Catalysts for the Selective Oxidation of Ammonia to Nitrogen

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David T. Wickham
Jeffrey Lind

TDA Research Inc. • Wheat Ridge, CO 80033 • www.tda.com

Overview

- Background of the Vapor Phase Catalytic Ammonia Removal (VPCAR) System.
- TDA approach to the identification of a selective catalyst.
- Results of our Phase I Project.
- Preliminary reactor design for the full scale VPCAR unit.

The Need for a New Water Purification System

- The cost of delivering a payload to Mars is much higher than to low Earth orbit.
- Therefore missions to Mars place higher emphasis on reducing launch weight.
- Thus, water purification systems currently used on the ISS may not be suitable for use on a Mars mission.

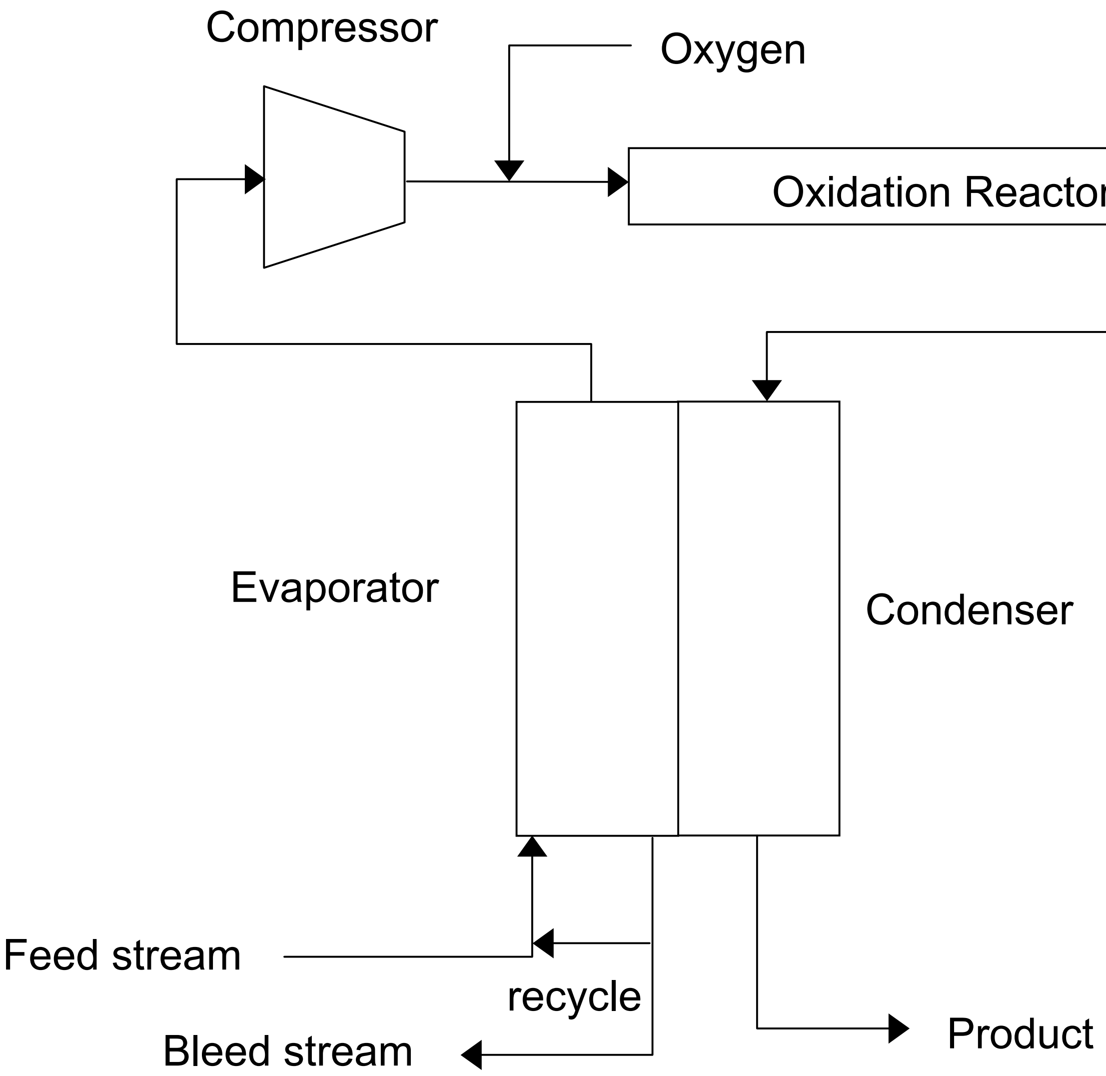
Comparison of Water Purification Methods

- **The ISS uses the Water Recycle System (WRS) to purify water.**
  - Employs expendable adsorption beds.
  - Resupply requirement is 0.32 kg/person day.
  - For a remote destination, resupply costs could exceed $800 M (960 day – 6 crew) (Flynn and Borchers 2000).
- **For Mars missions.**
  - Emphasis is on eliminating resupply requirement.
  - VPCAR system uses distillation to purify water.
  - Requires more energy, but does not rely on expendables.

Technical Challenges Associated with VPCAR

- Distillation does not eliminate volatile components such as ammonia (NH_3 SMAC = 7 mg/m^3, 9.2 ppm, Perry 1998).
- These must be oxidized in the catalyst bed – platinum catalysts are effective.
- Unfortunately, commercial platinum catalysts convert NH_3 to NO and NO_2 (NO_X).
- NO SMAC = 5.0 mg/m^3 (3.7 ppm) and NO_2 SMAC = 0.94 mg/m^3 (0.45 ppm).
- The goal of our Phase I is to identify catalysts that do not produce NO_X.

Schematic of the VPCAR System



Simplified from Flynn and Borchers, 2000

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Oxidation of NH_3

- **Selective oxidation of ammonia to nitrogen.**

$$2\ NH_3 + 3/2\ O_2 \rightarrow N_2 + 3\ H_2O$$

- **Oxidation of ammonia can also produce NO and NO_2.**

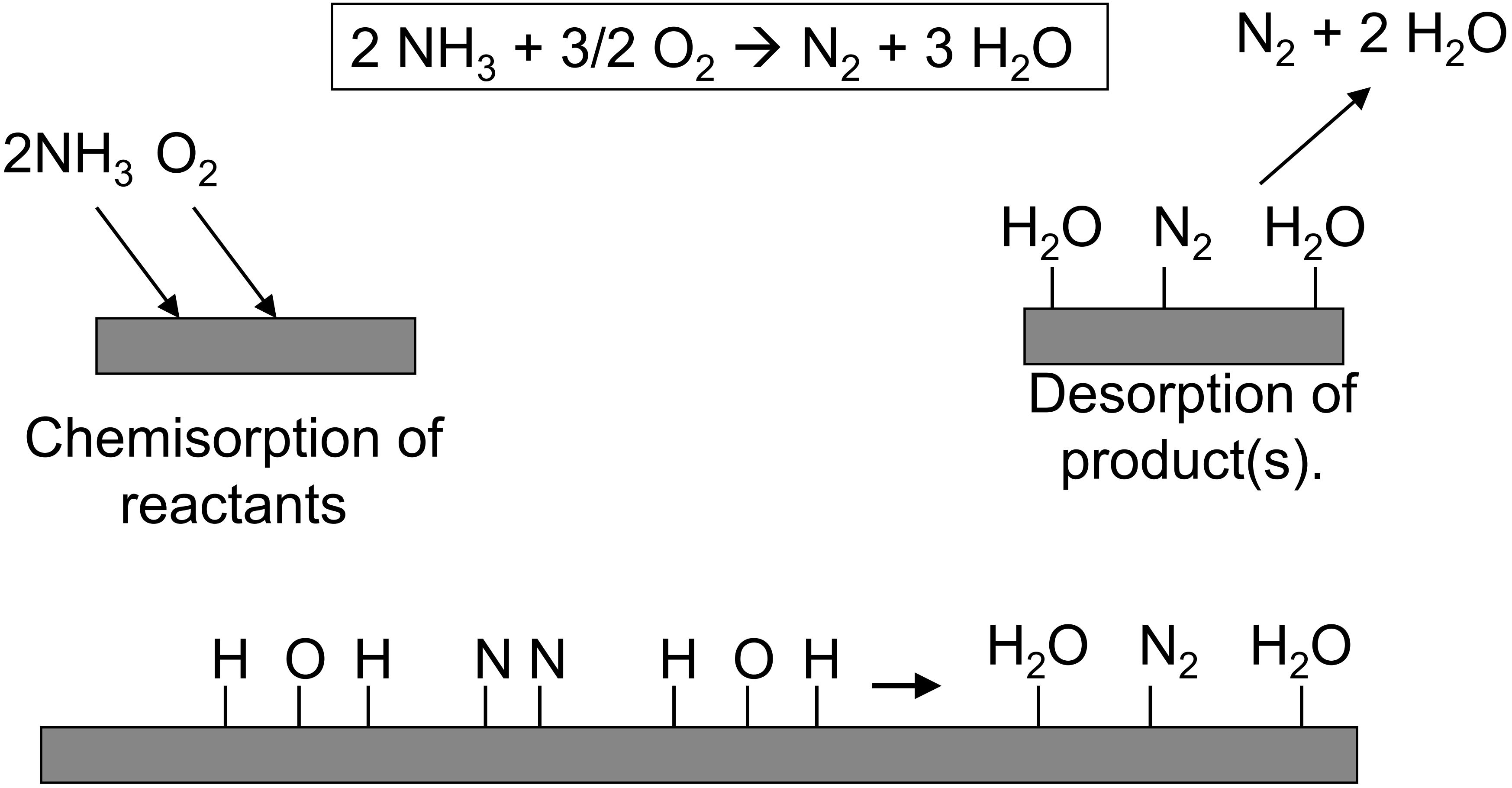
$$2\ NH_3 + 5/2\ O_2 \rightarrow 2\ NO + 3\ H_2O$$

$$2\ NH_3 + 7/2\ O_2 \rightarrow 2\ NO_2 + 3\ H_2O$$

We must identify a selective catalyst to eliminate NO or NO_2 (NO_X).

