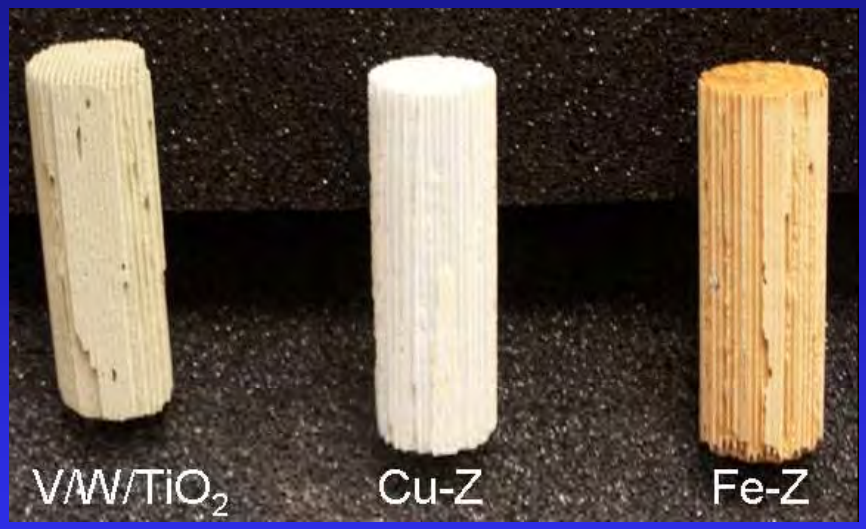
SCR DEACTIVATION KINETICS STUDY FOR CONTROL AND AGING APPLICATIONS

SwRI Internal Research Project



NH_3 STORAGE CAPACITY AND *Ed* DETERMINATION

Final Report

Presentation Outline

- Project Objectives
- BASF Fe-Zeolite catalyst - recap
  - NH_3 storage capacity (Ω) test conditions, results and conclusions
  - Deactivation energy (*Ed*) determination
- Johnson Matthey V/W/TiO2 'SINOx' Catalyst - recap
  - NH_3 storage capacity (Ω) test conditions, results and conclusions
  - Deactivation energy (*Ed*) determination
- BASF Cu-Zeolite catalyst – new data
  - NH_3 storage capacity (Ω) test conditions, results and conclusions
  - Deactivation energy (*Ed*) determination
- Overall Summary and Conclusions

Project Objectives

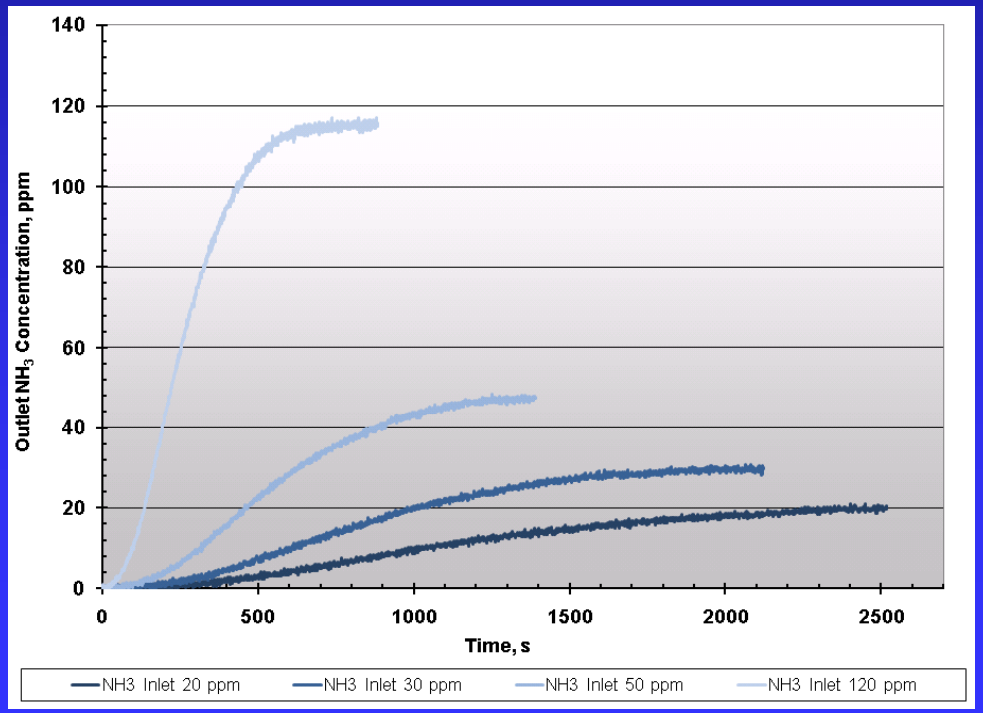
- SwRI Completed an Internal Research and Development Project to Better Understand SCR Catalyst Deactivation in Fall 2010
  - The project had three primary objectives:
    - Evaluate NH_3 storage capacity (Ω) as a function of aging time and temperature to provide data for on board SCR catalyst model-based control algorithms
    - Determine deactivation energies (*Ed*) for each SCR formulation to assist in accelerated thermal aging calculations using Arrhenius equation
    - Evaluate NO_x transient response with NH_3 transients for possible use as an On-Board Diagnostic (OBD) metric - presented in 2010. Not repeated here.

