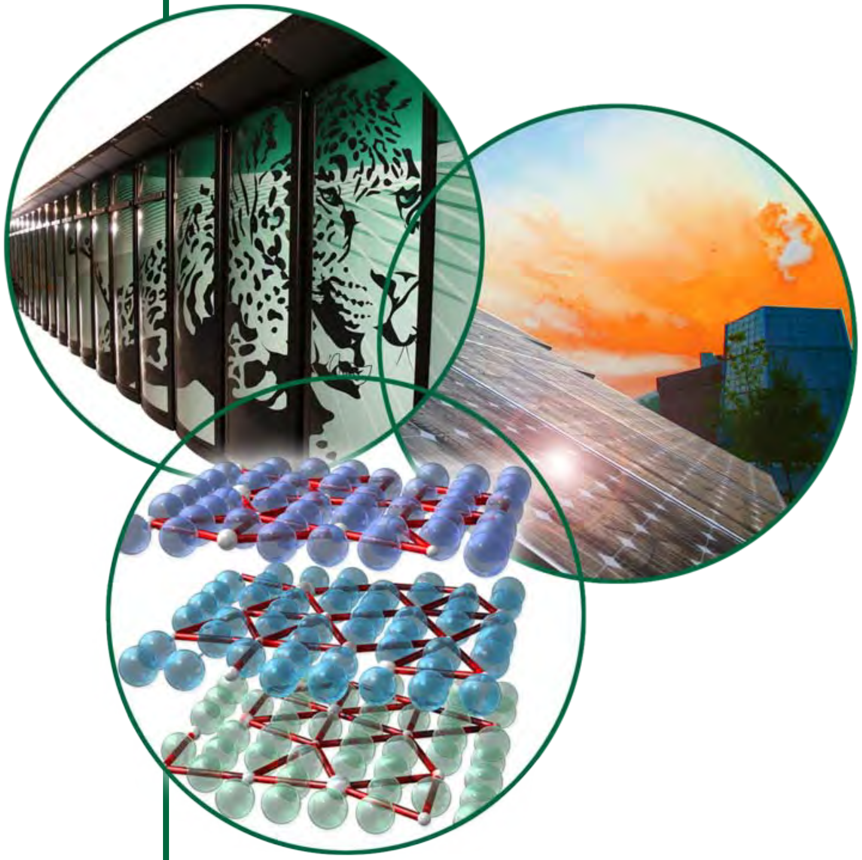
Project ID: PM028

Catalyst Characterization

2010 DOE Vehicle Technologies Annual Merit Review and Peer Evaluation Meeting

May 10, 2011



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Sponsored by
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U.S. DEPARTMENT OF ENERGY

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Background: **Exhaust Aftertreatment**

- **Ammonia containing compounds added to diesel exhaust to reduce NO_x to N_2**
  - **e.g., $NH_3 + NO + 1/4O_2 \Rightarrow N_2 + 3/2H_2O$**
  - **Excess ammonia is often needed resulting in NH3 escaping or "slip"**
  - **This ammonia must be removed by a secondary step.**
- **NH_3 slip is currently not regulated in US, however for sociability and environmental reasons, Cummins chose to use Ammonia Oxidation (AMOX) Catalyst* device to ensure that ammonia slip to ambient is minimal**
- **An AMOX catalyst can be used to convert the NH_3 slip to $N_2 + H_2O$**
  - **Candidate catalysts: zeolite-based and alumina-supported metal or metal oxide catalysts**
  - **Temperature and water content play a big role in the functioning and aging of these catalysts**

*** Also called Selective catalytic oxidation (SCO) or Ammonia Slip catalyst (ASC)**

Overview

Timeline

- Start: June 2002
- End: Sept. 2012
- 87% complete

Budget

- Total Project funding
  - DOE-$2.2M
  - Cummins-$2.3M
- Funding received:
  - FY10 $200k
  - FY11 $200k approved

Barriers* - Propulsion Materials Technology:

- Changing internal combustion engine combustion regimes → Optimize catalysts to minimize emissions
- Long lead times → NH_3 not regulated yet
- Cost-eff. emission control → Precious metal content

Barriers* - Combustion and Emission Control R&D:

- Lack of fund. knowledge → understanding degradation mechanisms
- Poor durability → degradation/aging resistant materials needed
- Market perception → Understanding improves public's acceptance

Partners

- Cummins Inc.
- Johnson Matthey

- FreedomCar and Vehicle Technologies Program, Multi-Year Program Plan 2011-2015, Dec 2010, pp. 2.3-4, 5, 8; 2.5-8, 9, 10.

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Objective

- **The purpose of this effort is to produce a quantitative understanding of the process/product interdependence leading to catalyst systems with improved final product quality, resulting in diesel emission levels that meet the prevailing emission requirements.**

Milestones

- **Milestone10: Initiate evaluation of feasibility of the advanced tools available at ORNL for quantitative analysis of the materials changes underlying the ammonia oxidation (AMOX) catalyst performance degradation with age.**

- **Milestone11: Continue AMOX catalyst characterization of a practically-relevant *zeolite catalyst* subjected to hydrothermal aging for lifetime prediction model input (09/2011).**

Relevance to barriers

- **Impact on barriers: Experimental characterization…**
  - **Of why, when, where and extent of hydrothermal aging degradation on the material system's performance. Understanding mechanisms provides *fundamental knowledge* which allows new engine regimes to mitigate aging**
  - **Input for models to predict behavior accurately. In turn, strategies to mitigate hydrothermal aging degradation can be formulated which *changes engine combustion regimes***
  - **Predictable behavior allow for better catalysts to be designed which improves *durability***
  - **Improved strategies minimize loss, save precious metals improving *cost-effective emission control***

Relevance to barriers (cont'd)

- **Impact on barriers: Experimental characterization…**
  - **Presently NH_3 emissions are not regulated…materials knowledge is needed <u>now</u> because of the *<u>long lead times</u>* required to put a material/component in place.**
  - **Net result of above is cleaner diesel which improves *<u>market perception</u>***

Integration

- **Integration within Vehicle Technology program:**
  - **Utilizes characterization tools acquired and maintained by the High Temperature Materials Laboratory (HTML) Program**

Relevance to Vehicle Technologies Goals

- **Advanced Combustion Engine R&D: By 2015, improve the fuel economy of light-duty gasoline vehicles by 25 percent and of light-duty diesel vehicles by 40 percent, compared to the baseline 2009 gasoline vehicle. Efficient emission control is a component of this.**
  - **With an efficient and durable AMOX catalyst, higher NOx conversion efficiencies can be attained, thus minimizing constrains on engine-out NOx emissions and allowing engines to be tuned for optimal fuel efficiency, cost and durability**
  - **Increases acceptance of clean diesel by the public. Larger acceptance results in larger percentages of conversion to diesel, with the resulting reduction in petroleum**