Steps in Ammonia Oxidation

$\boxed{2\ NH_3 + 3/2\ O_2 \rightarrow N_2 + 3\ H_2O}$

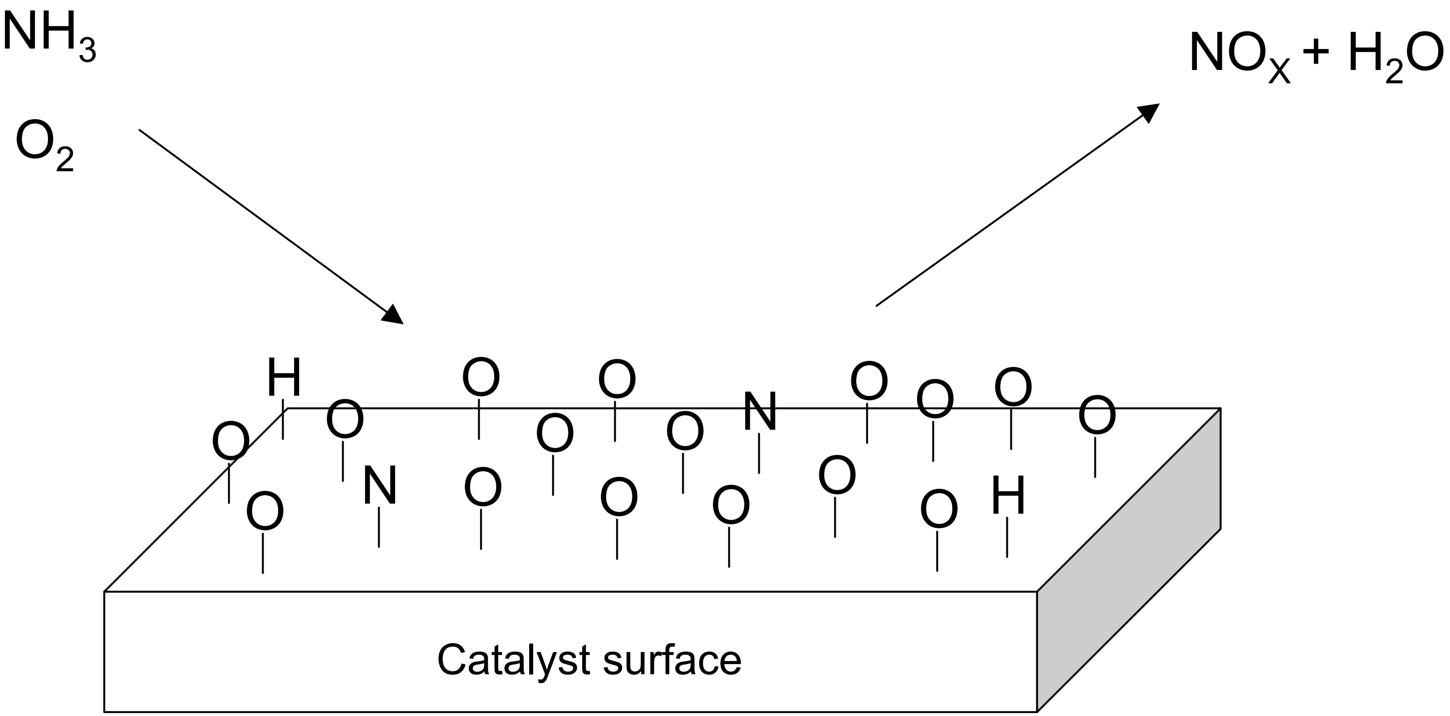


Chemisorption of reactants

Desorption of product(s).

Surface reaction between mobile adsorbed species.

Why NO_X is Produced During Ammonia Oxidation



In excess oxygen, there is a high probability that N and O will react to form NO or NO_2.

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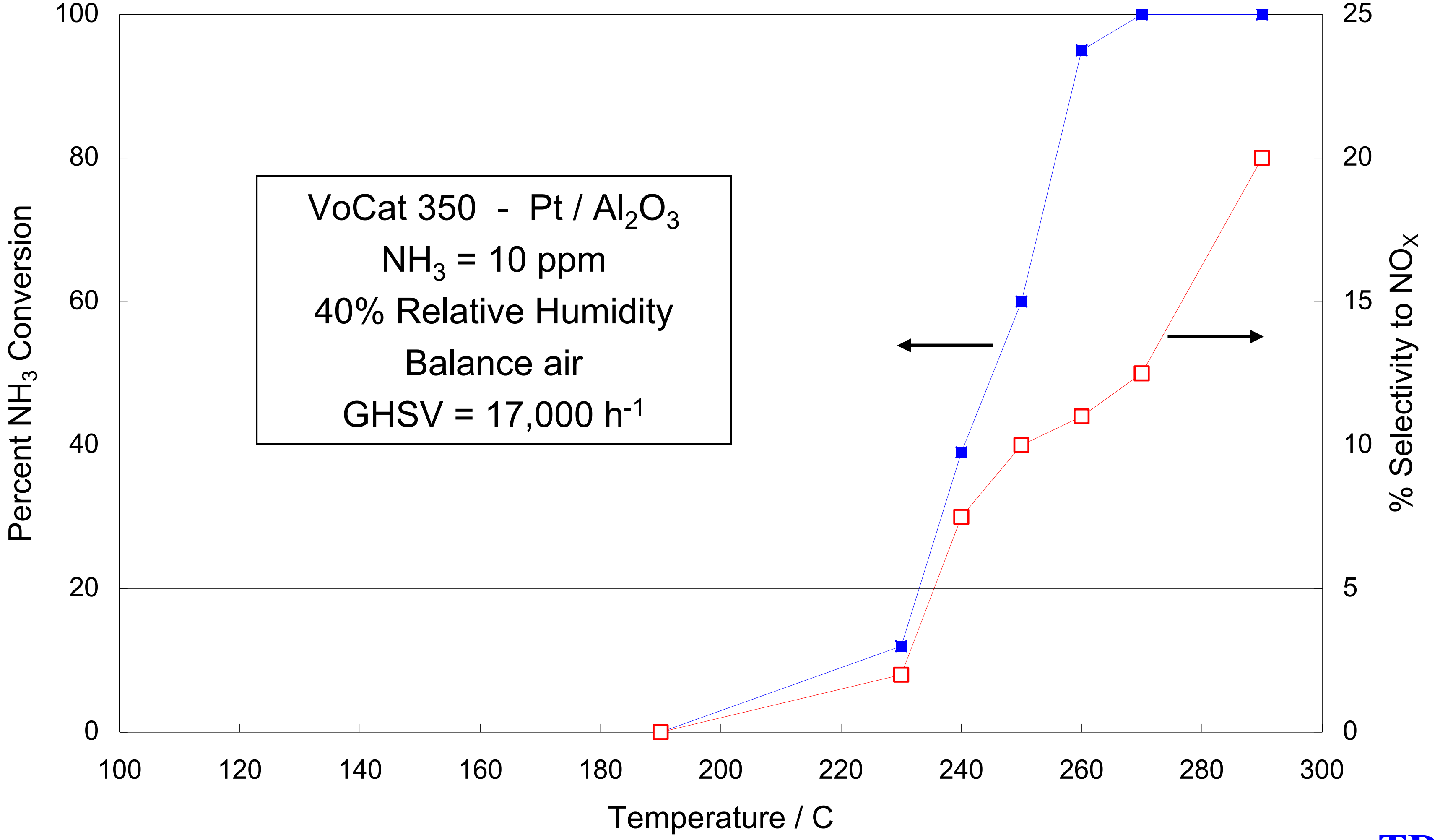
Previous Data on VoCat Shows High NO_X Formation



VoCat 350 - Pt / Al_2O_3

NH_3 = 10 ppm

40% Relative Humidity

Balance air

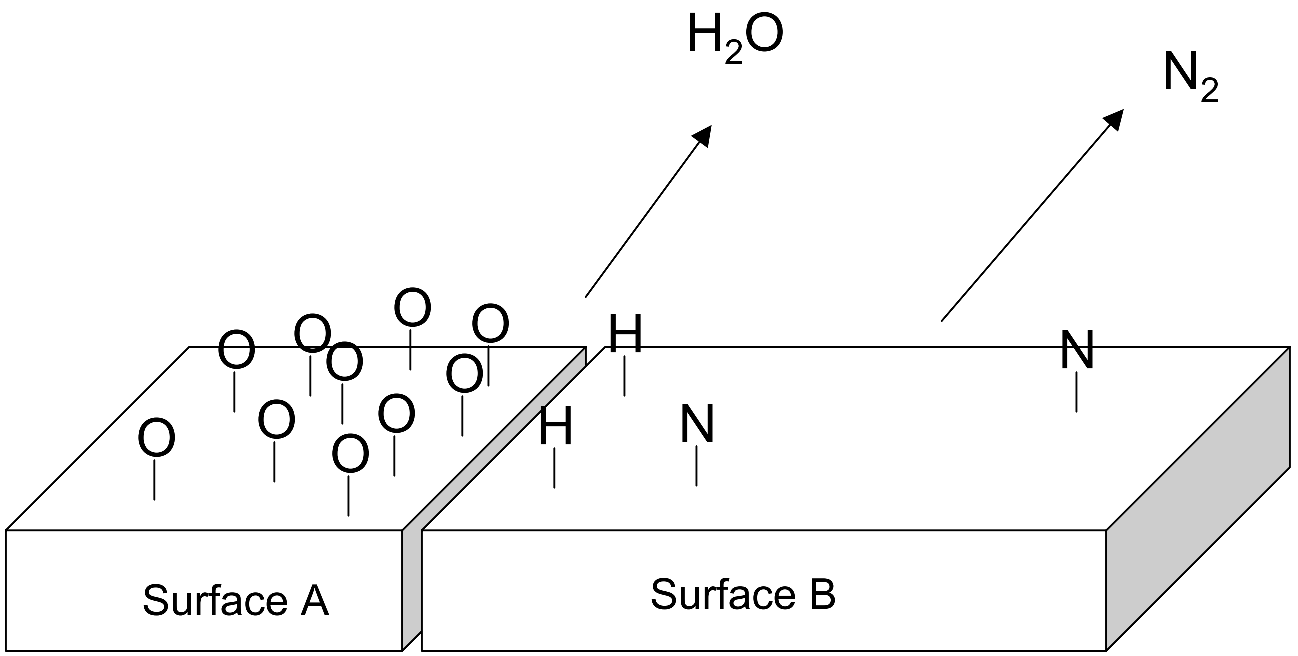
GHSV = 17,000 h^{-1}

From Wright et al. 1997

TDA's Approach to Preparing a Catalyst That Does not Produce NO_X

- Prepare a catalyst with two types of active surfaces in close contact with each other.
- Nitrogen adsorbs primarily on one surface.
- Oxygen is concentrated on the second active site.
- Reduces the reaction between oxygen and nitrogen, eliminating NO_X.

