Overview of Automotive Zeolite HC Trap, Challenges for Gasoline Fuel and Current Research Areas

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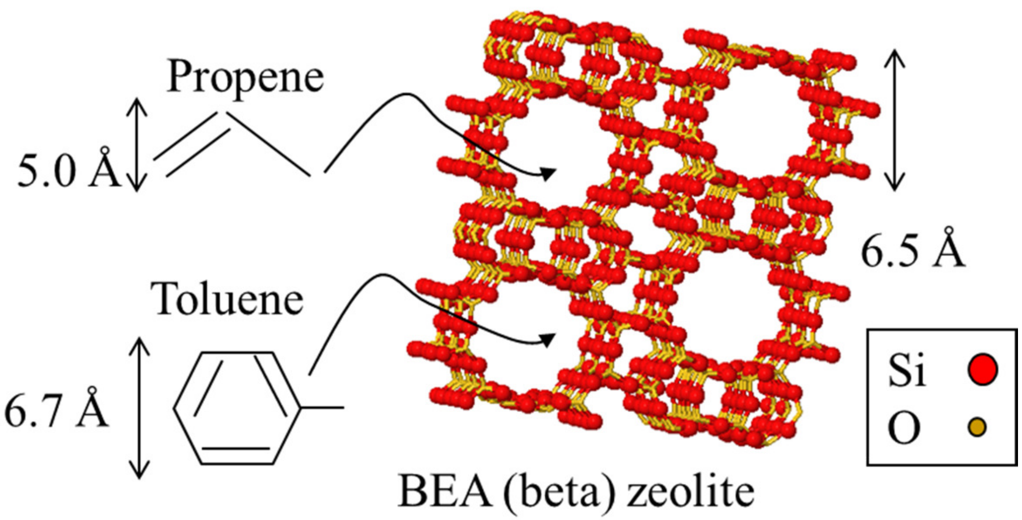
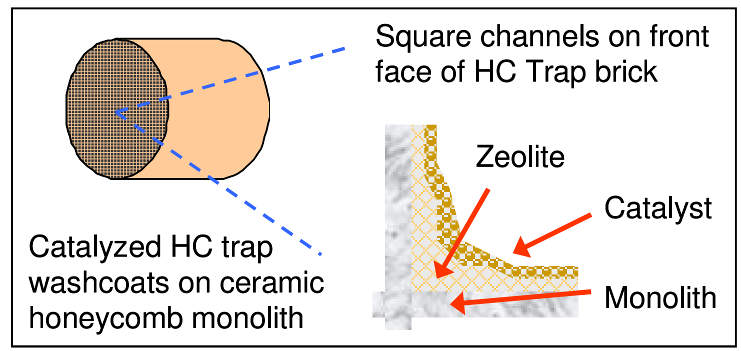
Regulations Impact on Vehicle Emissions

Emission challenges ahead	Possible Solutions
1. Annual decreases in fleet average tailpipe NMOG+NOx FTP75 emissions (PC/LDT1): – 2015 = 0.100 g/mi – 2025 = 0.030 g/mi	Vehicles that do not meet SULEV-30: Hydrocarbon (HC) Traps enable lower tailpipe NMOG emissions • Passive: adding zeolite to converter • Active: bypass trap plus exhaust valve
2. Uncertainty around increased national biofuel mandate : – 2015 = E10/E85 – 2025 = E??/E85	Excess ethanol emissions can be effectively captured and treated by HC traps to make vehicle exhaust system efficient for any biofuel mandate
3. Annual decreases in fleet average tailpipe particulate matter (PM) (PC/LDT1): – 2015 = 10 mg/mi – 2021 = 3 mg/mi – 2028 = 1 mg/mi	Gasoline direct injection vehicles that do not meet the PM standard with a filter could use port fuel injection with a HC trap to meet NMOG and PM emissions

What is a Hydrocarbon (HC) Trap?

HC Trap = A catalytic converter with an adsorbent material (i.e., zeolite) that has a pore size on the same order as the molecules to be stored. The adsorbent material releases the stored HC molecules with increasing temperature to be burned over the hot oxidation catalyst.