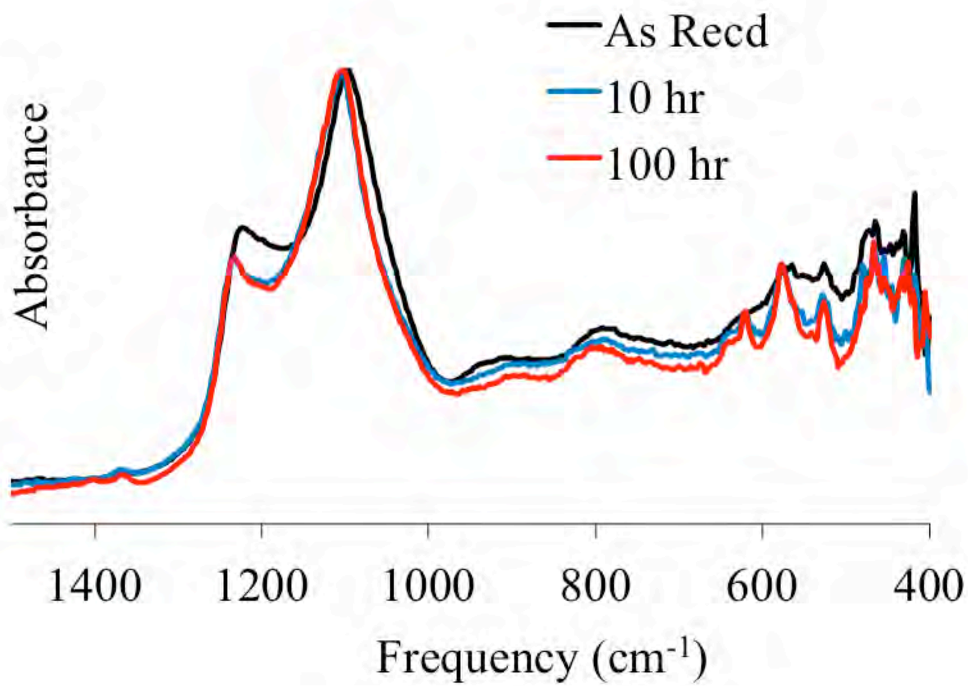
- **Achieve engine system cost, durability and emissions targets***
  - **Thrust is to characterize and improve the durability, resulting in the lowest overall cost and preventing emission release in service.**

* Vehicle Technologies Program, Multi-Year Program Plan 2011-2015, Dec 2010, pp. 2.3-2, 2.5-7.

Technical approach/strategy:

- **Experimentally characterize AMOX materials, supplied by Cummins, from all stages of the catalyst's lifecycle: fresh, de-greened, aged, regenerated, on-engine and off-engine, etc.**
  - **To study the effect of progressive aging hydrothermally age the sample at 650°C in 7% H_2O for 0, 2, 3, 5, 10, 25, 50, 100 hr**
- **Determinations include: crystal structure, morphology, phase distribution, particle size and surface species of catalytic materials.**
- **Seek the atomic mechanisms and chemistry of adsorption and regeneration processes**
- **Seek to understand the thermal and hydrothermal aging processes and other degradation mechanisms throughout the lifecycle of the catalytic material.**

Hydrothermal aging in 7% H_2O at 650ºC causes the zeolite structure to become more ordered as indicated by the narrower FT-IR band widths

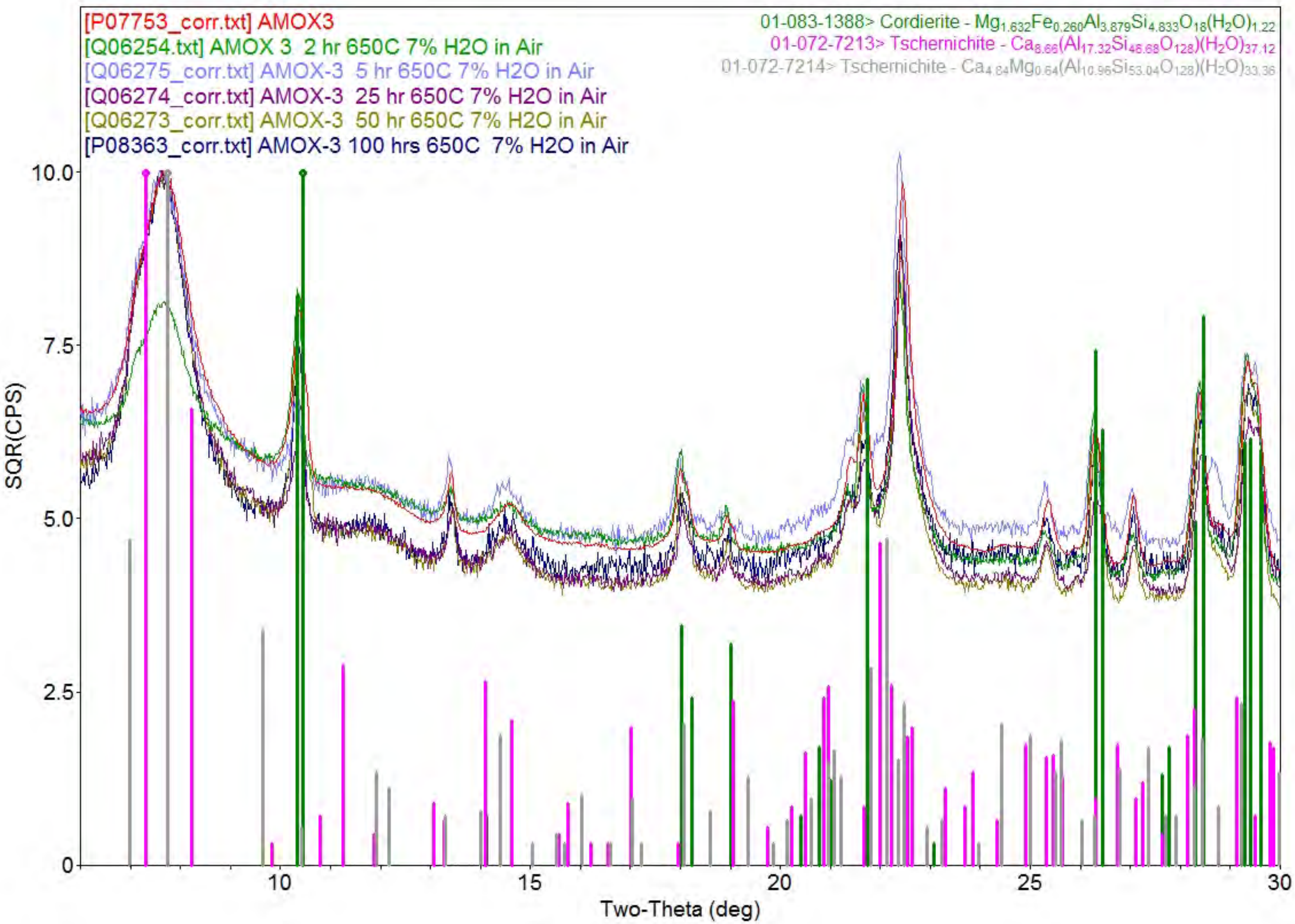


- **Fourier Transform-Infrared Spectroscopy (FT-IR) is sensitive to the skeletal modes of the zeolite framework that occur below 1400 cm^{-1}.***
- **This structural change occurs within the first 2 hours at temperature and subsequent aging for up to 100 hours does not significantly alter the zeolite structure.**