Simplified Schematic of Catalyst that is Selective for Nitrogen Production

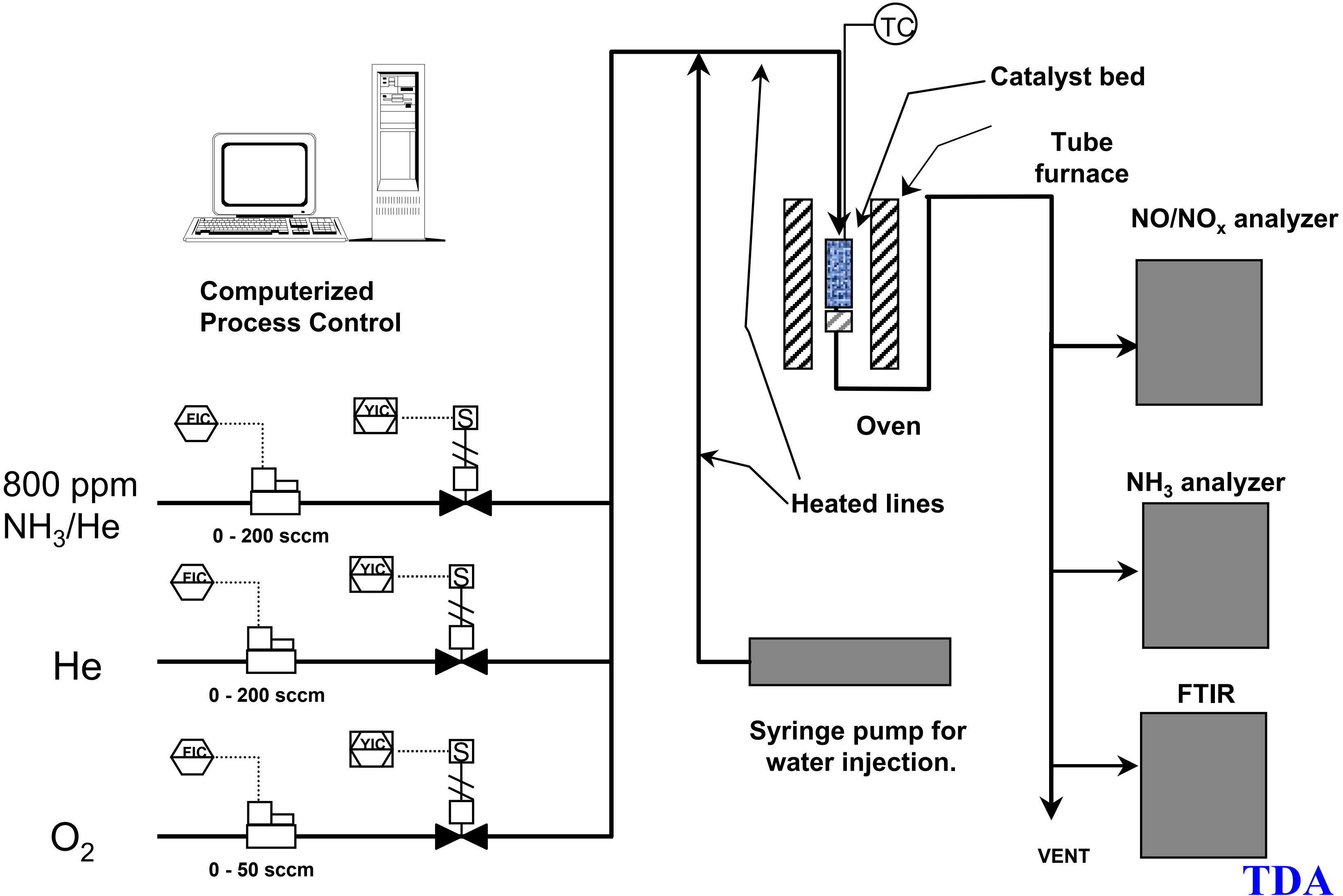


Separate adsorbed O from adsorbed N

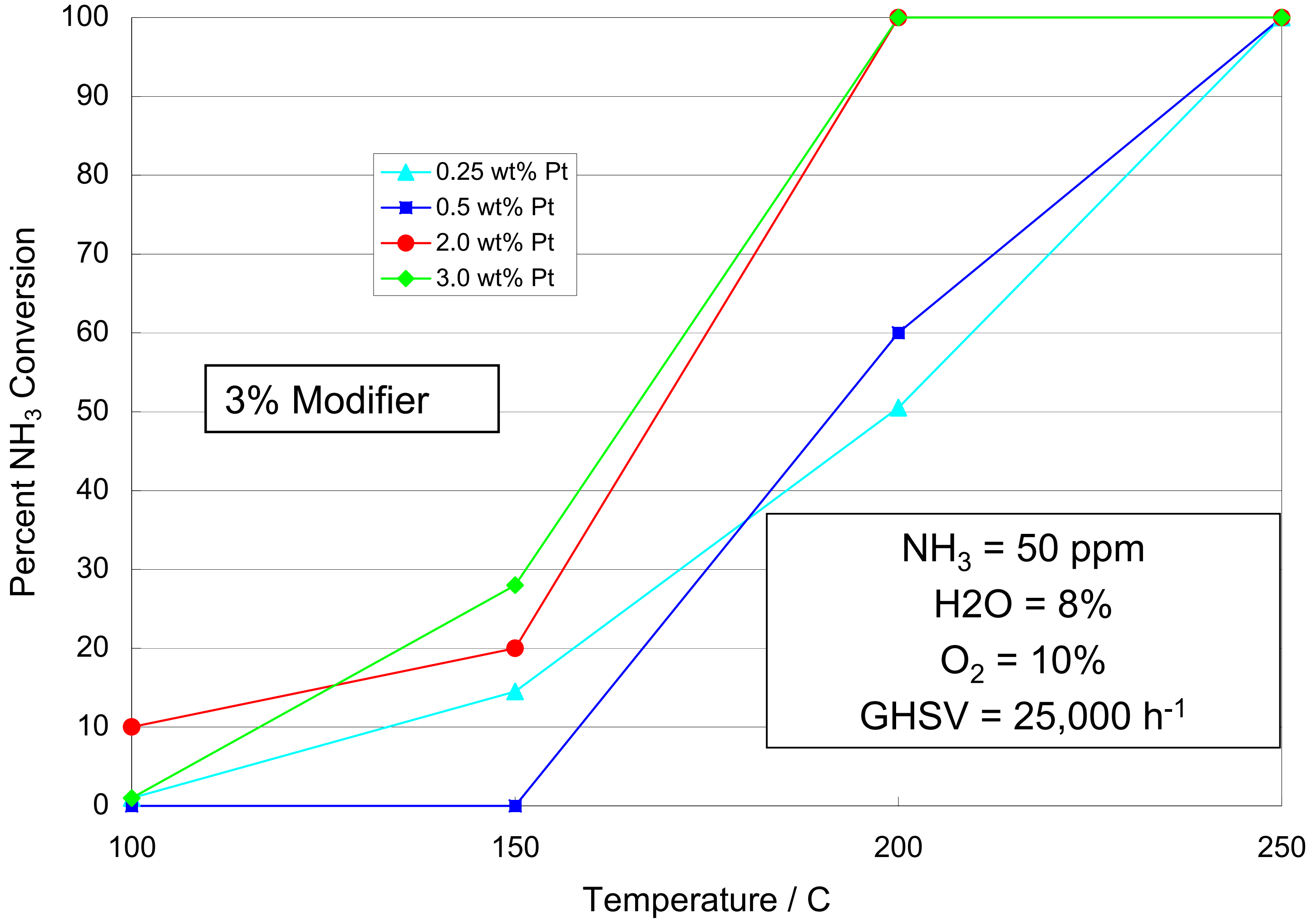
Phase I Test Plan

- **Prepare matrix of 25 catalysts consisting of platinum on modified supports.**
  - 0.25 to 3 wt% Pt; 3 to 15 wt% modifier.
  - Measure activity for ammonia oxidation and selectivity for NO_X.
- **Test in the presence of high water concentrations.**
- **Generate kinetic data to arrive at rate expression, which can be used to size the oxidation reactor.**