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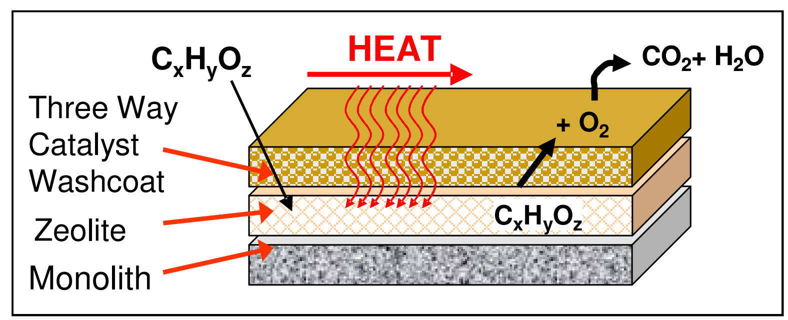
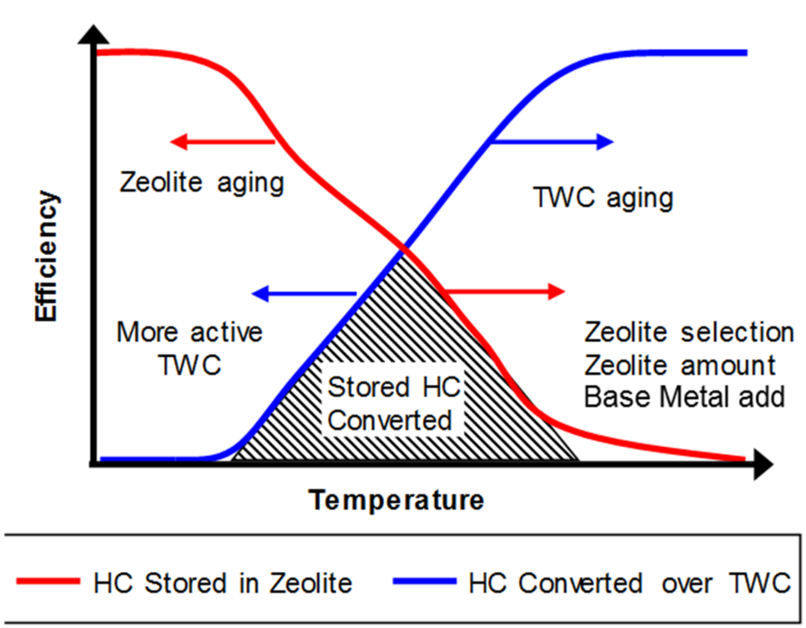


How Do HC Trap Attributes Affect Performance?

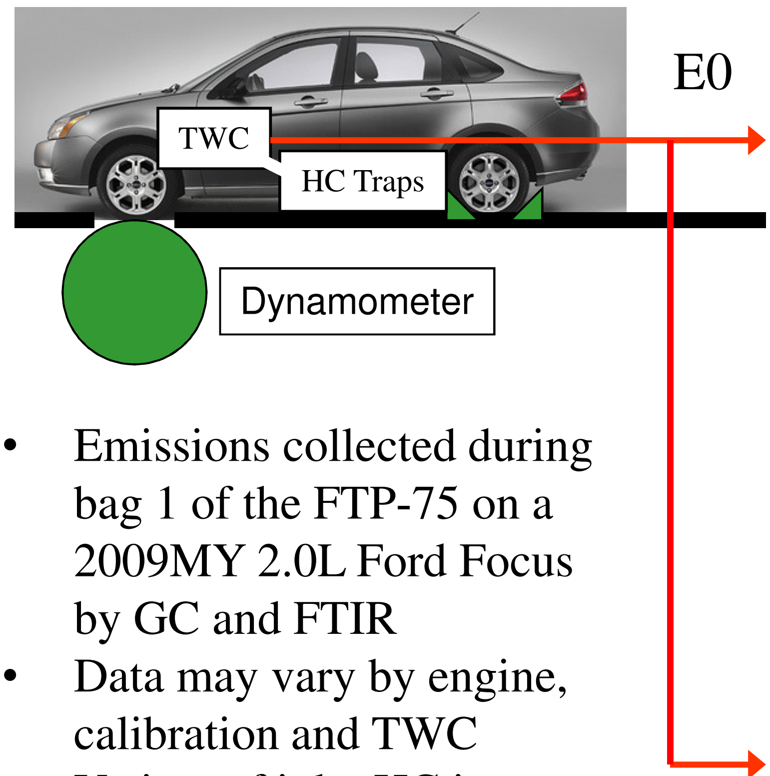
Goals: Minimize aging effects, improve performance, and lower PGM cost