*Paze´ et al., *J. Phys. Chem. B* **1997,** *101,* 4740-4751

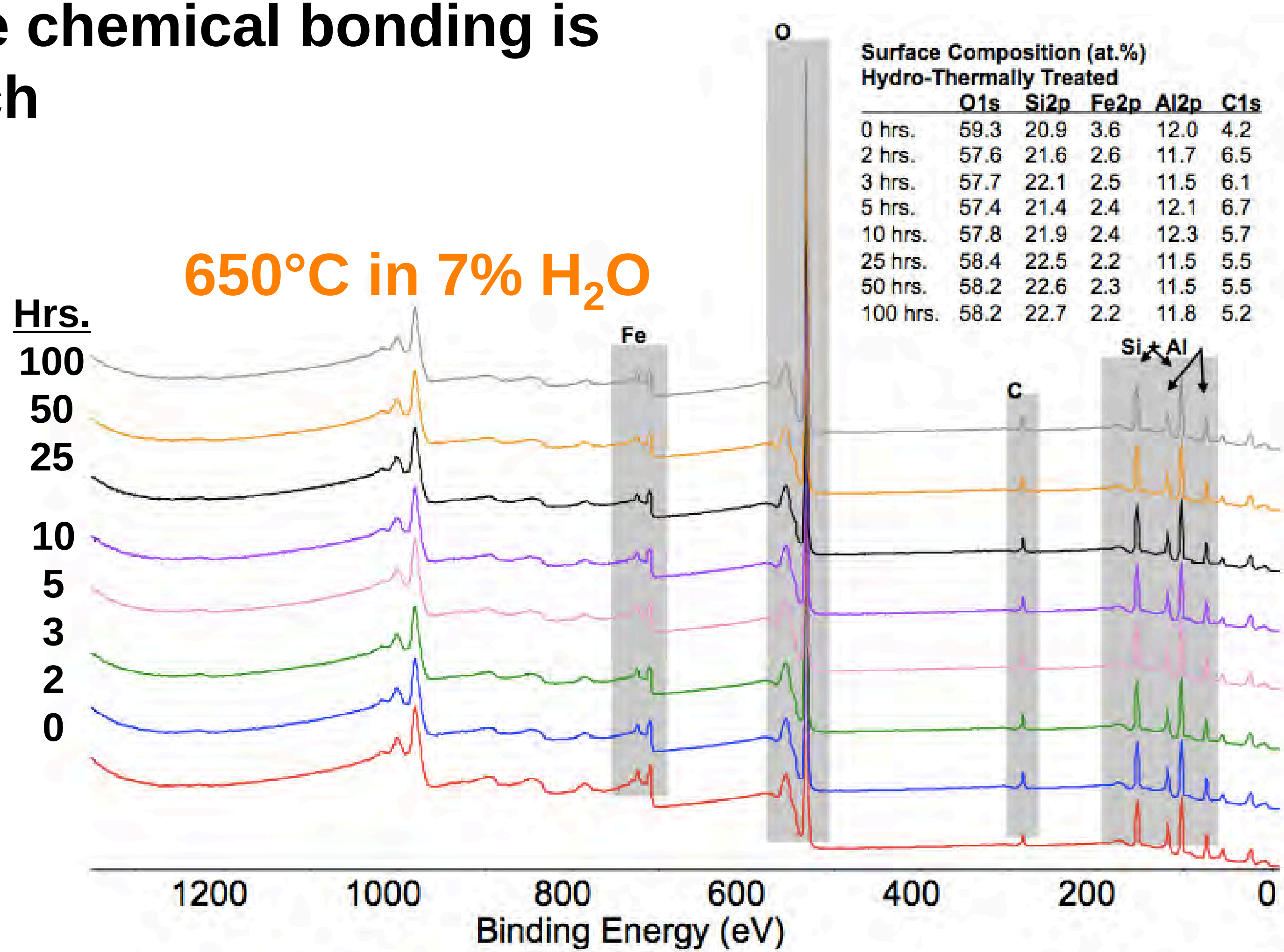
XRD showed slight narrowing of zeolite peaks, suggesting structure is more crystalline with aging.

Intensity Differences also seem to support this, save 50 hr which could be do to loss of catalyst powder



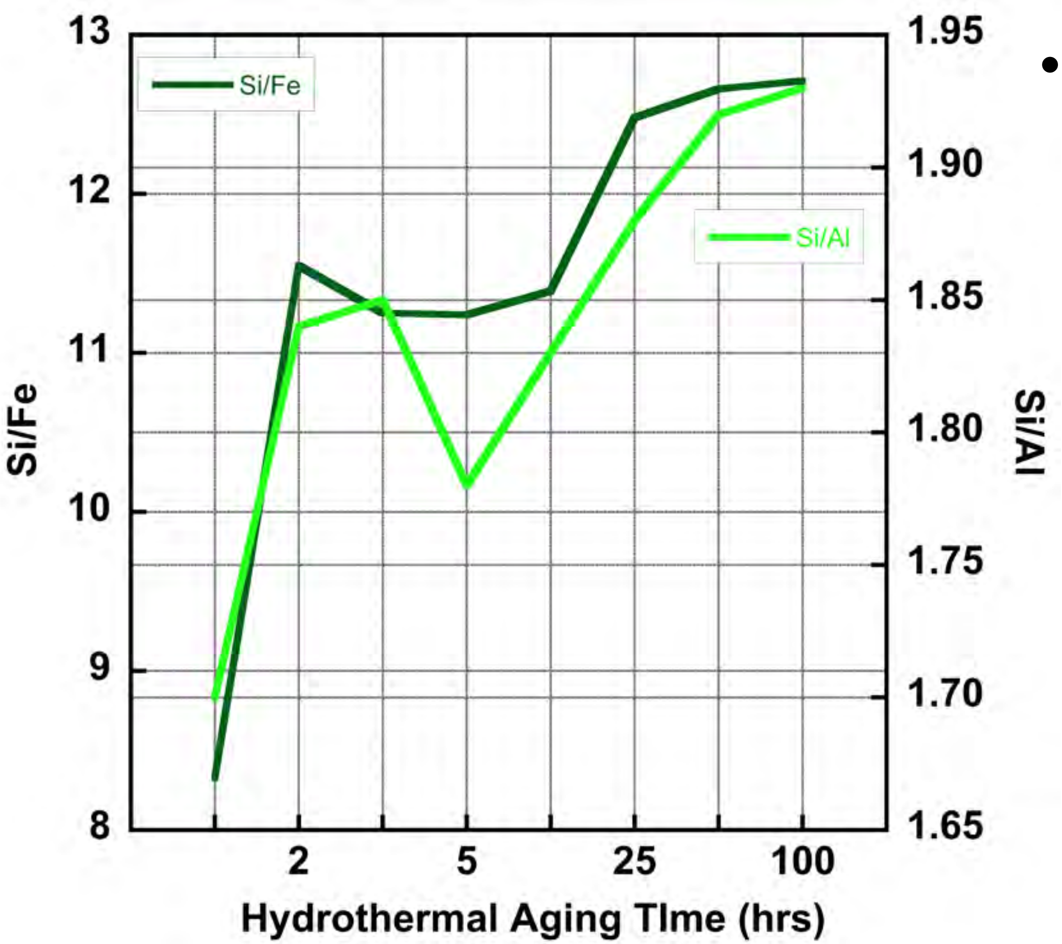
X-ray Photoelectron Spectroscopy shows similar chemistry and valence as a function of hydrothermal aging time