Automated Test Rig

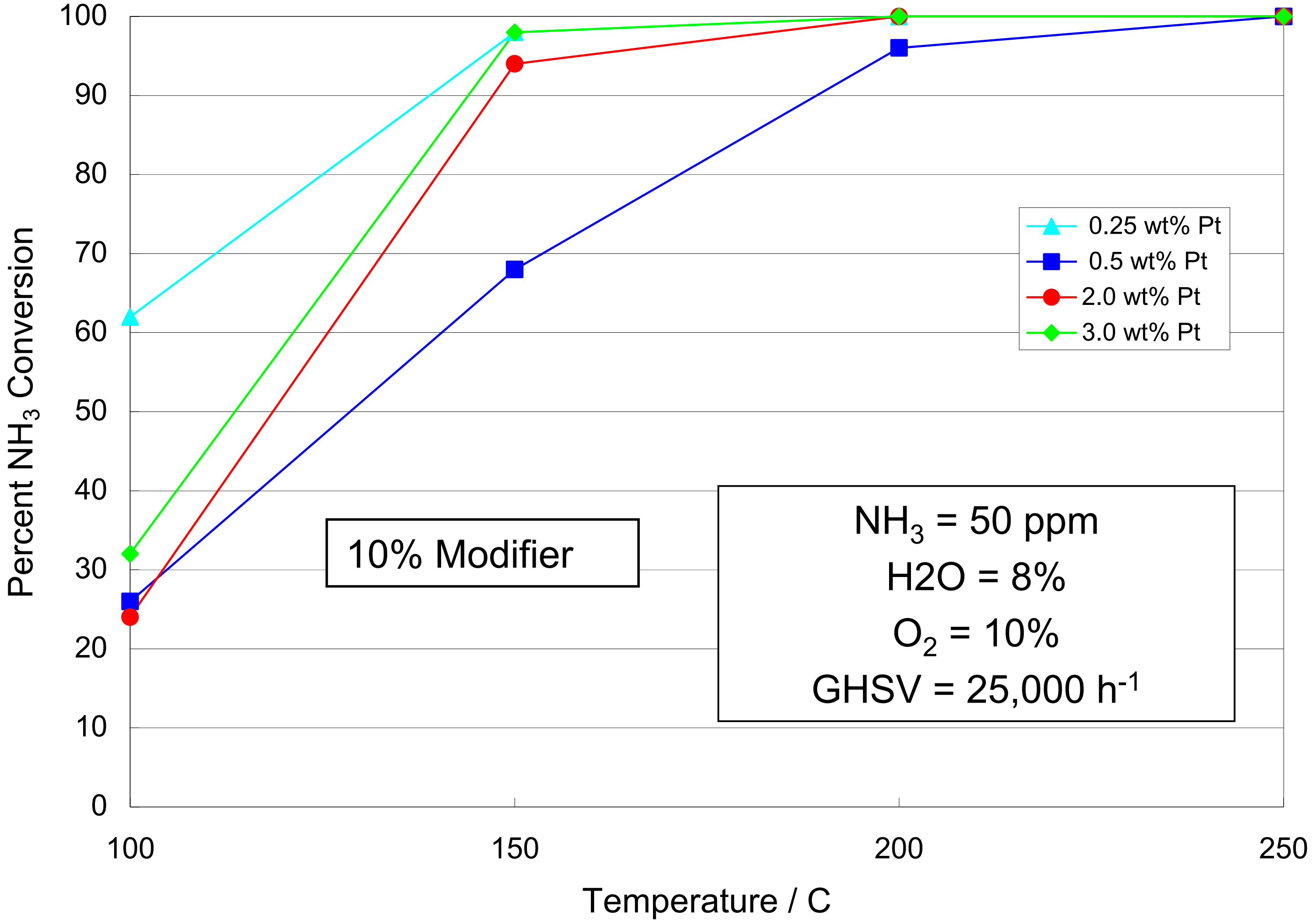


3% Modifier Results in Low Activity



NH_3 = 50 ppm
H2O = 8%
O_2 = 10%
GHSV = 25,000 h^{-1}

Catalysts with 10% Modifier Were the Most Active



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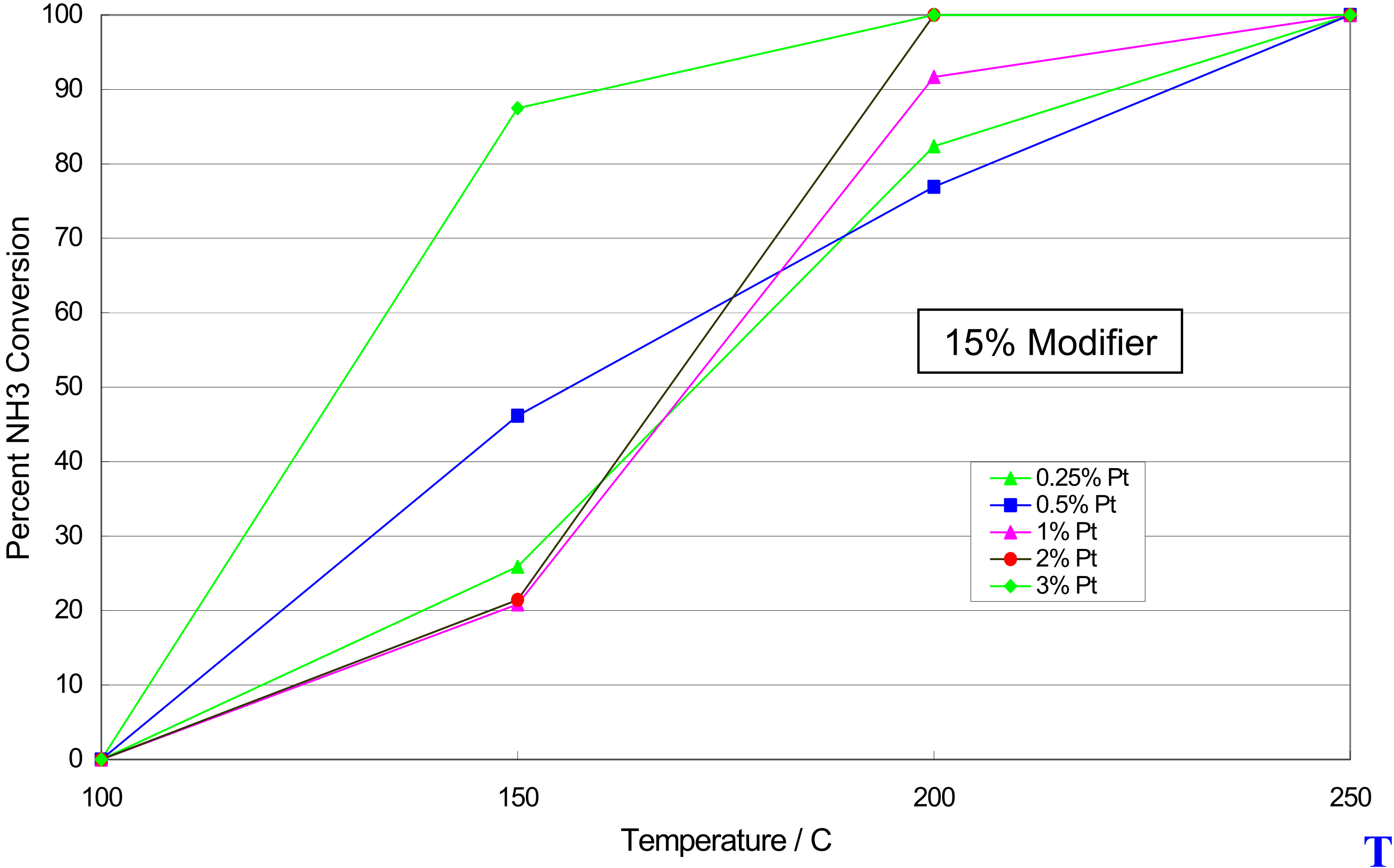
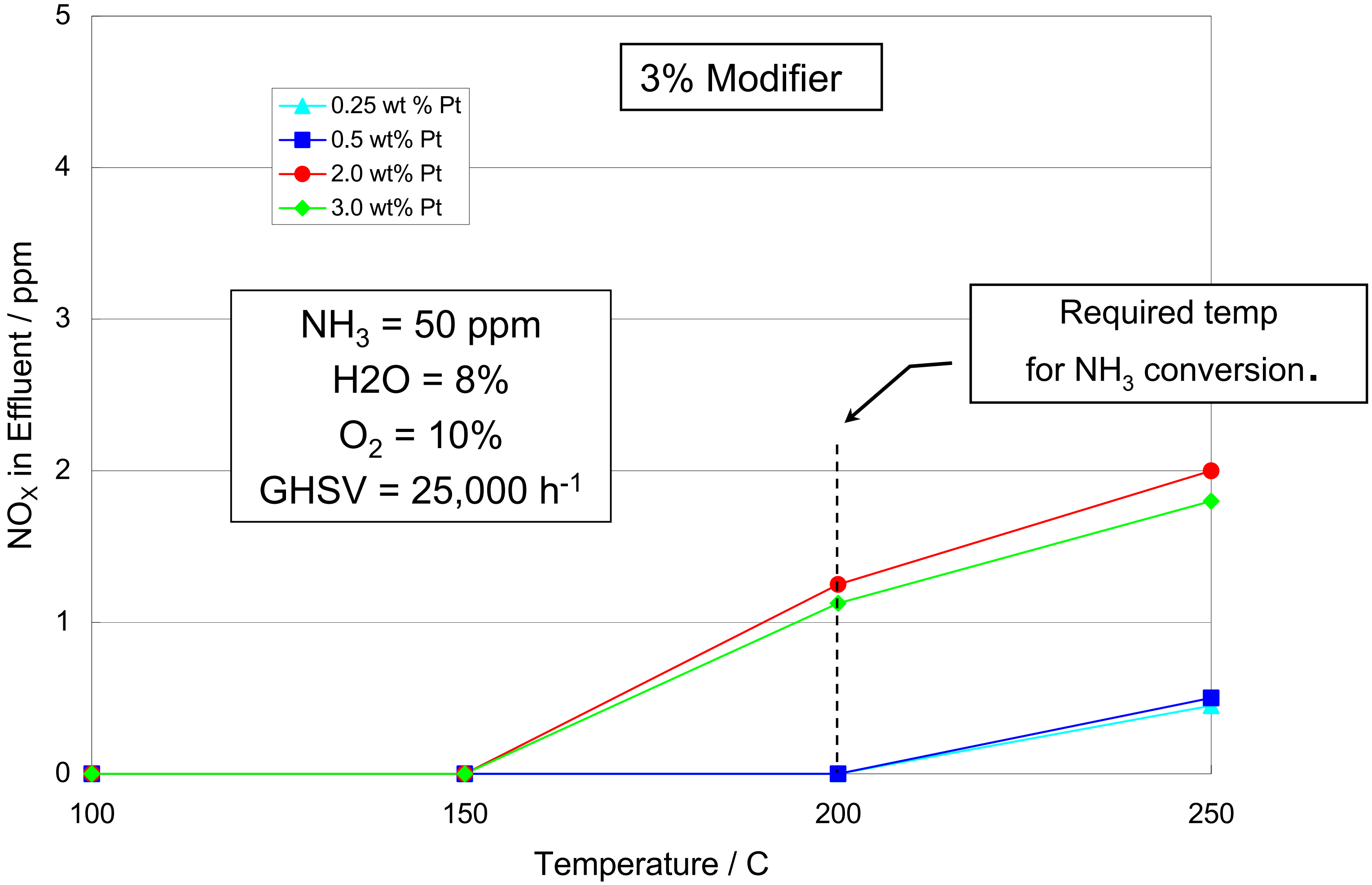
15% Modifier Reduced the Catalyst Activity



NO_X Levels over 1 ppm at 200°C with 3% Modifier



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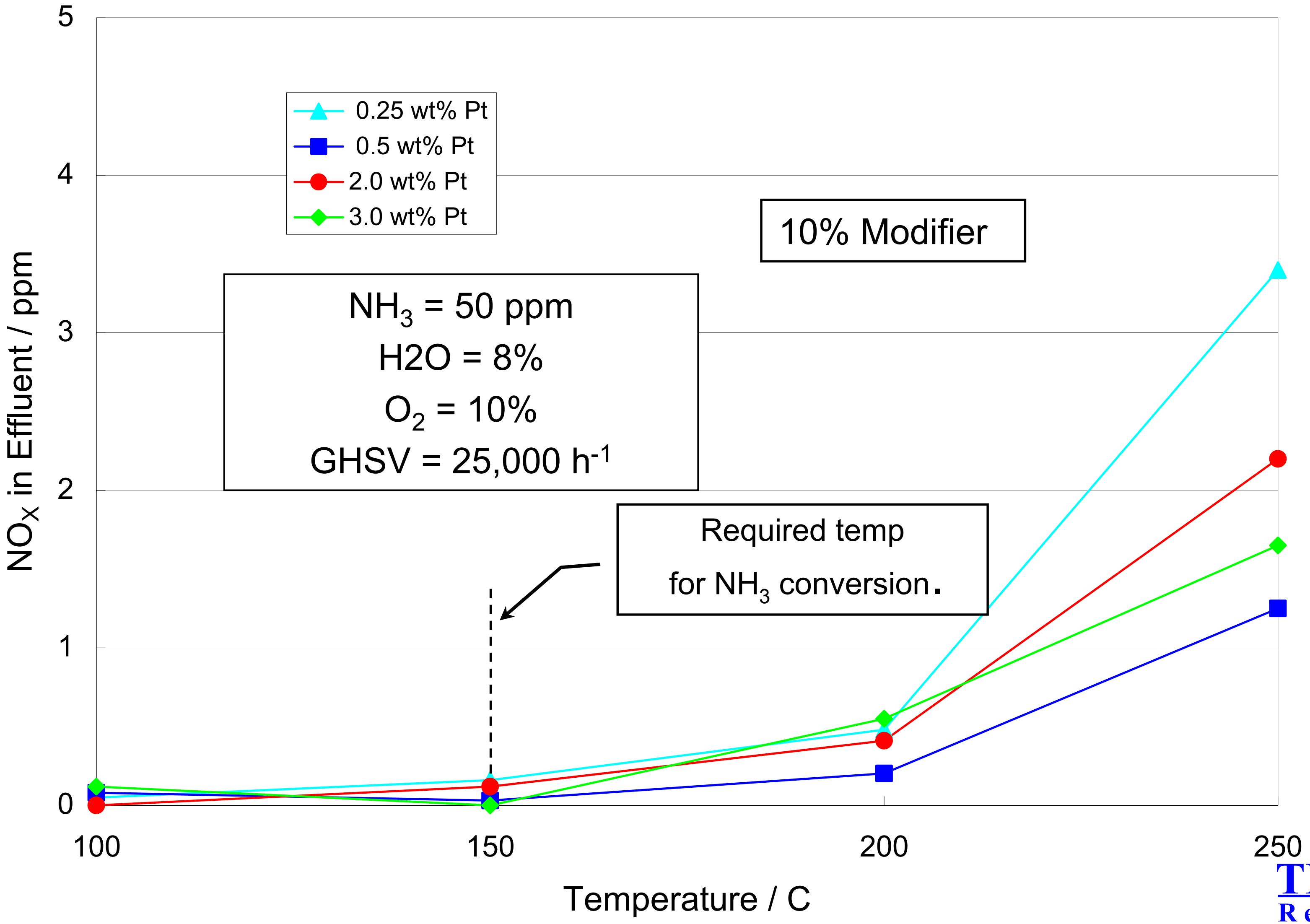
Very Little NO_X Production at 150°C with 10% Modifier



10% Modifier

NH_3 = 50 ppm
H2O = 8%
O_2 = 10%
GHSV = 25,000 h^{-1}

Required temp
for NH_3 conversion.