Catalyst Aging

- 1 inch diameter x 1 inch long core
- Aged in situ in SwRI Universal Synthetic Gas Reactor® (USGR®)
- Gas Mixture: 14% O_2, 5% CO_2, 6% H_2O, balance N_2
- Space Velocity: 60,000 hr^{-1}
- Fe-Zeolite
  - Preconditioned 2 hours, 350°C (Max. Ω)
  - Aged 2, 4, 8, 16 hours at 475, 550, 625, 700°C
- $V/W/TiO_2$
  - Preconditioned 2 hours, 600°C (Max. Ω)
  - Aged 2, 4, 8, 16 hours at 550, 600, 650, 700°C
- Cu-Zeolite
  - Preconditioned 8 hours, 775°C (Max. Ω)
  - Aged 2, 4, 8, 16 hours at 700, 775, 800, 850°C

Fe-Zeolite
NH_3 Adsorption Test Conditions

- Gas Mixture: 14% O_2, 5% CO_2, 5% H_2O, X ppm NH_3, balance N_2
- Test Temperature 200°C ± 0.5°C (tight control critical)
- Space Velocity 120,000 hr^{-1}
- Catalyst 'cleaned' of NH_3 Between Test Points (NO + NO_2 + NH_3 fast reaction used)
- NH_3 Setpoints 20, 30, 50, 120 ppm
- Note Single Point Equilibration Times as Long as 54 Minutes at 20 ppm NH_3 Concentration



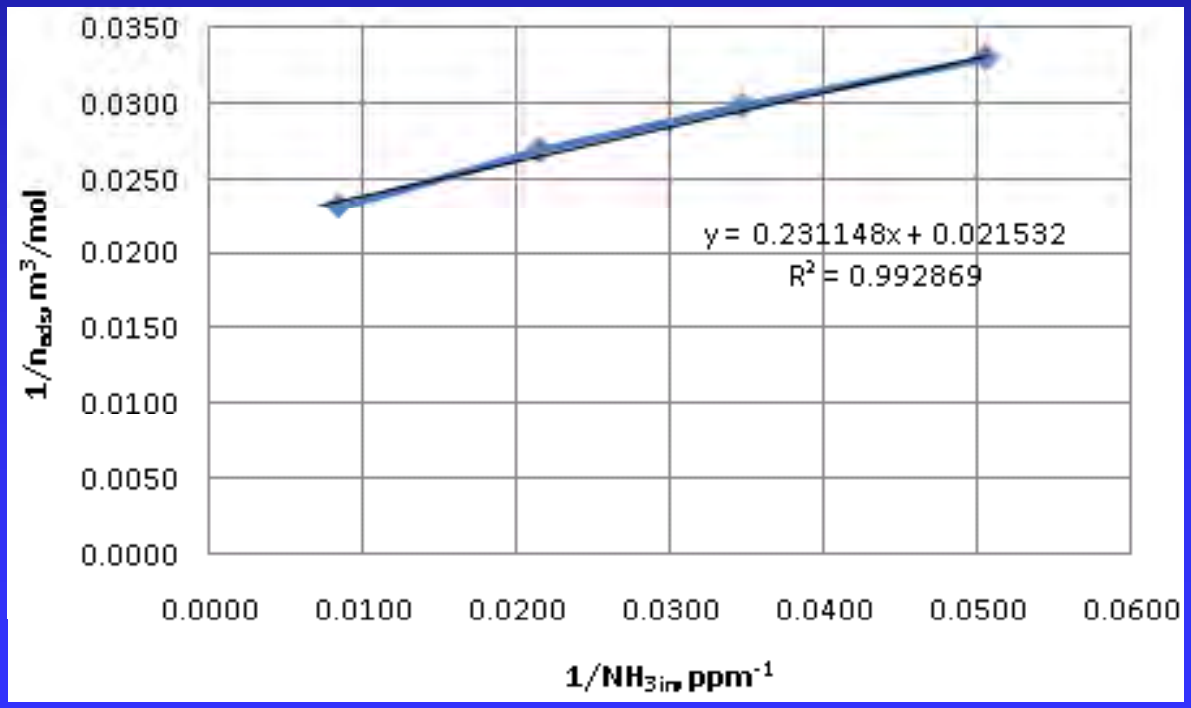
Fe-Zeolite
NH_3 Adsorption Test Results (1)