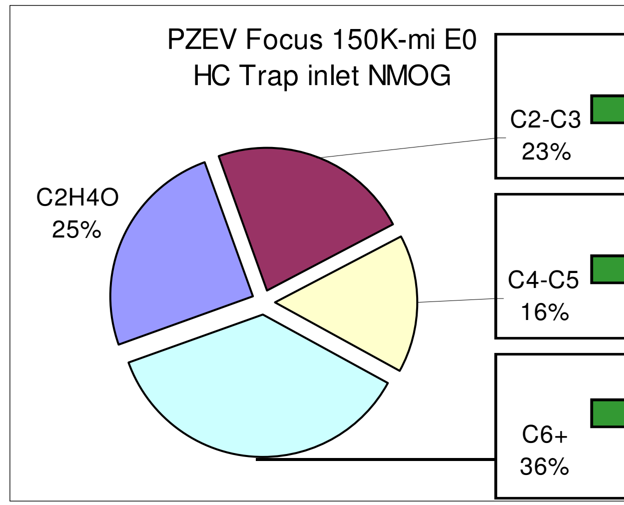


HC Trap attributes:

1. **Type of zeolite** (structure, pore size and acidity)
2. Increased **zeolite capacity** per unit volume
3. Improved **HC oxidation activity** by TWC layer
4. **Base metal** addition for improved HC trapping and reaction

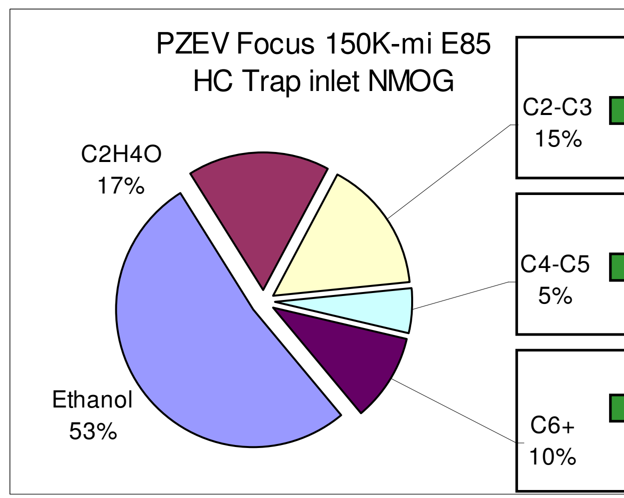
What NMOG Species Enter into UB Assembly?





Major Components

- C2-C3 23%: Ethylene 31%, Ethane 23%, Propylene 18%
- C4-C5 16%: Isopentane 51%, Isobutane 5%, Isobutene 14%
- C6+ 36%: Toluene 38%, Isooctane 8%, Benzene 11%



Major Components

- C2-C3 15%: Ethylene 59%, Ethane 14%, Propylene 6%
- C4-C5 5%: Isopentane 45%, Isobutane 20%, Isobutene 10%
- C6+ 10%: Toluene 32%, Isooctane 4%, Benzene 16%

- Emissions collected during bag 1 of the FTP-75 on a 2009MY 2.0L Ford Focus by GC and FTIR
- Data may vary by engine, calibration and TWC
- Variety of inlet HC is a challenge for one zeolite to do it all

Common Zeolites & HC Kinetic Diameters (in Å)