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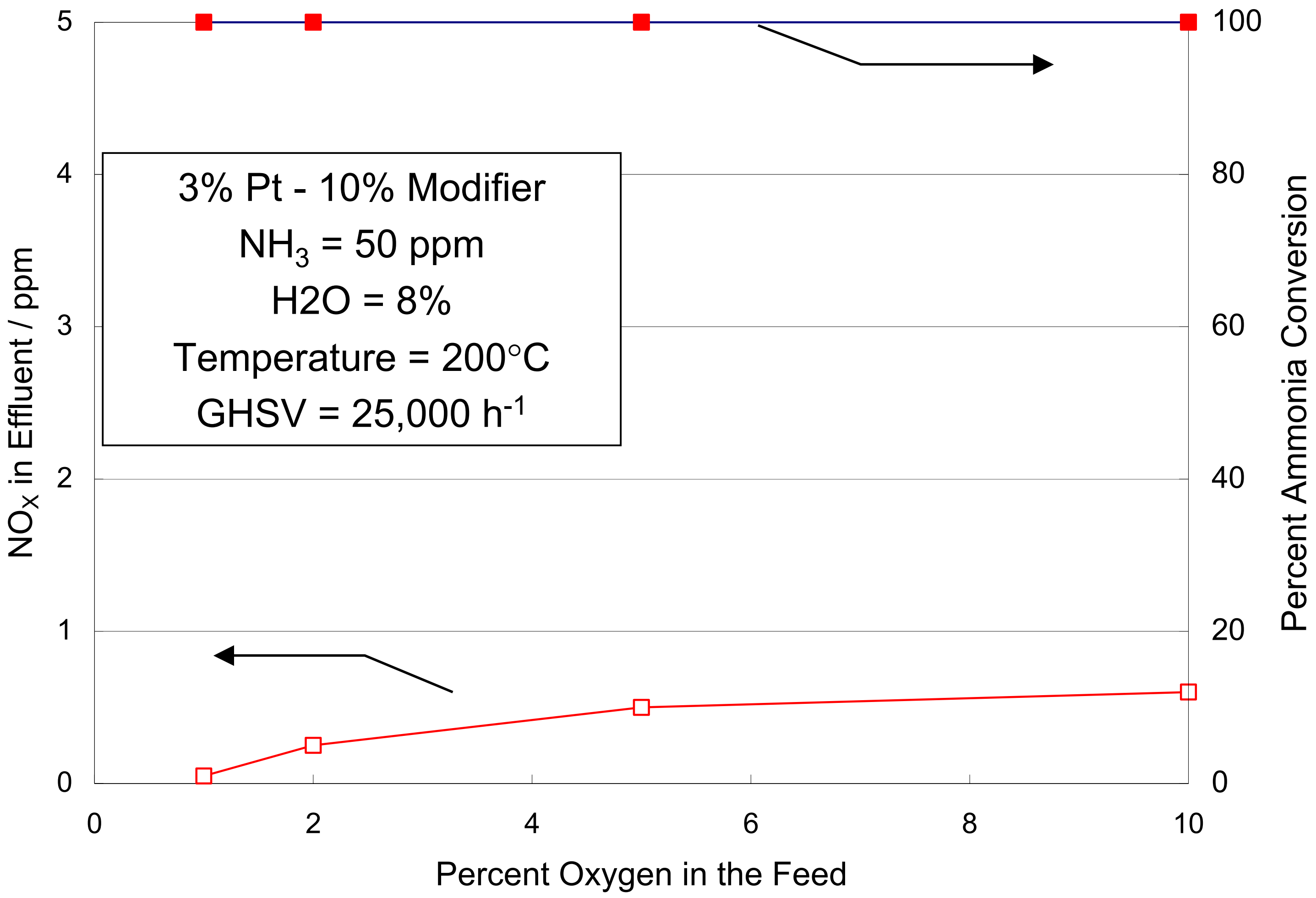
Reducing Oxygen Concentration Lowers NO_X



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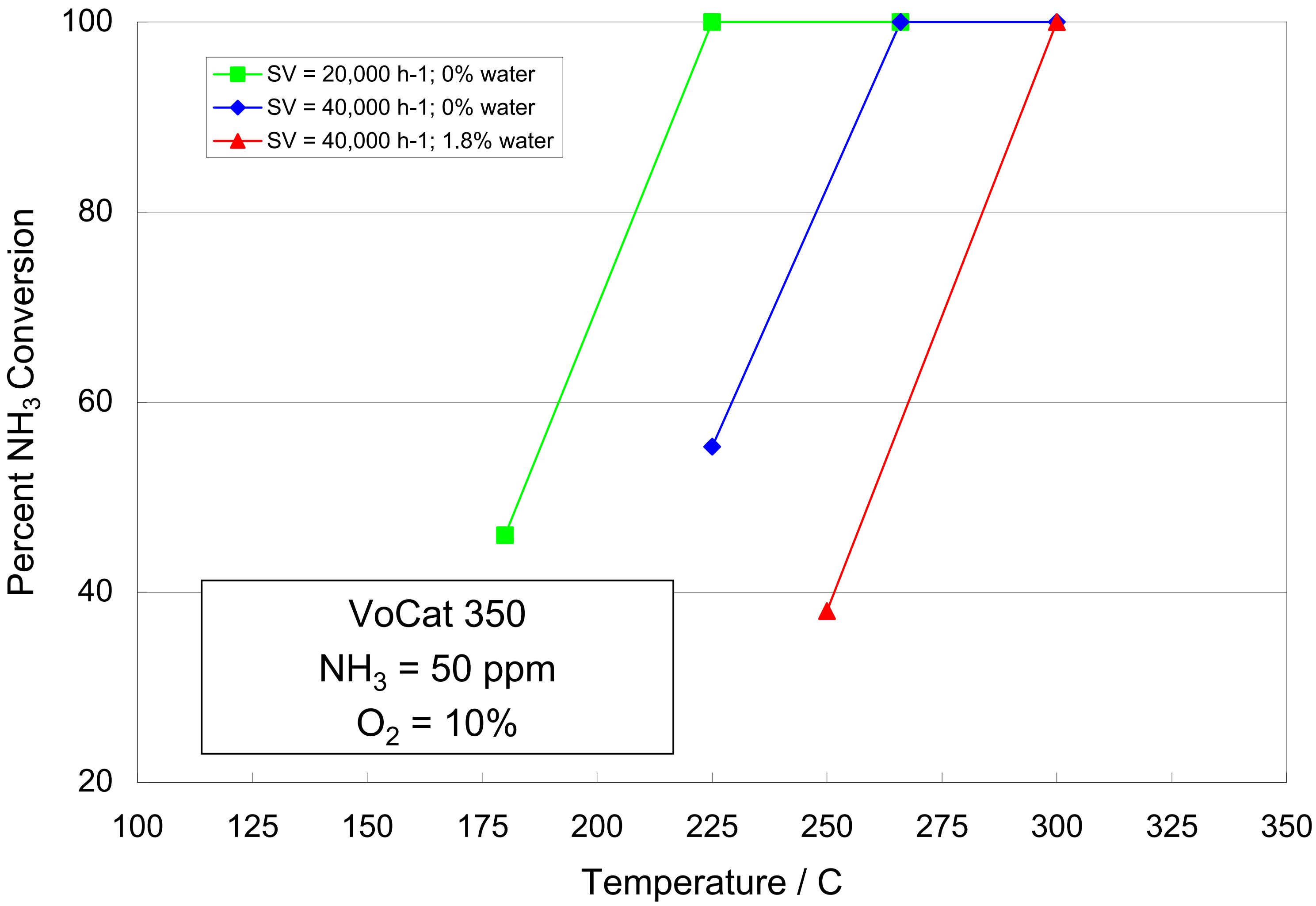
Comparison of TDA Catalyst to VoCat 350

- Best TDA catalyst consisted of 3% Pt 10% Modifier.
- VoCat 350 commercial oxidation catalyst consisting of Pt/Al_2O_3.
- We compared the activity of these catalysts at higher space velocities and in the presence of water.

VoCat Conversion is Affected by Water



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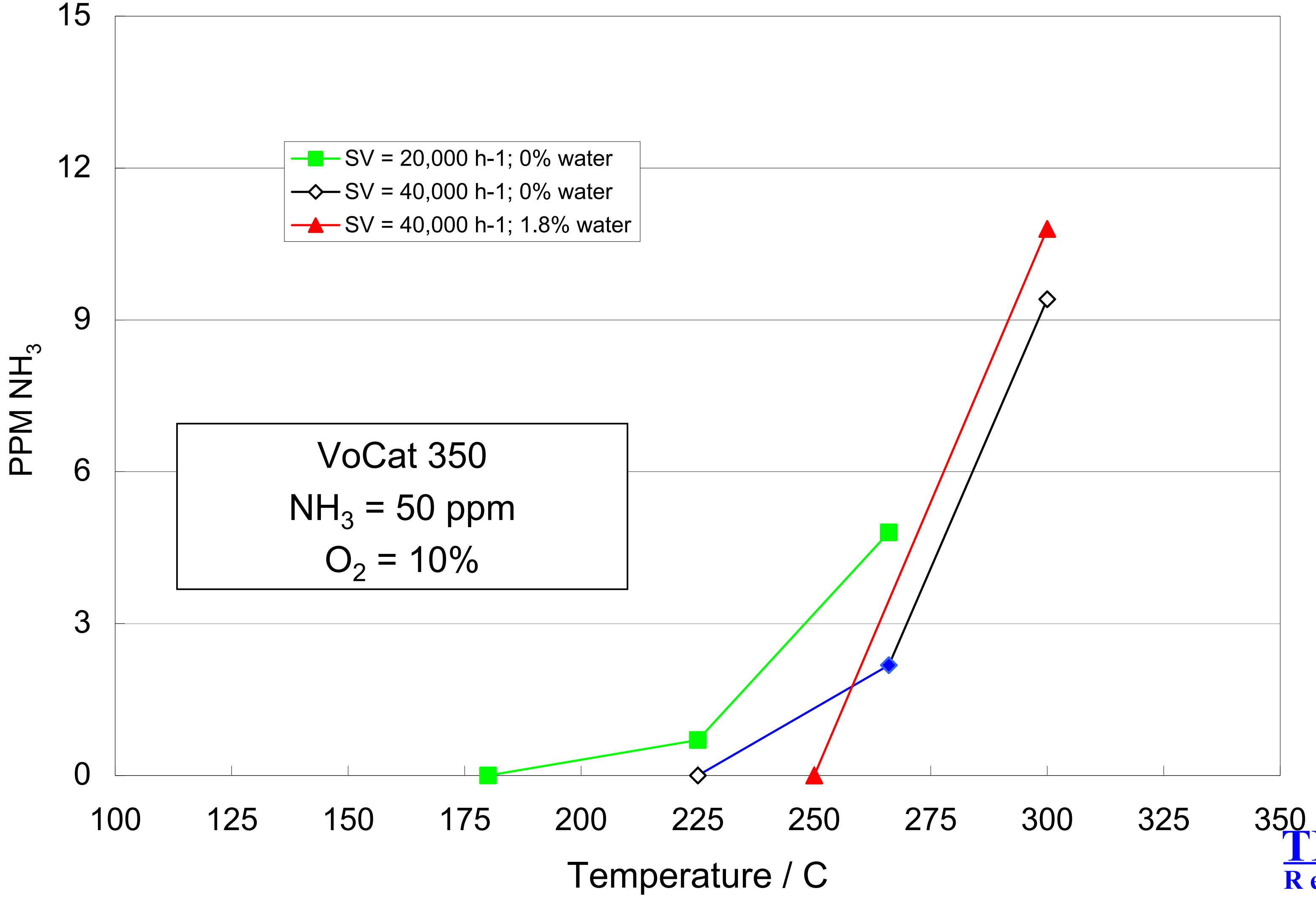
High NO_X at Temperatures Required for 100% Conversion