- **O, Si, Al, and Fe core level spectra show that the chemical bonding is similar in each**



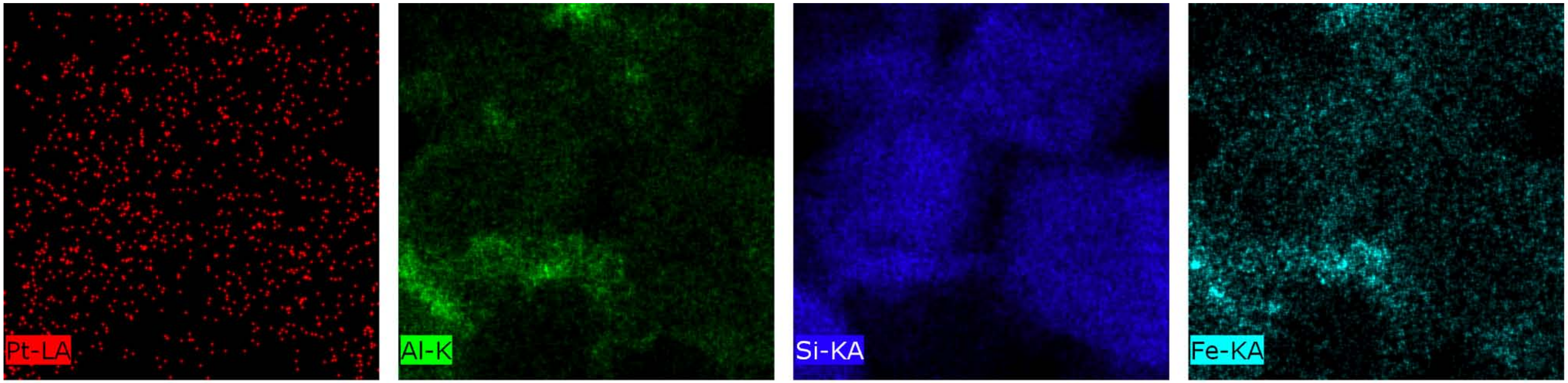
	O1s	Si2p	Fe2p	Al2p	C1s
0 hrs.	59.3	20.9	3.6	12.0	4.2
2 hrs.	57.6	21.6	2.6	11.7	6.5
3 hrs.	57.7	22.1	2.5	11.5	6.1
5 hrs.	57.4	21.4	2.4	12.1	6.7
10 hrs.	57.8	21.9	2.4	12.3	5.7
25 hrs.	58.4	22.5	2.2	11.5	5.5
50 hrs.	58.2	22.6	2.3	11.5	5.5
100 hrs.	58.2	22.7	2.2	11.8	5.2

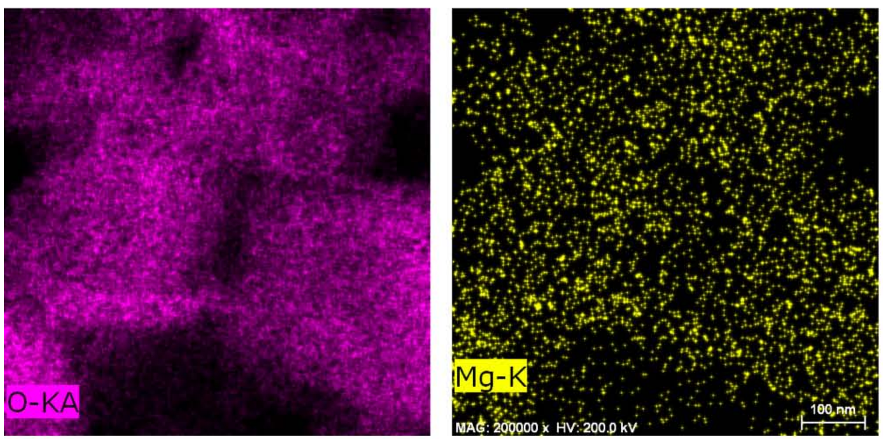
Si/Fe and Si/Al atomic ratios suggest that the surface is slightly depleted in Fe as the material is hydrothermally aged

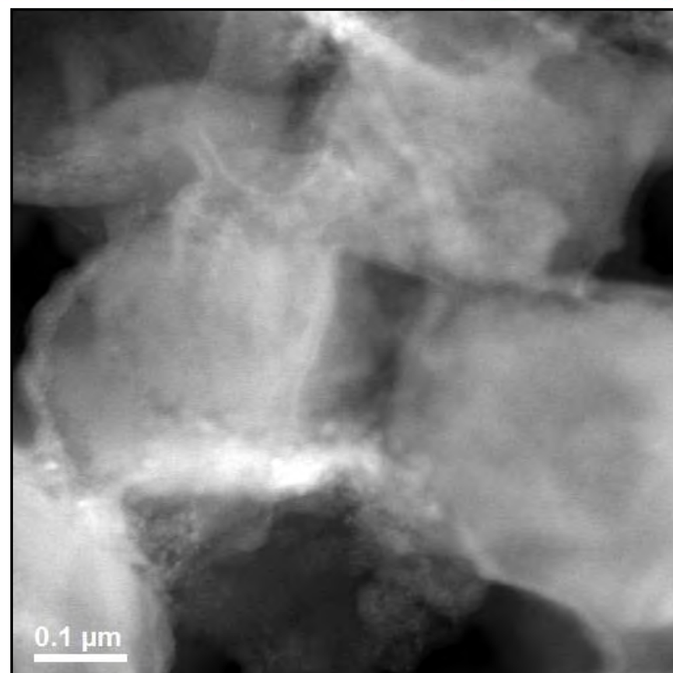


- While the Si/Al mirrors that of Si/Fe, it is an order of magnitude smaller change

Zero hours: The elemental maps show segregation of Al and Fe to boundaries and surfaces of primarily SiOx grains; Mg remains uniformly distributed

