (mph)

λ = intake air / theoretical air req.
Exhaust Gas Oxygen Content

$\lambda = \frac{\text{intake air}}{\text{theoretical air req.}}$

Ford 2011MY Diesel (9500 lbs)

Ford 3.5L GTDI (5250 lbs)

Chassis FTP-75 Cycle
Diesel Lean NOx Control Options

- HC SCR using Pt
- Lean NOx Trap with Pt, Pd and Rh
- EtOH SCR using Ag
- Urea SCR with Cu/zeolite
Basics of Urea SCR

*urea decomposition:*

\[
\begin{align*}
\text{urea} & \xrightarrow{\text{heat}} \text{HNCO} + \text{NH}_3 \\
\text{HNCO} & \xrightarrow{\text{heat}} \text{CO}_2 + \text{NH}_3
\end{align*}
\]

*NO\textsubscript{x} reduction:*

\[
\begin{align*}
4\text{NO} + 4\text{NH}_3 + \text{O}_2 & \rightarrow 4\text{N}_2 + 6\text{H}_2\text{O} \\
6\text{NO}_2 + 8\text{NH}_3 & \rightarrow 7\text{N}_2 + 12\text{H}_2\text{O} \\
2\text{NH}_3 + \text{NO} + \text{NO}_2 & \rightarrow 2\text{N}_2 + 3\text{H}_2\text{O}
\end{align*}
\]

- Urea is injected into the exhaust pipe upstream of the catalyst as an aqueous solution at 32.5 wt% (eutectic)
- Non-toxic, commodity chemical that forms ammonia
- Tradename in U.S. is “Diesel Exhaust Fluid” – DEF
- SCR needs oxygen for high conversions
Cu/zeolites are best at low temperatures

Fe/zeolites perform well at high temperatures

Vanadium based SCR are not appropriate for US Diesels with Filters
What are Zeolites?

- Zeolites are composed of aluminum oxide and silicon oxide in a crystalline structure.
- Some zeolites are found in nature but most are synthesized for high purity.
- Zeolites are in widespread use as water softeners, absorbents, desiccants, oil refining.
- Also called “molecular sieves” due to varying cage sizes on the angstrom scale.

Beta (BEA) Chabazite (CHA)

www.iza-structure.org/databases/
Small Pore Zeolites Enabled Use of Cu Automotive Catalyst

- Cu/CHA development enabled Cu/zeolite for automotive use
- Related patents and publications:

Chabazite (CHA)

www.iza-structure.org/databases/

Schneider, CLEERS Telecon, Sept 2011
A Few Challenges Faced During Commercial Urea SCR System Development

• Stabilization of Pt
• Stabilization of Cu/zeolite
• HC poisoning/coking of Cu/zeolite
• Sulfur effects on Cu/zeolite
• Urea specifications and refill
Thermal Stability of DOC

- Addition of Pd to Pt has a stabilizing effect for HC oxidation during cold-start

- Pd also stabilizes Pt for NO oxidation but has no inherent activity itself

HC Light-Off Conversion
2-Mode 100 hrs / 300 ppm S + 20 mgP/gal

% NO\textsubscript{2} of Total NO\textsubscript{x} vs Temperature (C)

NO\textsubscript{2}:NO\textsubscript{x} vs Temperature (C)
Precious Metal Poisoning of SCR

- Pt from upstream DOC can volatilize and interfere with SCR function
- Prime indicators are increased NH₃ oxidation and N₂O production
- Front section of catalyst most affected and can be regenerated
- Pt DOC may be stabilized with addition of Pd and lower exotherm Ts

EVALUATION of DYNAMOMETER AGED FeSCR CATALYST

Lab flow reactor Pt poisoning of Cu SCR by upstream DOC

SAE 2008-01-2488
SAE 2009-01-0627
Thermal Stability of SCR Catalyst

- Thermal stability of Cu/zeolite recently improved from 750 to 900°C (Cu/beta → Cu/CHA)
- NO\textsubscript{2} no longer needed for low temp conversion
- Lower cost aftertreatment now possible

\[4\text{NH}_3 + 4\text{NO} + \text{O}_2 \rightarrow 4\text{N}_2 + 6\text{H}_2\text{O}\]

**FIGURE 7.** NO\textsubscript{x} conversion of best in class SCR catalyst formulations from 2005 – 2007 after hydrothermal aging for 1 hour at 900°C.

*SAE 2008-01-1025*
HC Poisoning/Coking of Zeolitic SCR

SCR Catalyst Durability: HC

HC Inhibition

HC Storage/Exotherm

Both issues were resolved by transition from Cu/beta to Cu/CHA

* HC poisoning is reversible after 500°C, lean

DEER 2004
Sulfur Effects on Cu/zeolite

- Sulfur affects NOx activity below 300°C
- Sulfur can be removed by lean filter regeneration conditions >650°C
- Amount adsorbed between regens can be tolerated based on 15 ppm-wt S in diesel fuel

DEER 2004
Urea Specifications and Refill

- OEMs and suppliers formed USCAR working group to define specifications
- Aqueous urea is sold as “Diesel Exhaust Fluid” or “DEF”
- Current refill uses bottles, drums, totes, and bulk dispensers
  - ~ $2.79/gal in bulk
  - ~ $4.65/gal in bottles
  
  [Website](http://www.dieselexhaustfluid.com/

- Websites offer DEF locations

[Website](http://www.factsaboutscr.com)
Diesel MDV Impact on Sustainability

Comparison of Class 2b / Class 3 peak torque brake specific CO$_2$ for medium-duty vehicles 1998 - 2011 calendar years.

- Data from EPA HD database.
- Figure from Wallington, et al., in review.

At light/moderate loads the CO$_2$ advantage for SCR-equipped diesel will be > 10%.

Urea SCR used on majority of diesels in 2010+. 
Diesel MDV Impact on Sustainability
Precious Metal Usage on Ford Super Duty Trucks

Increasing Emission Stringency

DOC only
DOC + CDPF
DOC +SCR+CDPF

2011MY J1
2011MY J2

Diesel-Gasoline PGM Gap

2011MY TWC

Pd-rich

Total PGM
Pt Equiv
Potential Use of Base Metal Catalysts: Addition of SCR to TWC or LNT System

- **TWC+SCR**
- **LNT+SCR**

*Li et al., 2009*

- **SCR may be a key enabler for lean burn**
- **SCR may enable lower PGM usage**

- Use of SCR depends on lean burn gasoline dev. & LD diesel usage
- Advanced lean aftertreatment depends on availability of low sulfur fuel

SAE 2009-01-0285

Sept 29, 2011
Potential Use of Base Metal Catalysts: NO → NO₂ Oxidation Function

**Pd BMO DOCs**

- **Pd needed for HC oxidation**

**Pt-free Perovskite LNTs**

- **PGM needed for HC and NOx reduction**

- Low temperature NO oxidation benefits lean NOx reduction.
- Base metals can replace a portion of the precious metals.
Summary

• TWC is limited to Pt, Pd and Rh after 30+ years of research and development

• Diesel aftertreatment content has seen rapid growth in last 5 years from DOCs to filters to lean NOx control

• Pd-rich DOCs and Cu/zeolite lean NOx aftertreatment are now in production on medium duty diesel trucks

• Other potential uses of base metals are now in research stages and depend greatly on lean burn engine development

• The availability of lower sulfur fuel enables high efficiency lean NOx aftertreatment
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