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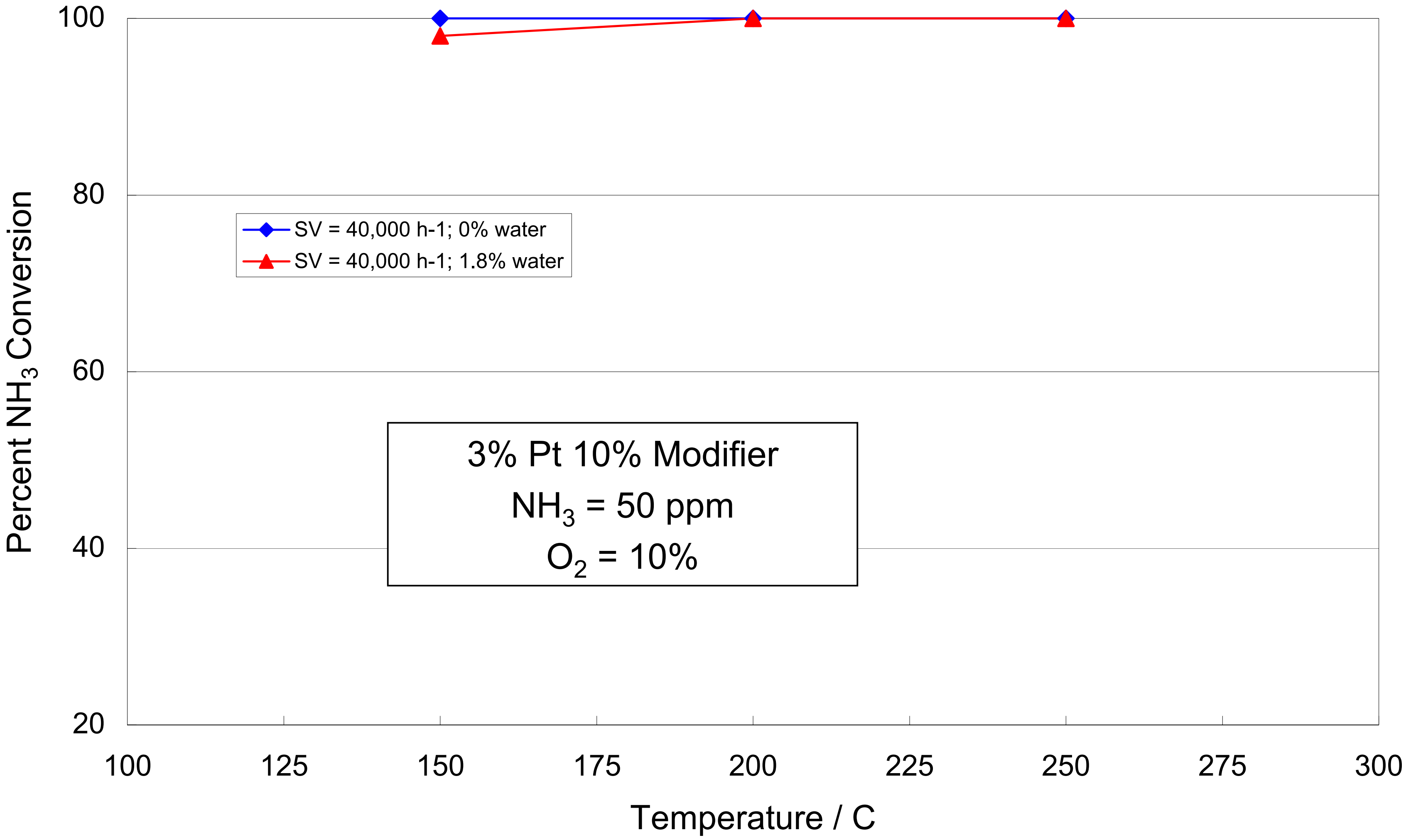
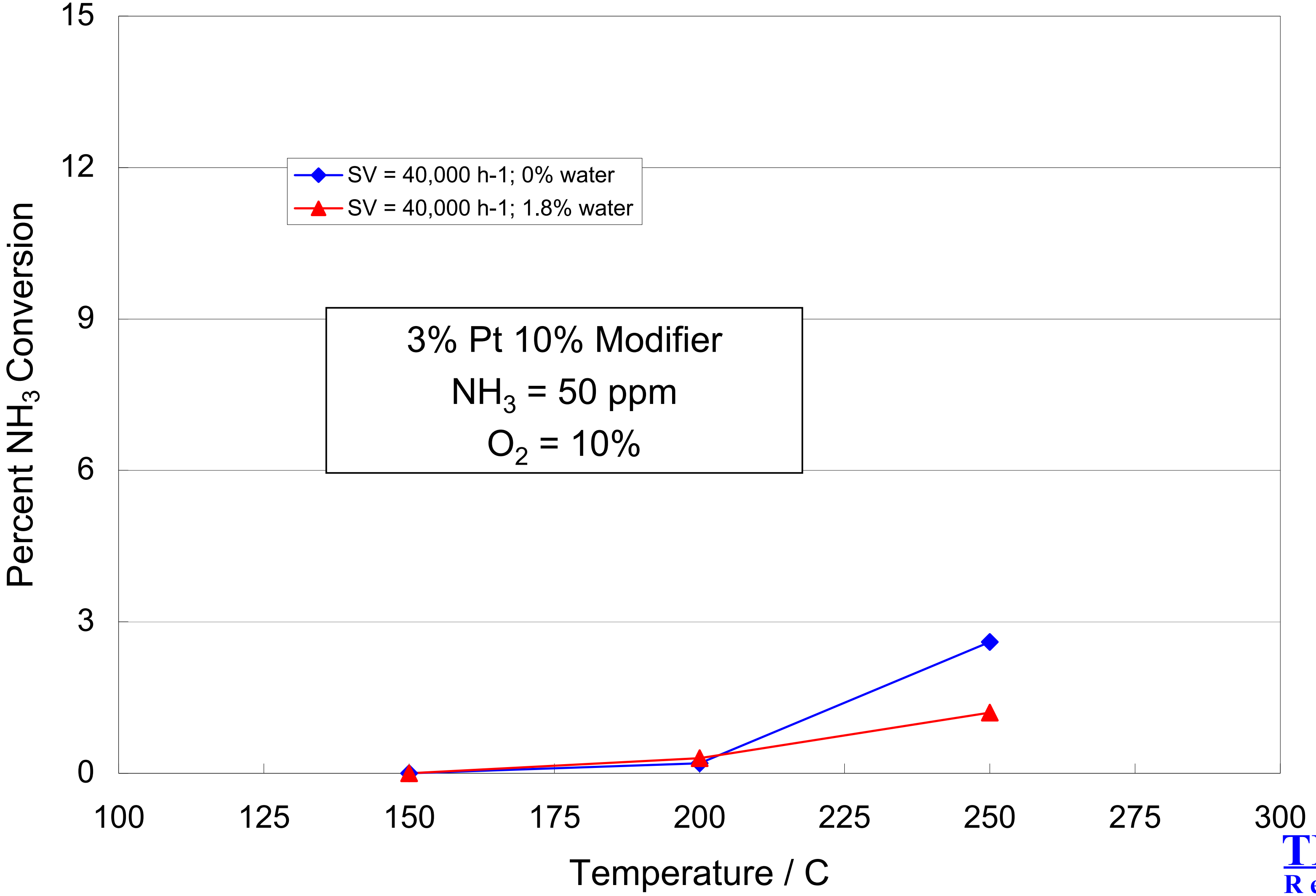
Conversion on TDA Catalysts Higher than Obtained on VoCat



3% Pt 10% Modifier
NH_3 = 50 ppm
O_2 = 10%

Low NOX at Temperatures Producing 100% Conversion



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Tests to Characterize Activity of the TDA Oxidation Catalyst

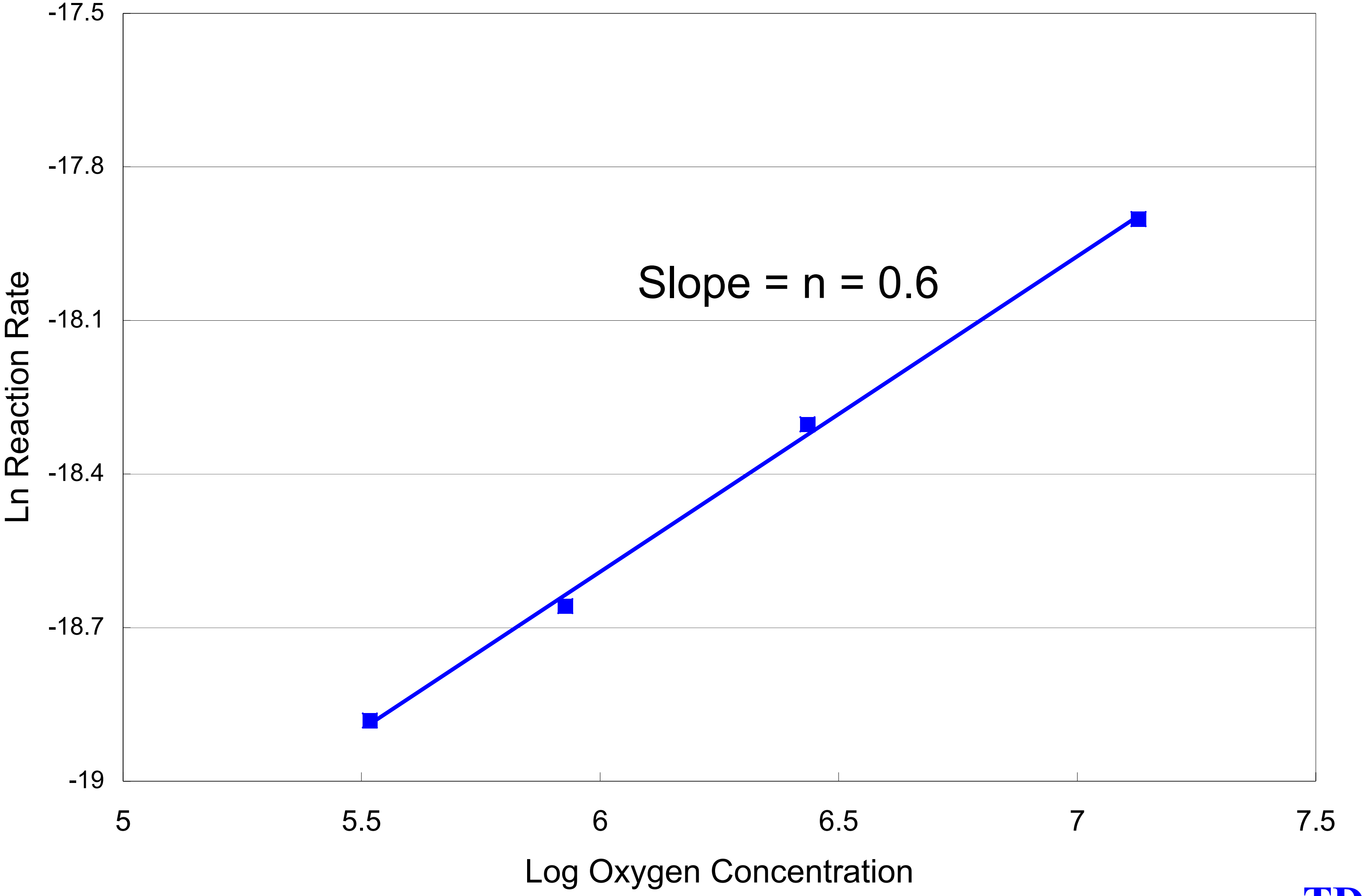
- **Characterize reaction kinetics.**
  - Measure dependence of reaction rate on oxygen and ammonia partial pressure.
  - Determine dependence of reaction rate on reaction temperature.
- **Use data to calculate conversion in the full scale VPCAR system.**

Rate Equation

$$\text{Rate} = v \exp[-Ea/RT] * P_{NH3}{}^{m} * P_{O2}{}^{n}$$

Solve or m,n Ea, and v.