- Data fitted to Langmuir adsorption isotherm model by plotting the data in Langmuir coordinates

$$1/n_{ads} = 1/\Omega + 1/(K_{eq} \times \Omega) \times 1/C_{NH_3}$$

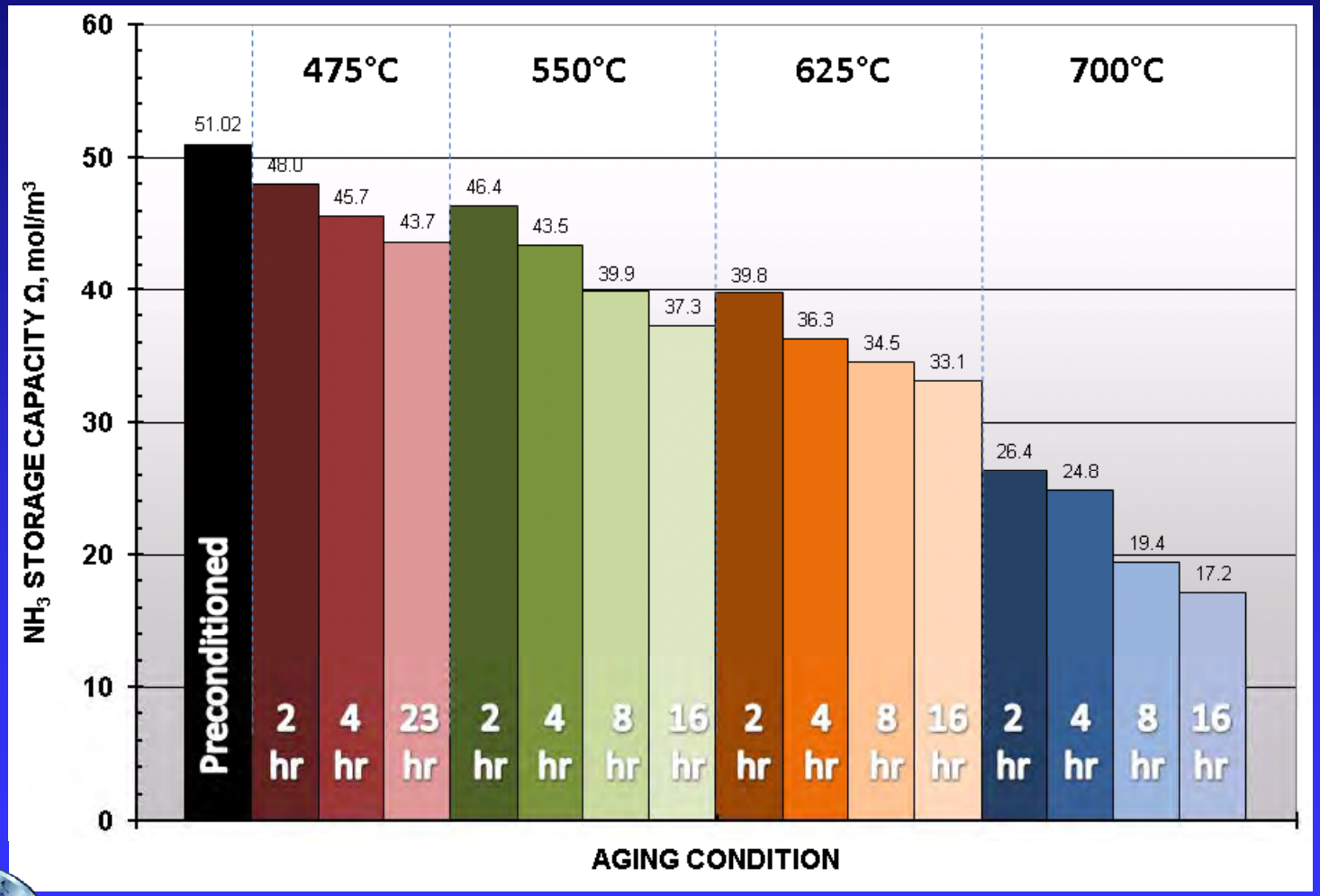
Plotting $1/n_{ads}$ as a function of $1/C_{NH_3}$ yields a line with slope $1/(K_{eq} \times \Omega)$ and intercept $1/\Omega$