Common Zeolites	IZA code	Pore diameter	Ring size	Pore structure
Y-type	FAU	7.4x7.4	12	3D
Beta	BEA	6.6x6.7 5.5x5.6	12 12	3D
Mordenite	MOR	6.5x7.0 3.4x4.8 2.6x5.7	12 8 8	1D
ZSM-5	MFI	5.3x5.6 5.1x5.5	10 10	3D
Ferrierite	FER	4.2x5.4 3.5x4.8	10 8	2D

HC species by size

- o-Xylene (7.4)
- Toluene (6.7)
- Benzene (6.7)
- Iso-octane (5.6)
- Iso-pentane (5.6)
- Iso-butene (5.6)
- Propylene (5.0)
- Ethanol (4.4)
- Acetaldehyde (4.4)
- Ethylene (4.2)
- Acetylene (2.4)

Large

Medium

Small

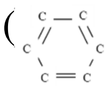
Small HC species can't be trapped effectively, so Beta zeolite with its 3D structure is best

Challenges with Conventional Passive HC Traps

HC species unlikely to be stored or converted effectively by HC traps

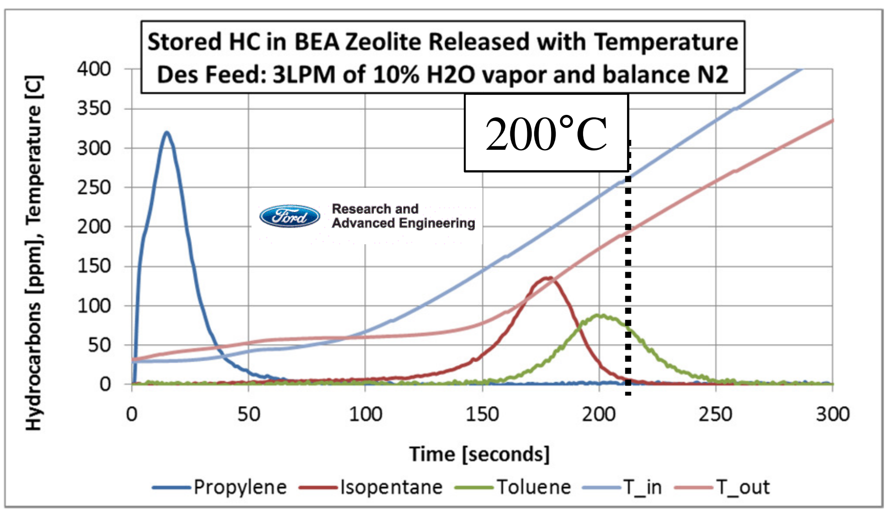
- Methane
- Alkanes (C-C): Isopentane, Isooctane
- C_2-C_3 Alkenes (C=C): Ethylene, Propylene
- Acetaldehyde

HC species traditionally stored and converted well by HC traps

- Ethanol
- C_{4+} Alkenes (C=C): Hexene
- Aromatics (): Benzene, Toluene

Why are these HCs a challenge?

1. Low release temperature



2. High oxidation temperature

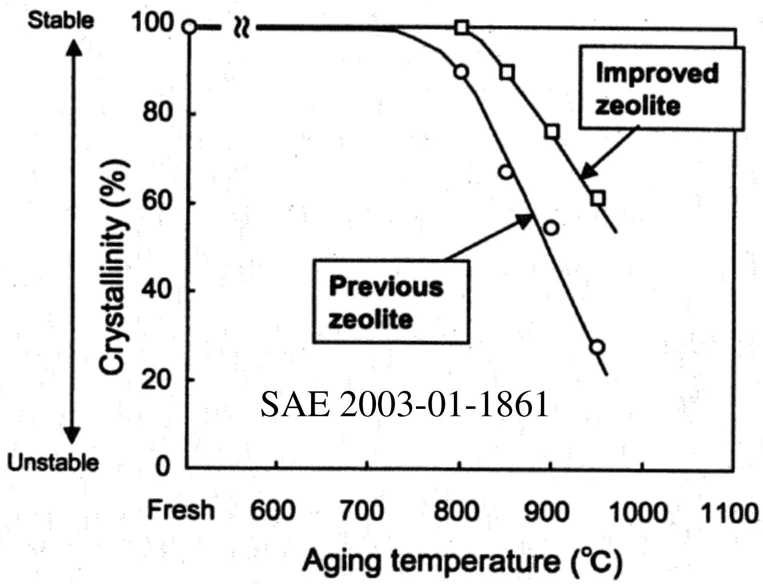
Temperatures (°C) required for 50% conversion of hydrocarbons when reacted individually (A), or together in the four hydrocarbon mixture (B), in the presence of carbon monoxide[a]