Rate is About 0.6 Order in Oxygen Pressure



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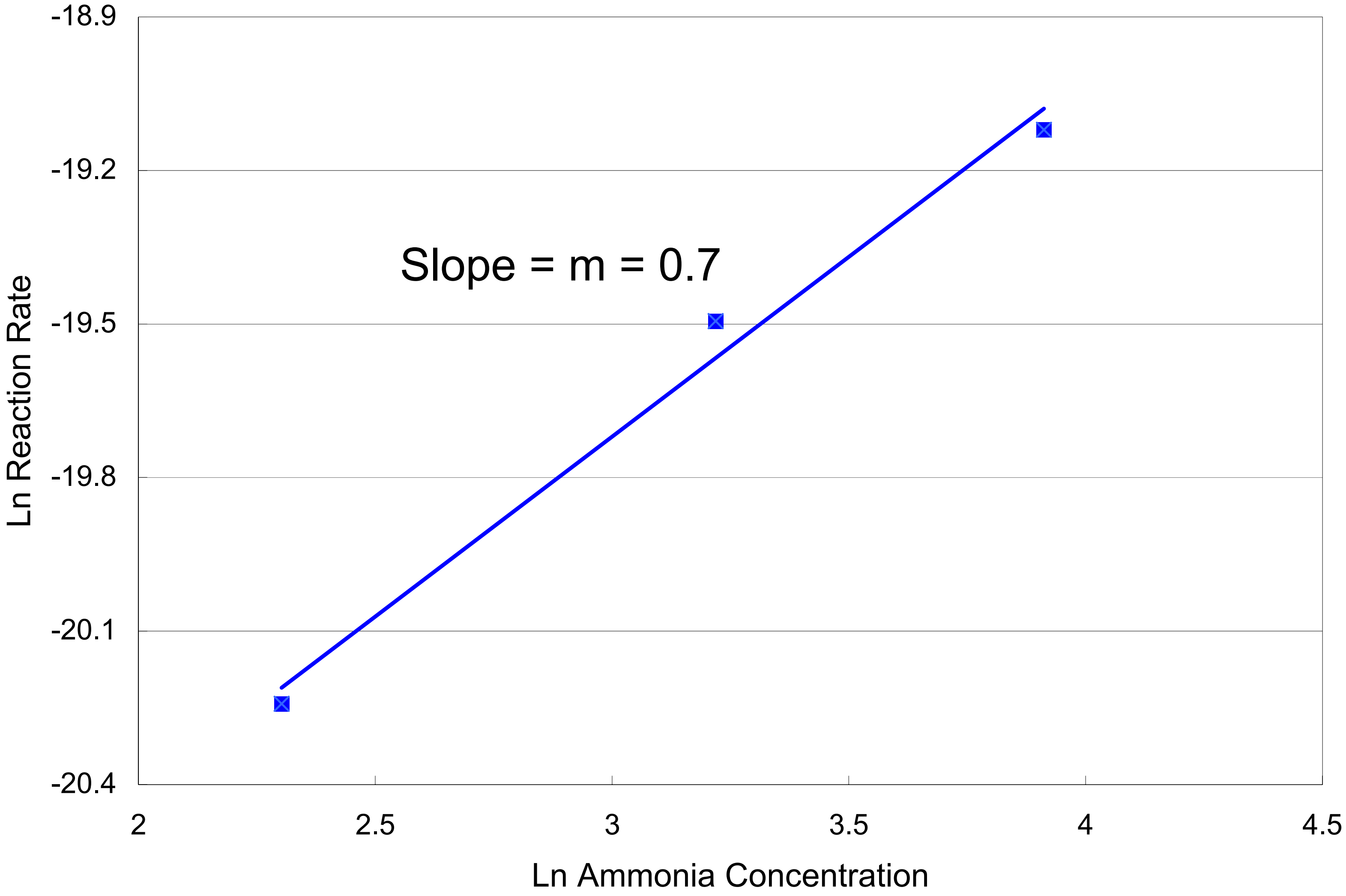
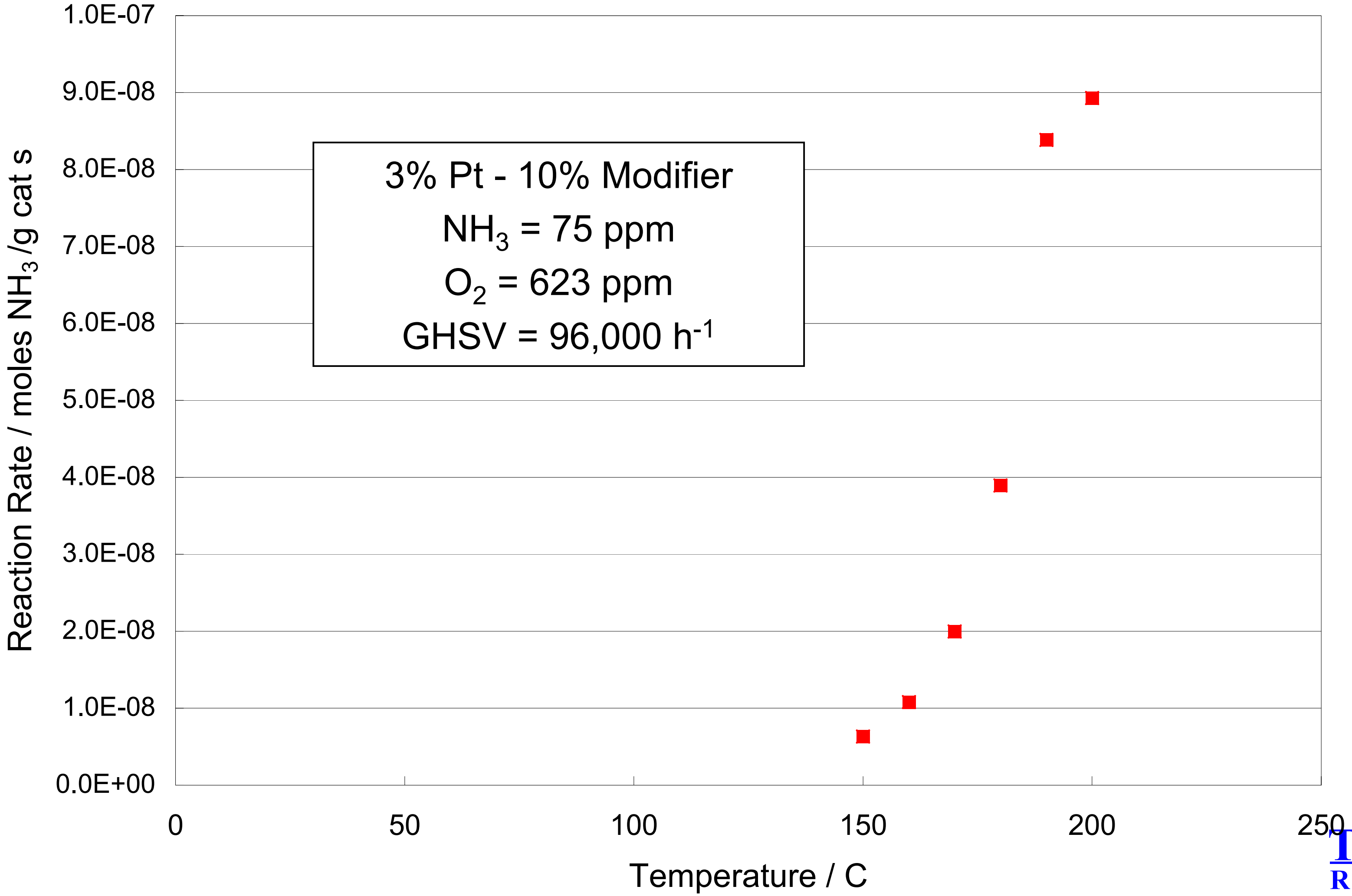
Similar Analysis on Ammonia