  - R2 = 0.99, therefore NH_3 adsorption obeyed a Langmuir type isotherm well



Fe-Zeolite
NH_3 Adsorption Test Results (2)

- NH_3 Storage Capacity Decreased with Aging Time and Temperature



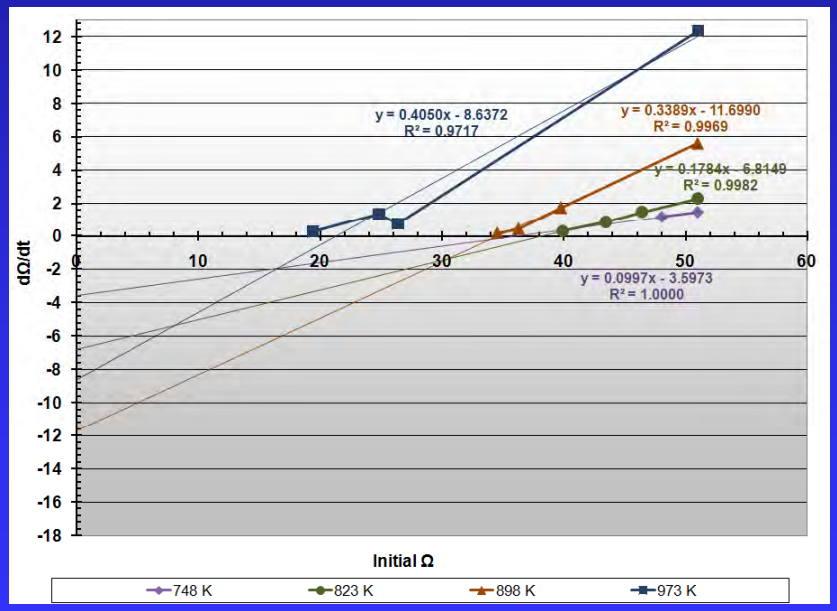
Fe-Zeolite
Deactivation Energy Determination, *Ed* (1)

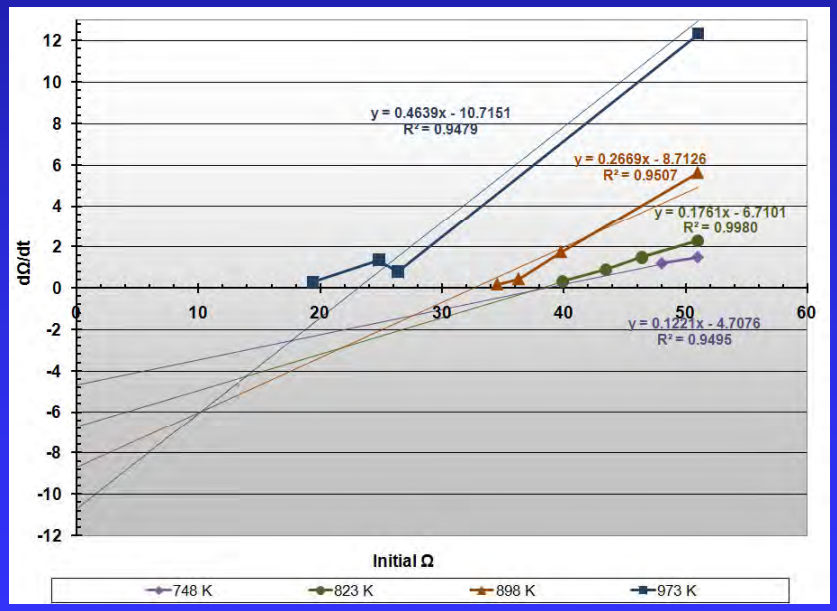
- 1st Order Rate Equation Returned 'Straight' Lines with Variable Intercepts