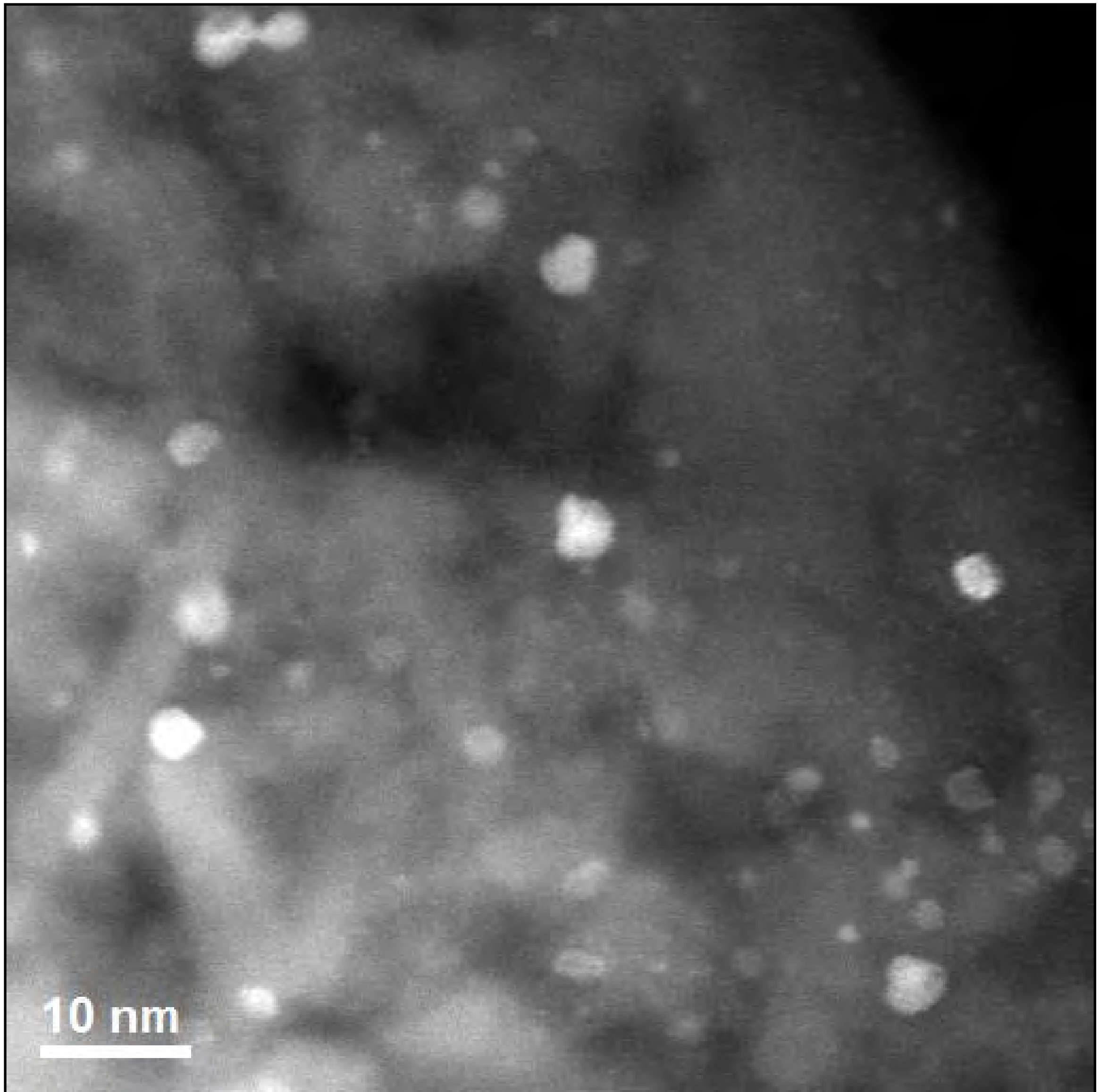




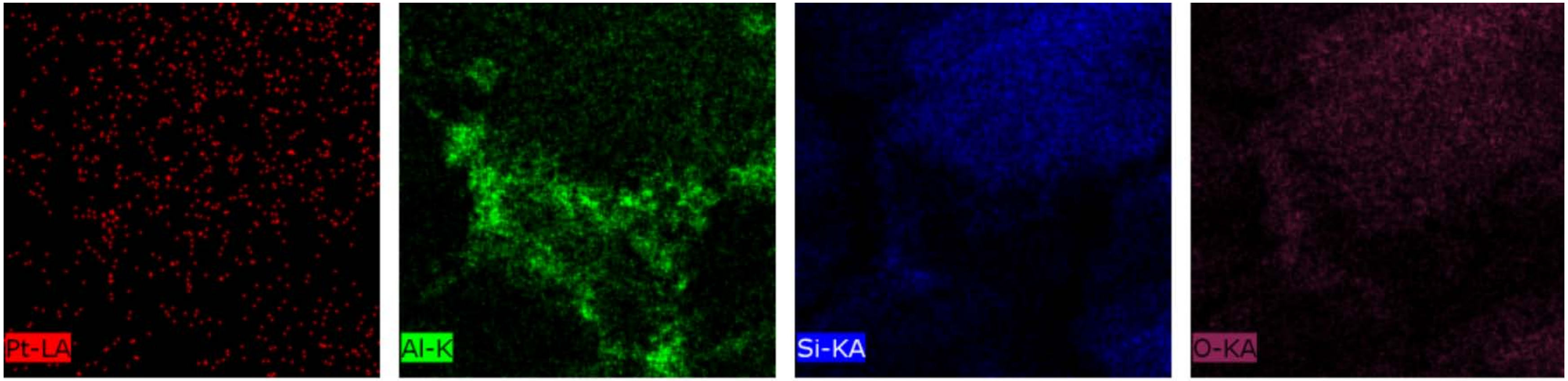


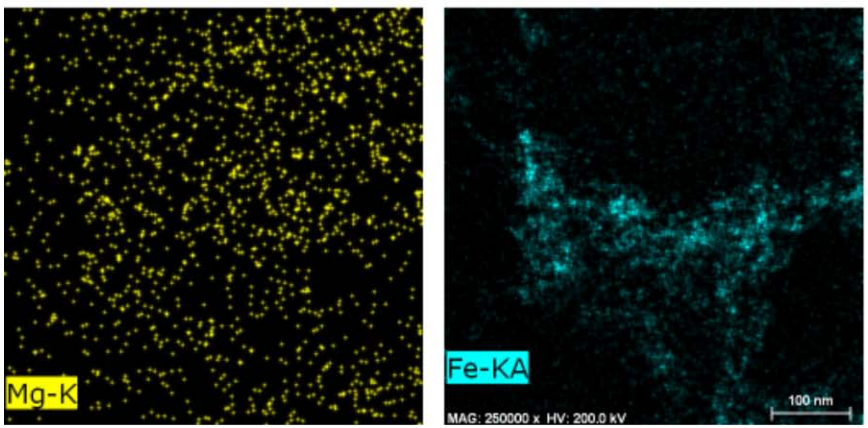
Dark-field image

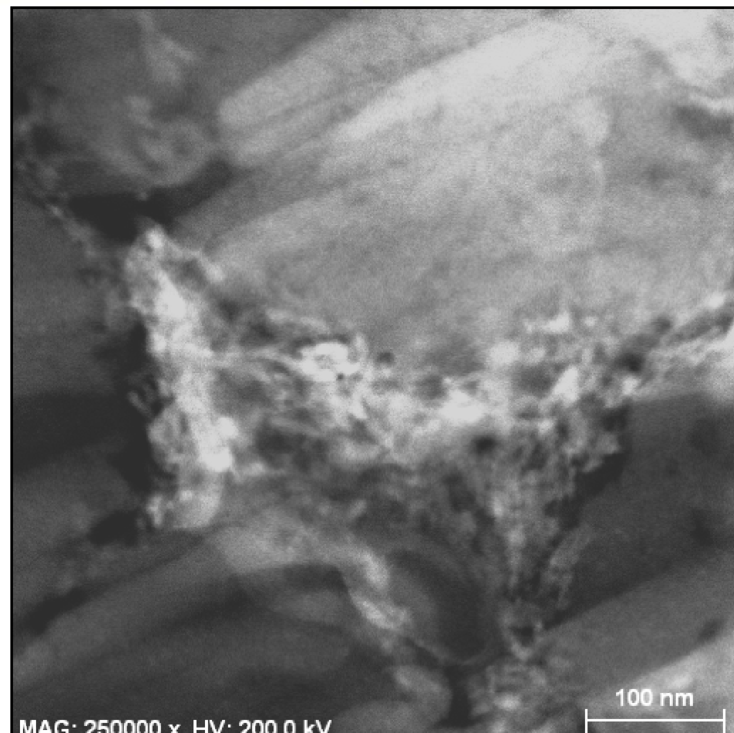
Zero hours: HAADF image showing nominal Pt particles 1-4 nm



10 hours: Elemental maps from prior area, showing segregation of Al with Fe, and primary grain composition of SiOx; Note Pt is background







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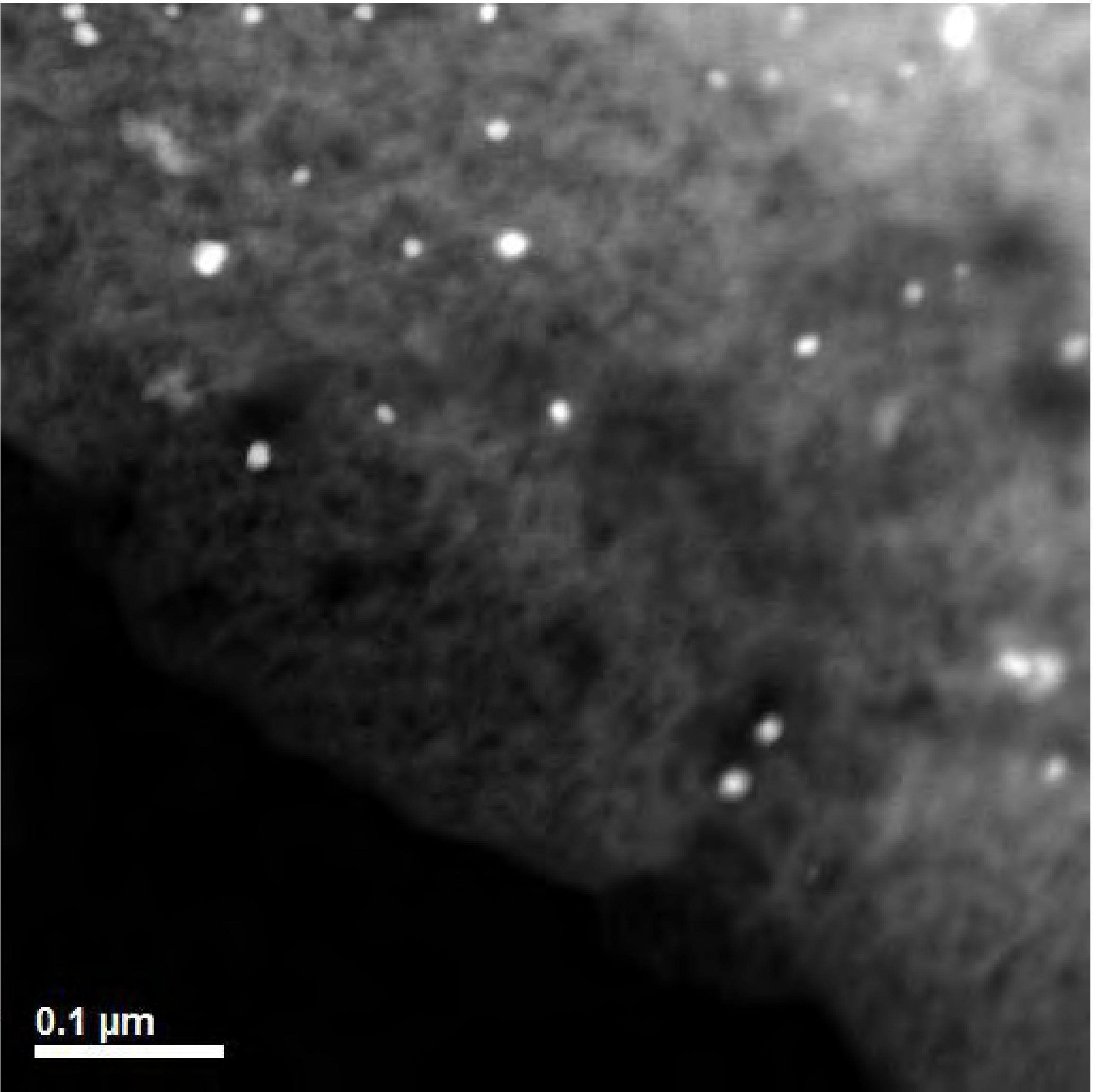
10 hours: HAADF image showing nominal Pt particles 10-30 nm; Pt particles effectively the same size after 100 hrs



Technical Approach/strategy: Addresses barriers

- **The above provides an understanding of materials behavior and property data to models which *increases knowledge to optimize regimes*. This *improves durability* making emission control *more cost effective*.**

Collaborations and coordinations with other institutions: Tech transfer

- **Efforts contributed to refinement of aftertreatment systems Dodge Ram Pickup truck**
- **Provide guidance for system design, cost (reduce precious metal content, and optimization.**
- **Reduce materials and functionality margins for related to catalyst aging.**

Collaborations and coordinations with other institutions: Partners

- Cummins (Industry):
  - Cummins' role is to collaborate and guide the work along the most useful path to achieve durability, cost and emissions targets
  - Supplies samples; share experimental results on samples (e.g. catalyst performance results during aging); exchange of technical information to assist with each others analyses; face to face meetings at least 2X/year

- JM Johnson Matthey (Industry):
  - Johnson Matthey's role is to consult and exchange of technical information