Slope = m = 0.7

Rate Changes Rapidly above 150°C



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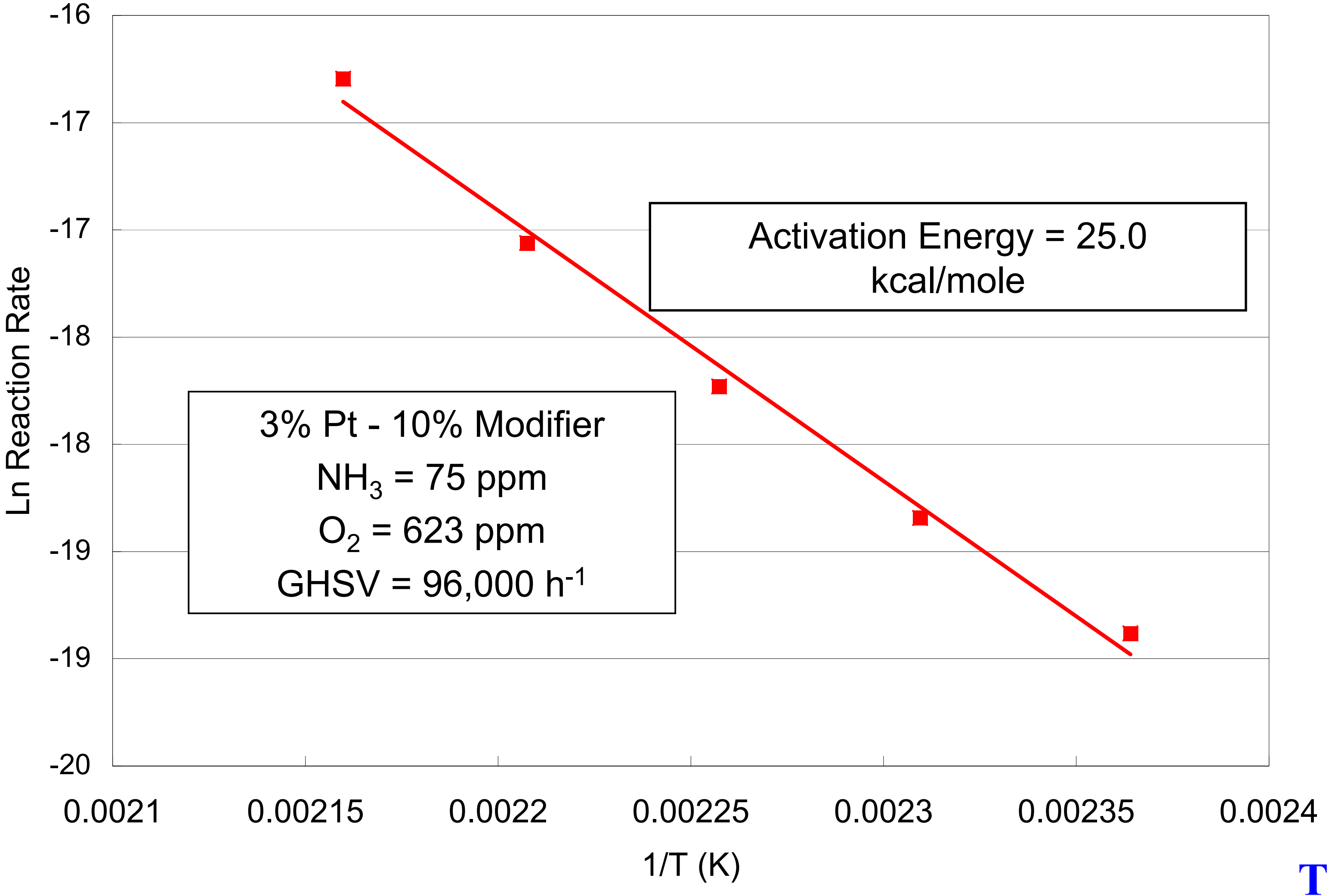
Temperature Dependence of the Ammonia Oxidation Reaction



Activation Energy = 25.0 kcal/mole

3% Pt - 10% Modifier

NH_3 = 75 ppm

O_2 = 623 ppm

GHSV = 96,000 h^{-1}

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Rate Equation

$$\text{Rate} = v \exp[-Ea/RT] * P_{NH3}^{m} * P_{O2}^{n}$$

$m = 0.6$, $n = 0.7$

$Ea = 25.0$ kcal/mole

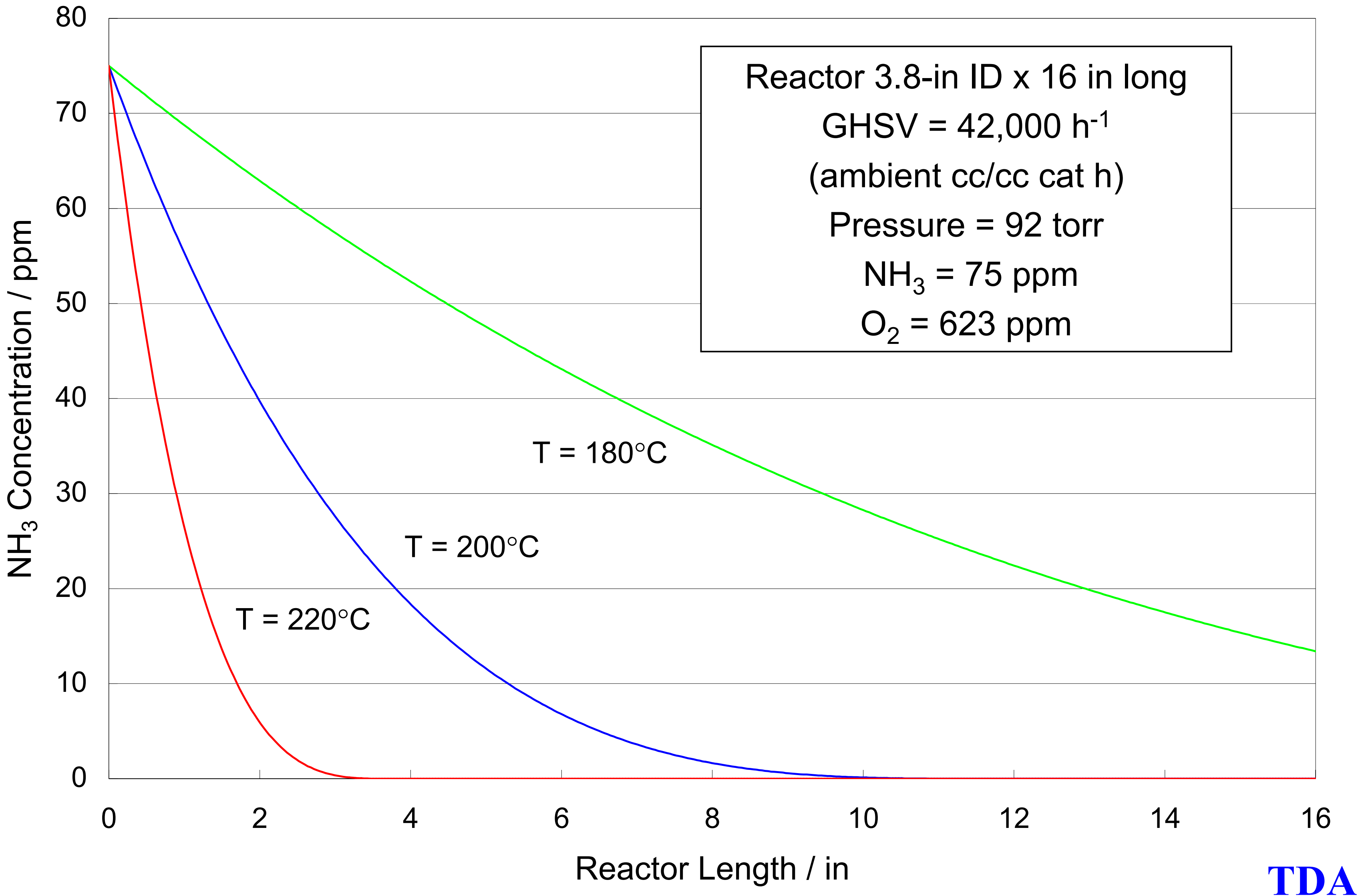
$v = 1.95$ E9 moles/g cat s atm$^{1.2}$

Operating Conditions in the Full Scale System*

- Catalytic reactor is 3.8-in ID x 16-in long.
- Operating pressure = 92 torr.
- Nominal water flow = 13.2 lb/h.
- O_2 flow = 0.13 lb/h (723 ppm at 0.82 atm).
- Operating temperature = 250°C.

* From Hamilton Sundstrand

Preliminary Reactor Design



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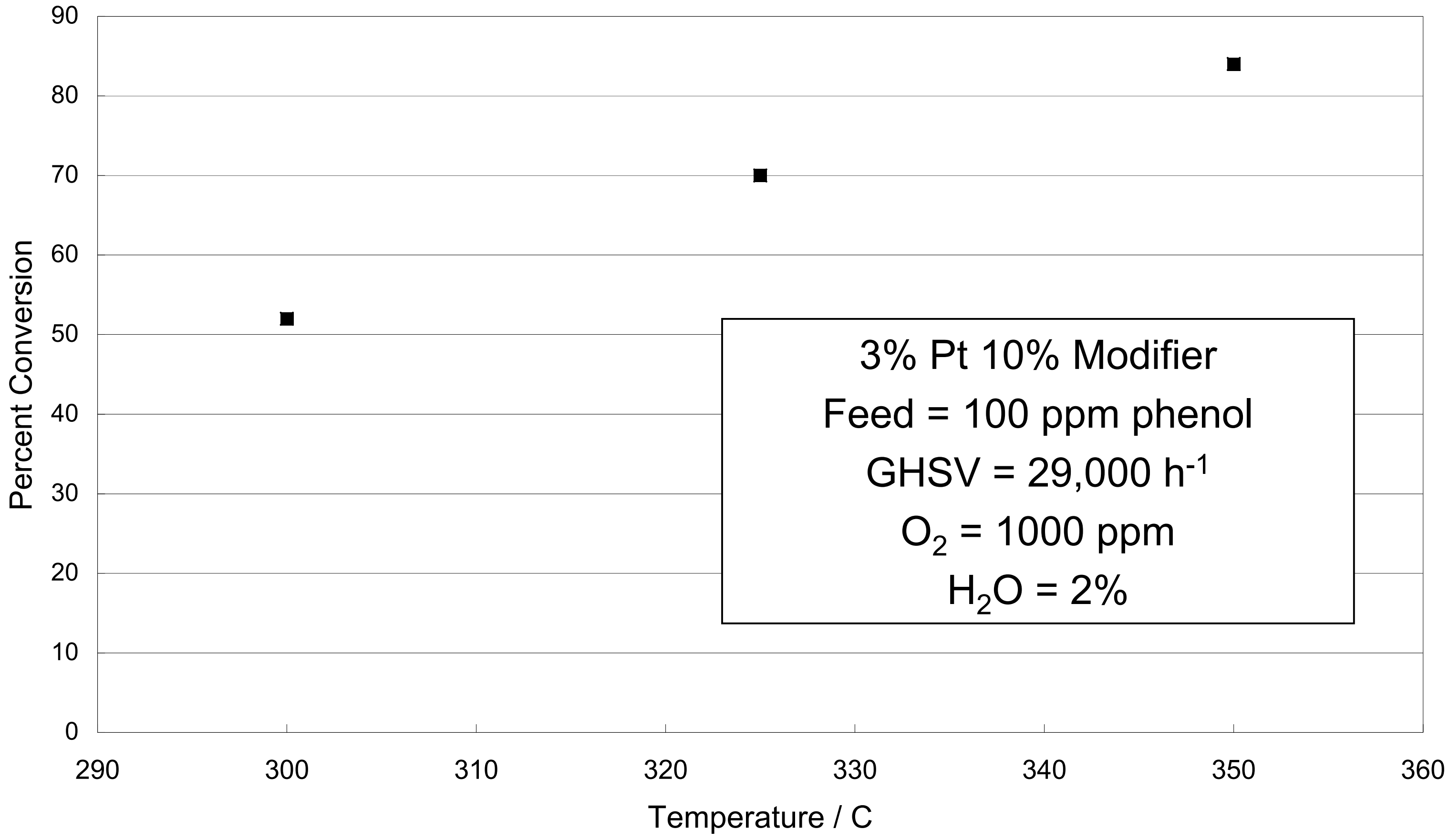
The Catalyst will Oxidize HC’s at Higher Temperature



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Summary and Conclusions

- TDA has identified a catalyst that is very active for ammonia oxidation and produces very little NO_X.
- The data suggest that the optimum catalyst composition is 3%Pt and 10% modifier.
- The catalyst is more active than the commercial oxidation catalyst and produces less NO_X.
- A preliminary reactor design for the full scale VPCAR shows that the catalyst will achieve 100% conversion at 195°C (< the design temperature).
- Very little NO_X should be produced under these conditions.

Acknowledgements

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