Rate Equation $- d\Omega/dt = k\Omega_1 + (x - yT)$

Ω NH_3 storage capacity, mol/m^3 t time, hours k rate constant T temperature, K
x constant y constant

- Linear regression trendlines processed to obtain x and y constants

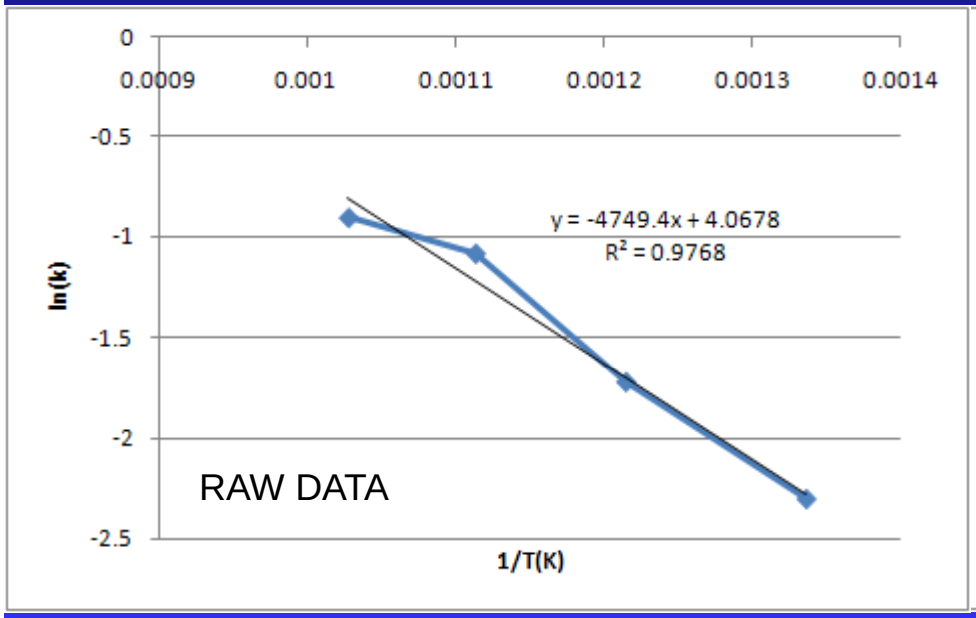


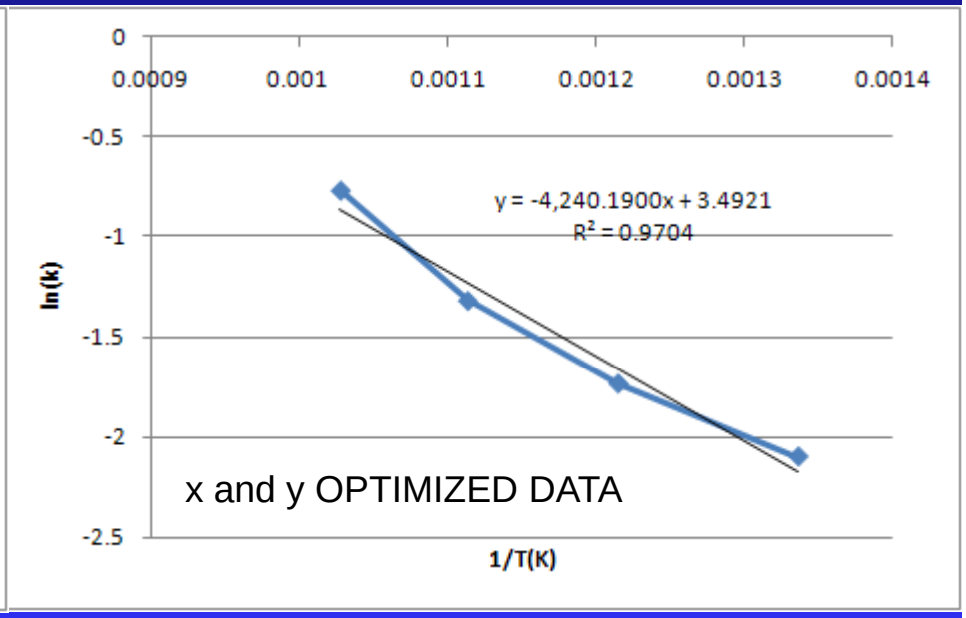


Fe-Zeolite
Deactivation Energy Determination, *Ed* (2)