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Future Work

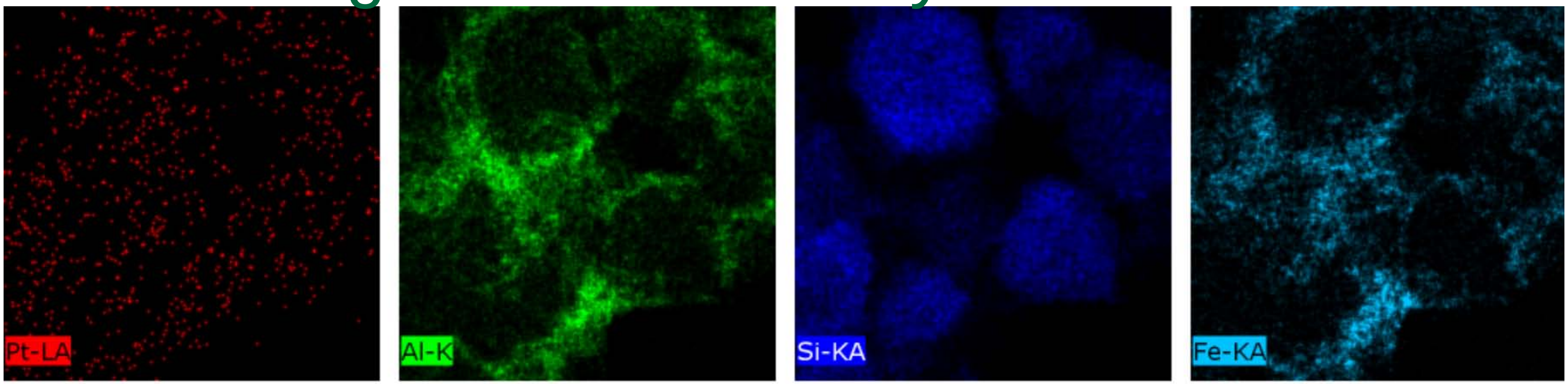
- **Continue ammonia oxidation (AMOX) catalyst characterization of a practically-relevant *zeolite catalyst* subjected to hydrothermal aging for lifetime prediction model input.**
  - **To study accelerated hydrothermal aging, hydrothermally age the samples for 1 and 2 h at 600, 650, 700, 800, 900°C in 7% H_2O**
- **Utilize new in-situ capabilities.**
- **Assist Cummins to competitively produce engines which attain the required prevailing emission levels and beyond while maintaining the advantage of the diesel's inherent energy efficiency (FY11 & FY12).**

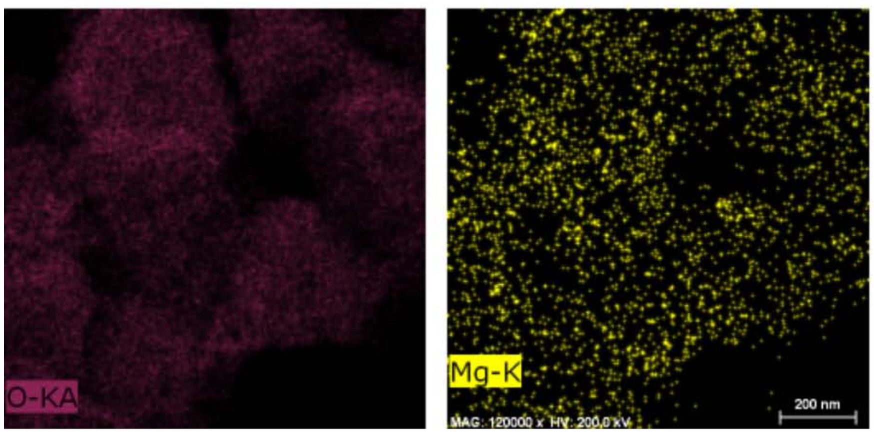
Summary: Characterizations provides *fundamental knowledge* reduces *long lead times* supporting lifetime predictions which *changes engine combustion regimes, improves durability, efficiency; reduces cost; improves market perception…VT goals*

- **Hydrothermal aging appears to increase order and crystallinity in the Fe-Zeolite (FTIR+XRD)**
- **XPS indicates that the surface is slightly depleted in Fe**
- **Pt particles size ↑ from 3 to 20 µm from 0 to 10 hrs at 650°C in 7% H_2O**

Technical Backup slides

100 hours: Al and Fe segregation, qualitatively, may have increased with increasing time under hydro treatment.





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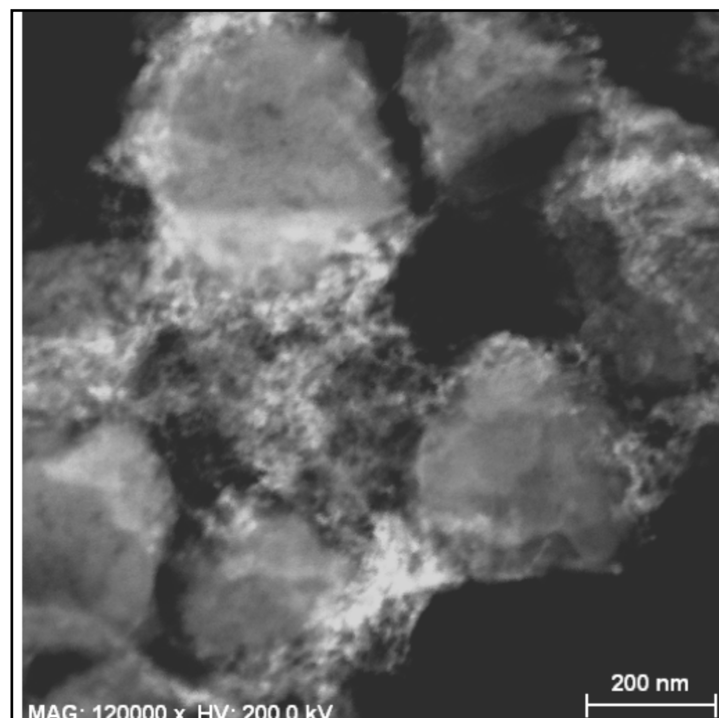
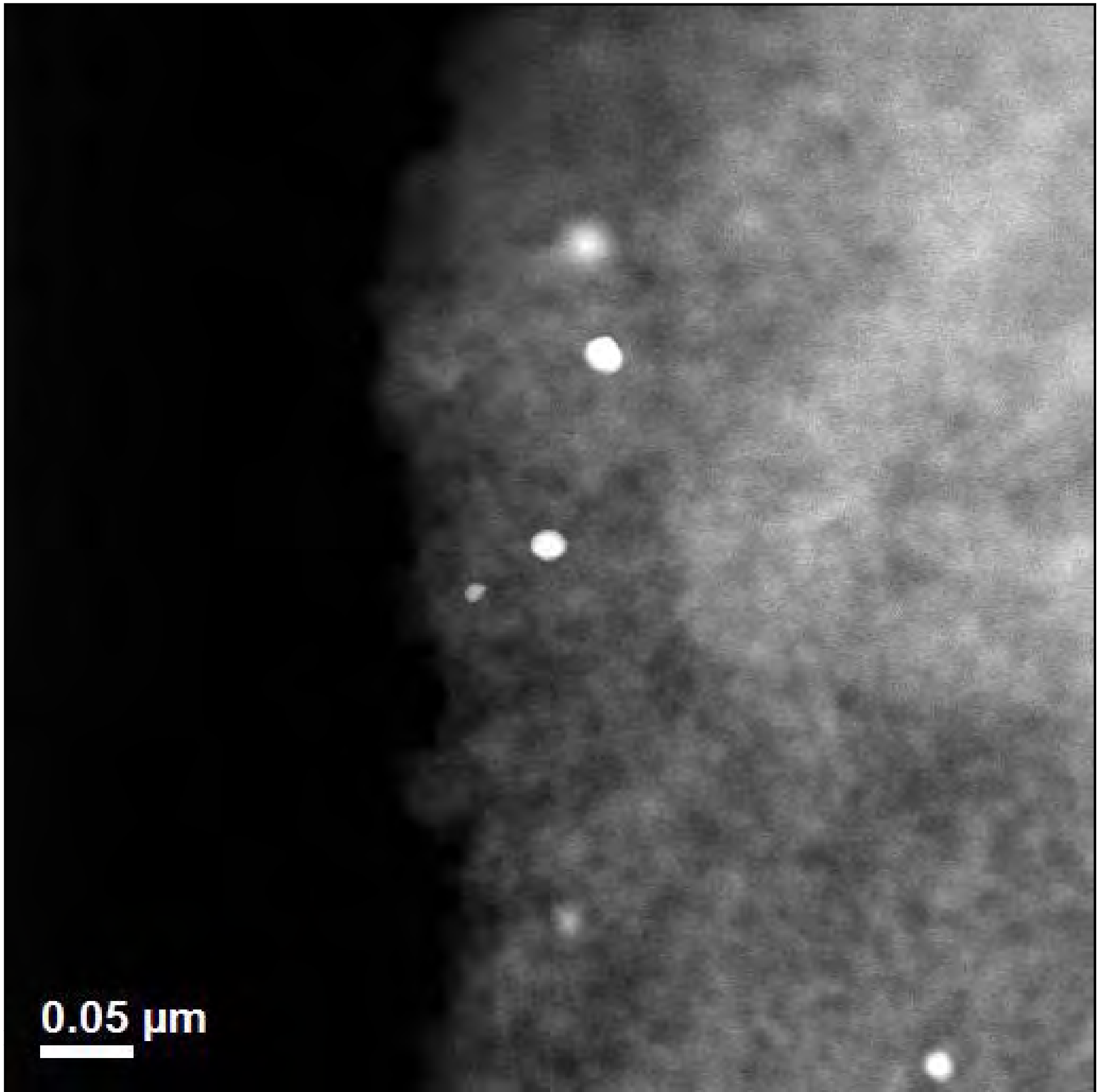