	$1.5wt\%Pt/Al_2O_3$	$1.5wt\%Pd/Al_2O_3$	$1.0wt\%Rh/Al_2O_3$
A: Individual reactions with CO present			
Hexene	308	260	201
Toluene	309	264	201
Benzene	301	254	218
B: In four hydrocarbon mixture with CO present			
Hexene	312	260	201
Toluene	326	279	202
Benzene	327	284	249
Isooctane	328	286	287

Applied Catalysis B: Environmental 26 (2000) 47–57

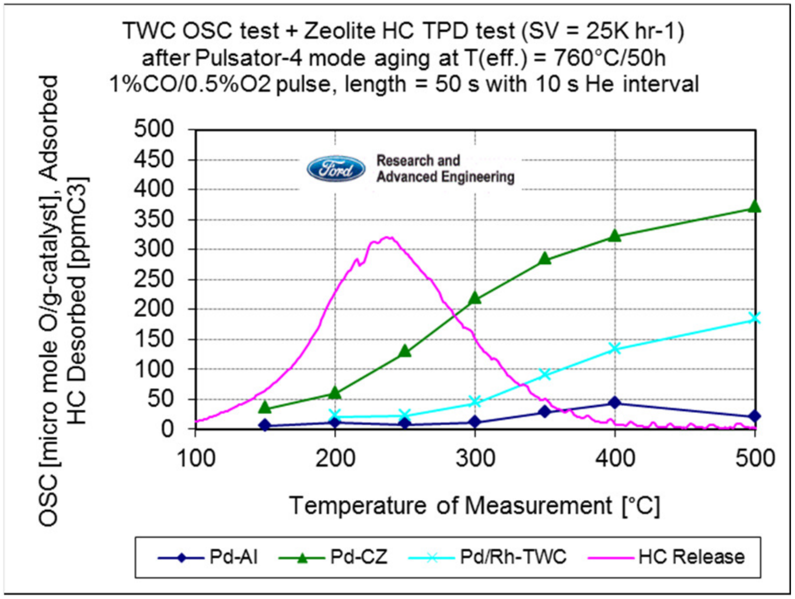
Challenges with Conventional Passive HC Traps

3. Low thermal durability → Do not exceed 850°C!



SAE 2003-01-1861

4. Poor alignment for desorbing HC and available oxygen storage capacity (OSC)



5. Competitive adsorption with Water → Water is favorably stored in acidic zeolite and can displace weakly adsorbed HC species (ethylene and propylene).

Applied Catalysis B: Environmental
46 (2003) 97–104
Applied Catalysis A: General
382 (2010) 213–219

What Does Langmuir Adsorption Model Theory Predict for an Optimized HC Trap Design?

- Mass balance of HC in zeolite:
  - HC load rate = HC adsorption rate – HC desorption rate

$$\frac{d\theta}{dt} = \left[k_{ads} \cdot c_{HC,wc} \cdot (1-\theta)\right] - \left[\frac{k_{ads}}{K_{EQ}} \cdot \theta\right]$$

- We can improve overall HC trap function by maximizing adsorption capacity and minimizing the desorption rate
  - Maximize the equilibrium constant for adsorption, K_{EQ} ($= k_{ads}/k_{des}$), by adjusting the zeolite attributes
  - Minimize fractional loading, θ ($= n/N$), by increasing the number of adsorption sites (N) in the zeolite
- We want a big trap that does not desorb HC readily
- Coking reactions are not covered by this model