Arrhenius Equation Plots $k = A e^{-(Ed / RT)}$

- Raw Data - *Ed* = 39.49 kJ/mol A = 56.83
- x and y Optimized Data - *Ed* = 35.26 kJ/mol A = 32.85 x = 15.268 y = 0.0267





Fe-Zeolite
Deactivation Energy Determination, *Ed* (3)

- MS Excel Solver Used to Obtain Best Fit Constants
- Best fit - *Ed* = 43.16 kJ/mol A = 118 x = 45.05 y = 0.06454

	MEASURED Ω			
	TEMPERATURE, Kelvin			
Aging, Hrs	748.15	823.15	898.15	973.15
2	48.0	46.4	39.8	26.4
4	45.7	43.5	36.3	24.8
8	nd	39.9	34.5	19.4
16	nd	37.3	33.1	17.2

Test Data

	CALCULATED Ω			
	TEMPERATURE, Kelvin			
Aging, Hrs	748.15	823.15	898.15	973.15
2	45.8	45.2	39.6	28.4
4	41.8	42.2	38.2	29.2
8	35.6	38.1	32.5	17.7
16	28.9	38.9	35.1	15.5

Calculated Values using Rate Equation

- $d\Omega/dt = k\Omega_1 + (x - yT)$

and Best Fit Constants

	PERCENTAGE ERRORS			
	TEMPERATURE, Kelvin			
Aging, Hrs	748.15	823.15	898.15	973.15
2	4.6	2.6	0.4	7.7
4	8.6	2.9	5.3	17.6
8		4.5	5.8	9.0
16		4.2	6.0	9.6
Average % error =		6.3		

Comparative Errors

Fe-Zeolite
Summary and Conclusions (1)

- Aging of Catalyst for 2, 4, 8 and 16 Hours at 475, 550, 625 and 700°C Decreased NH_3 Storage Capacity (Ω)

Using 1st Order Rate Equation

- Deactivation Energy *Ed* determined to be 43 kJ/mol
- Pre-Exponential Factor A determined to be 118

Fe-Zeolite
Summary and Conclusions (2)

- Possible to Predict NH_3 Storage Capacity In-Field using Two Equations:

$$t_c = t_{c-1} + e^{\left[-\frac{Ed}{R}\left(\frac{1}{T2}-\frac{1}{T1}\right)\right]}$$

Equation 1

where t_c is the cumulative effective aging time, t_{c-1} is the previous cumulative effective aging time, *Ed* is the deactivation energy value (43 kJ/mol), *R* is the molar gas constant (0.00831451 kJ/mol/K), *T*1 is the given effective aging temperature and *T*2 is the current actual measured temperature

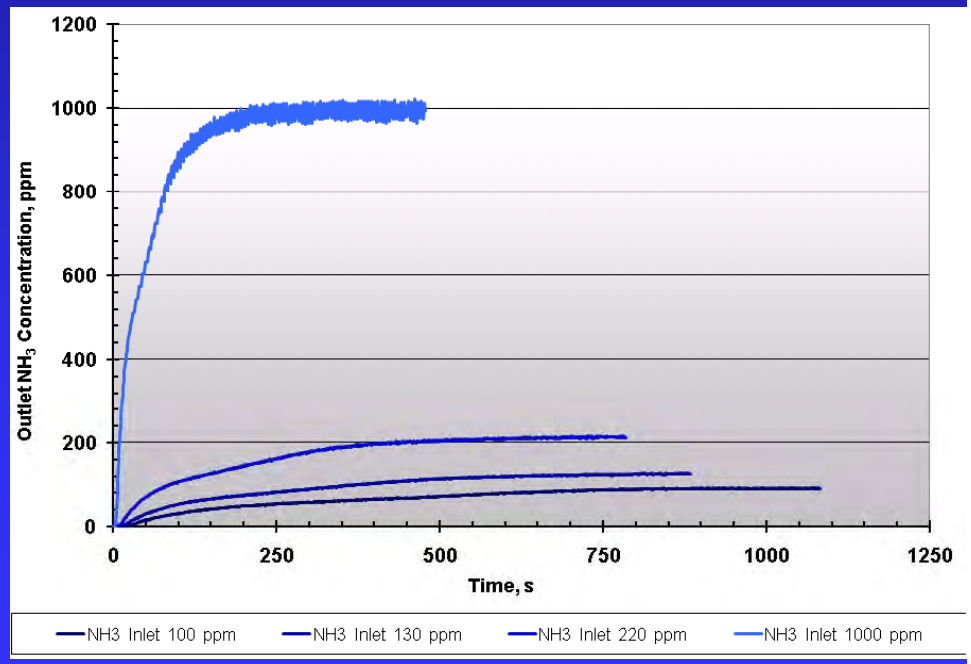
$$\Omega = \Omega_0 - t_c * \left[\left(A * e^{\left(\frac{Ed}{RT1}\right)}\right) * \Omega_0 + (x - yT_1)\right]$$