100 hours: HAADF image showing nominal Pt particles 10-30 nm



What is a zeolite?*

- **Classical definition: a crystalline, porous aluminosilicate**
- **Current definition: porous oxide structures with well-defined pore structures and a high degree of crystallinity**
- **Large number of structures possible**
- **Pores/Channels-molecular sieves**

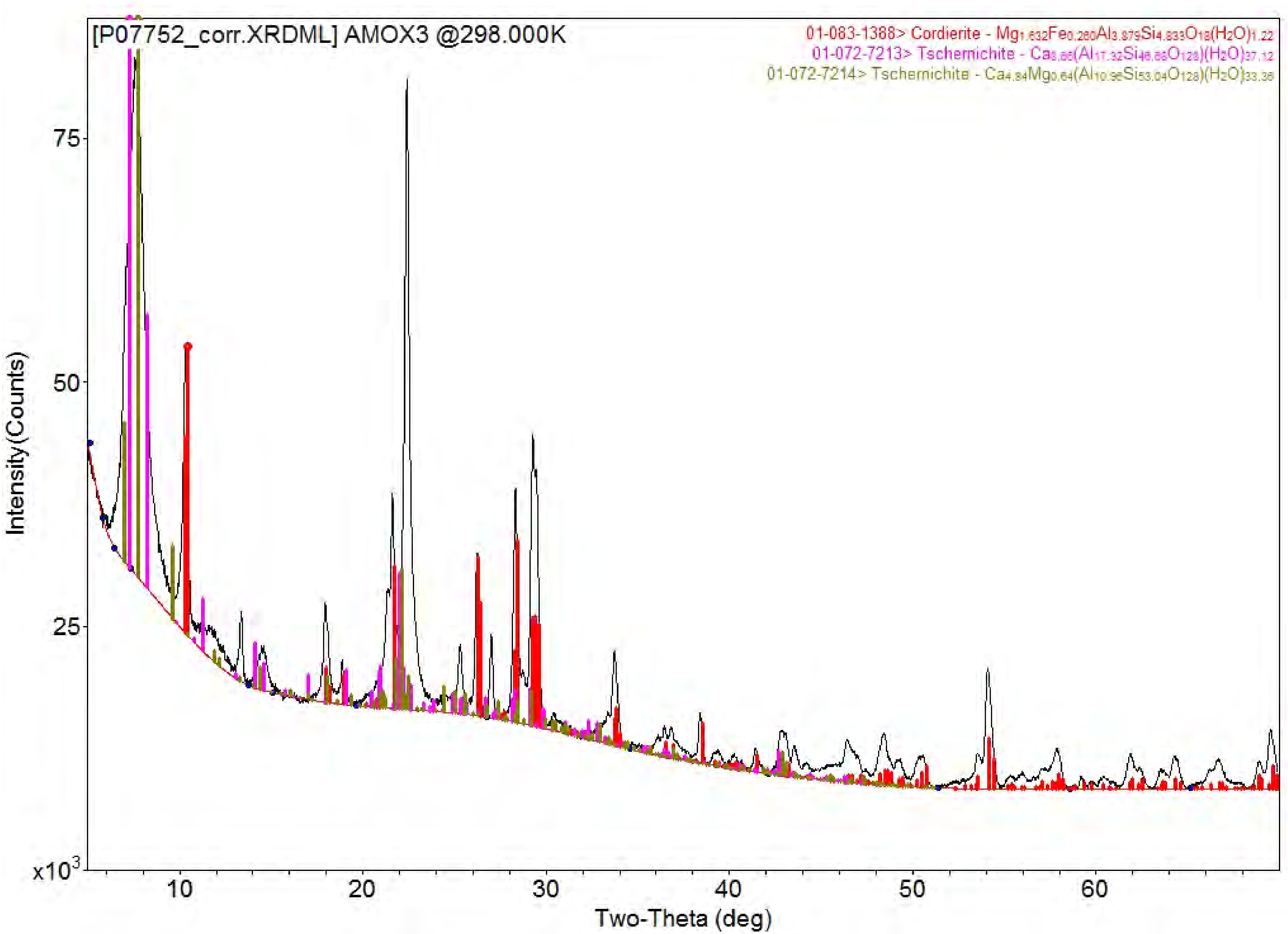
*** www.personal.utulsa.edu/~geoffrey-price/zeolite/zeo_narr.htm**

Chemical interactions of zeolites

- **Si-O4 tetrahedra and $(Al\text{-}O4)^{-1}$ tetrahedra**
  - **Charge compensation with cations in pores**
- **Uses:**
  - **Ion exchange as in water softeners**
  - **Cation=H+, becomes a strong acid-catalytically active**
  - **Other metal cations-shape selective catalysis**

*** www.personal.utulsa.edu/~geoffrey-price/zeolite/zeo_narr.htm**

X-Ray Diffraction: AMOX catalyst is a Zeolite on a cordierite substrate



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