Where:

k_{ads} and k_{des} are rate constants that contain heat of adsorption and desorption as:

$$k_i = k_{0,i} \cdot \exp\left(\frac{-Ea_i}{R \cdot T}\right)$$

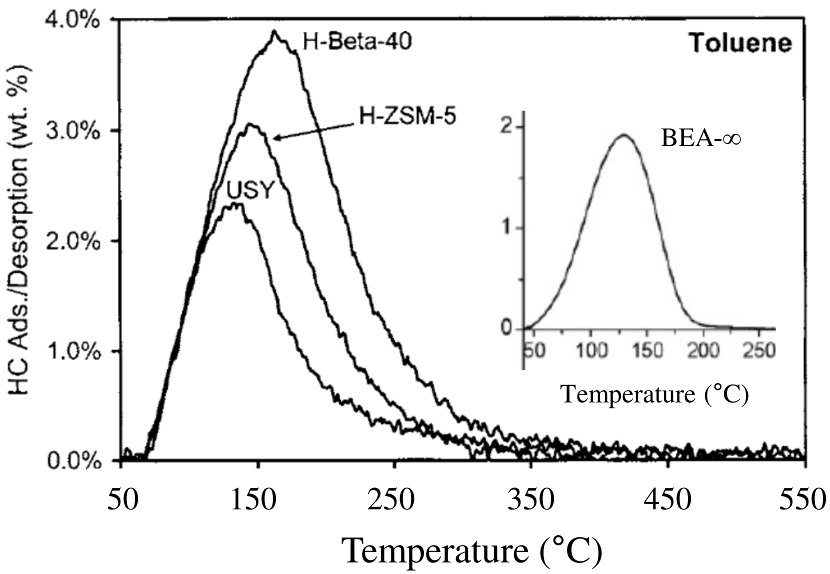
$c_{HC,wc}$ is the concentration of gas phase HC species in the washcoat layer void space

θ is the concentration of adsorbed HC molecules (n) divided by the total number of adsorption sites (N)

HC Trap Research in Scientific Literature

Zeolite Type

Stored toluene desorption from zeolites (Stud. Surf. Sci. Catal. 158 (2005) 1375-1382) and pure silica BEA-∞ (*Sep. Purif. Tech.* 54 (2007) 1-9)



- Si/Al_2 ratio effects HC retention. Pure silica BEA-∞ is not effective for storing toluene compared to BEA-40

Zeolite Acidity

Treatment of E85 fuel emissions from a 2L Focus by changing the underbody converter from a TWC to HC traps (SAE-2013-01-1297)

Table 5. Underbody Outlet HC through Bag 1 on E85

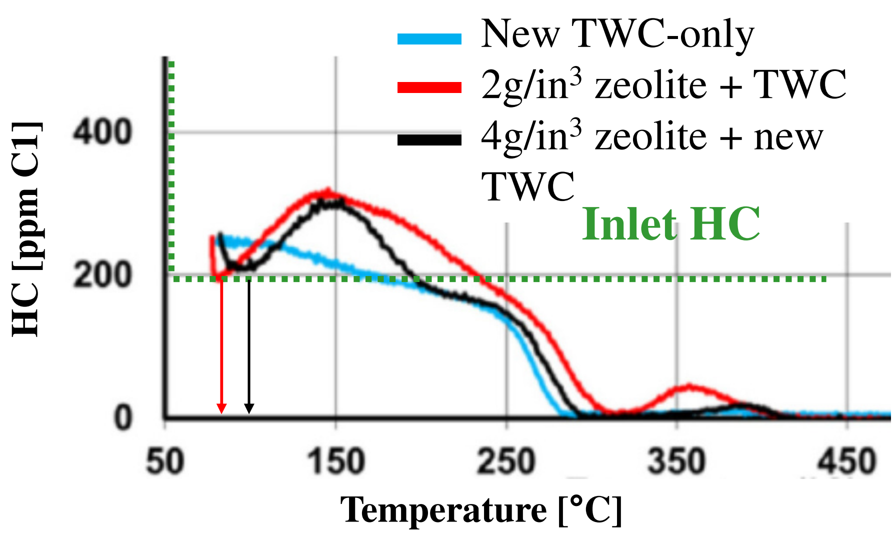
UB System	NMHC [mg/mi]	Ethanol [mg/mi]	HCHO [mg/mi]	C_2H_4O [mg/mi]	NMOG [mg/mi]
TWC-only 2 x 100g/ft^3	35.7 +/- 1.5	46.1 +/- 7.4	2.8 +/- 0.1	10.5 +/- 0.7	95.0 +/- 8.3
OEM Trap 300g/ft^3+135g/ft^3	33.8 +/- 7.7	21.9 +/- 7.0	1.4 +/- 0.1	11.1 +/- 2.6	68.3 +/- 13.1
Acidic Trap 2 x 100g/ft^3	24.7 +/- 7.3	7.8 +/- 7.4	13.4 +/- 12.3	15.3 +/- 6.5	61.2 +/- 14.4

- OEM two-brick HC Trap was loaded at 300g/ft^3 and 135g/ft^3
- More acidic zeolite had lower tailpipe emissions of HC species an enabled a PGM reduction to 100g/ft^3

HC Trap Research in Scientific Literature

Zeolite Loading + TWC

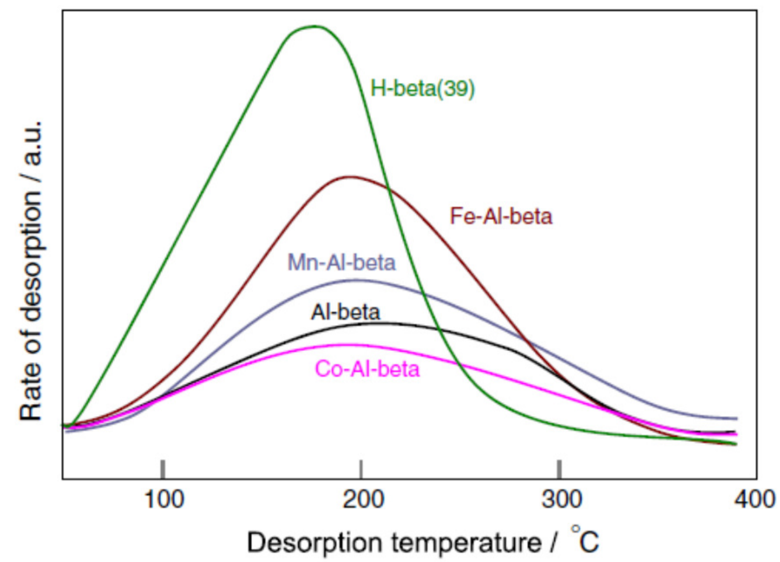
Mix of propylene, iso-pentane, and toluene fed at 1500 ppm C1 for 30 seconds, then reduced to 200 ppm C1 with temperature ramp (SAE 2014-01-1509)



- Increasing Zeolite load from $2g/in^3$ to $4g/in^3$ shifted HC release profile by 20°C to reduce unconverted HC
- New TWC lowered temperature needed to oxidize stored HC by 20°C

Base Metal Addition

Desorption of Toluene from Me-Beta-100 (*Catal. Lett.*, vol. 118, pgs. 72-78, 2007)



- Base metals decrease PGM demand on TWC to be active below 200°C
- Zeolite must have durable ion exchange site versus hydrothermal aging around 800°C

Conclusions

- Beta zeolite is capable at capturing all gasoline HC emissions, but retaining them above 200°C in a wet environment for possible oxidation is the challenge (it gets even worse after useful life aging!)
- Increasing of the zeolite acidity, loading and base metal content can increase the HC trap ability to hold stored HC to higher temperature
- Modification of the TWC washcoat composition for the underbody converter environment can lower the temperature required for HC oxidation and provide the required oxygen in an oxygen deficient environment