Equation 2

where Ω is the current NH_3 storage capacity to be calculated, Ω_0 is the initial maximum NH_3 storage capacity (51.02 mol/m^3), t_c is the effective aging time calculated using Equation 1, A is the pre-exponential factor (118), *Ed* is the deactivation energy value, R is the molar gas constant, T_1 is the given effective aging temperature and x and y are constants (45.05 and 0.06454)

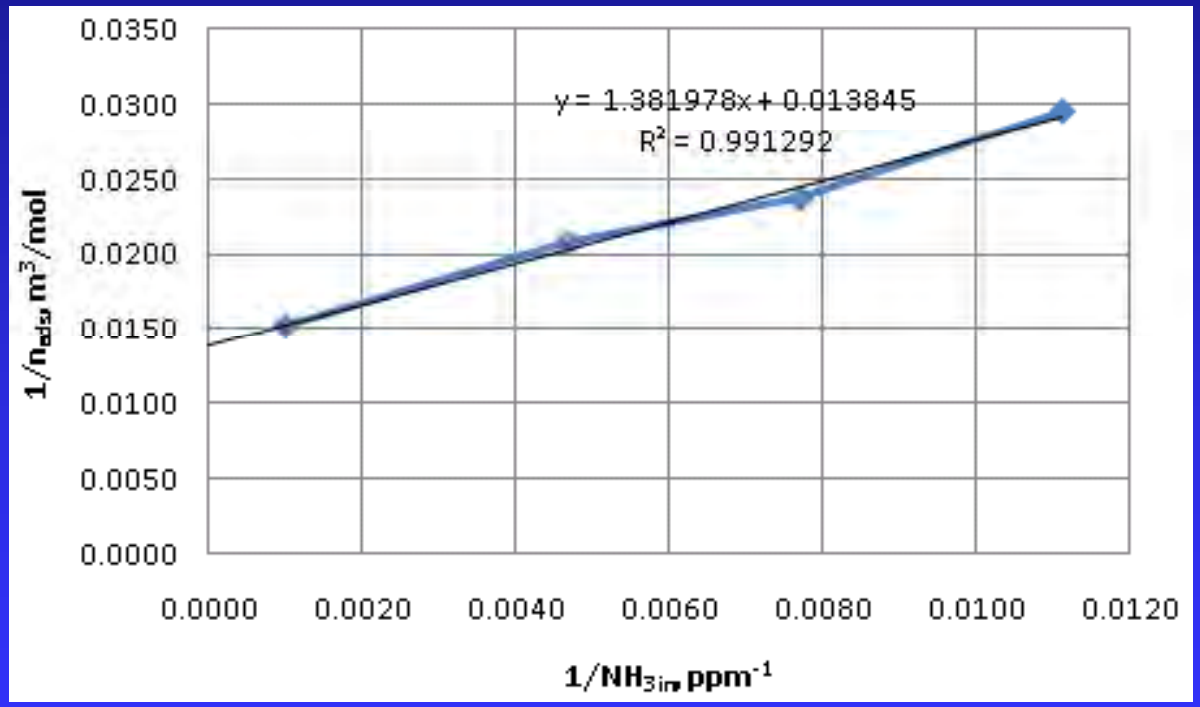
$V/W/TiO_2$
NH_3 Adsorption Test Conditions

- Gas Mixture: 14% O_2, 5% CO_2, 5% H_2O, X ppm NH_3, balance N_2
- Test Temperature 200°C
- Space Velocity 120,000 hr^{-1}
- Catalyst 'cleaned' of NH_3 Between Test Points (NO + NO_2 + NH_3 fast reaction used)
- NH_3 setpoints 100, 130, 220, 1000 ppm
- Note Single Point Equilibration Times Still as Long as 37 Minutes Despite 100 ppm Lowest NH_3 Concentration



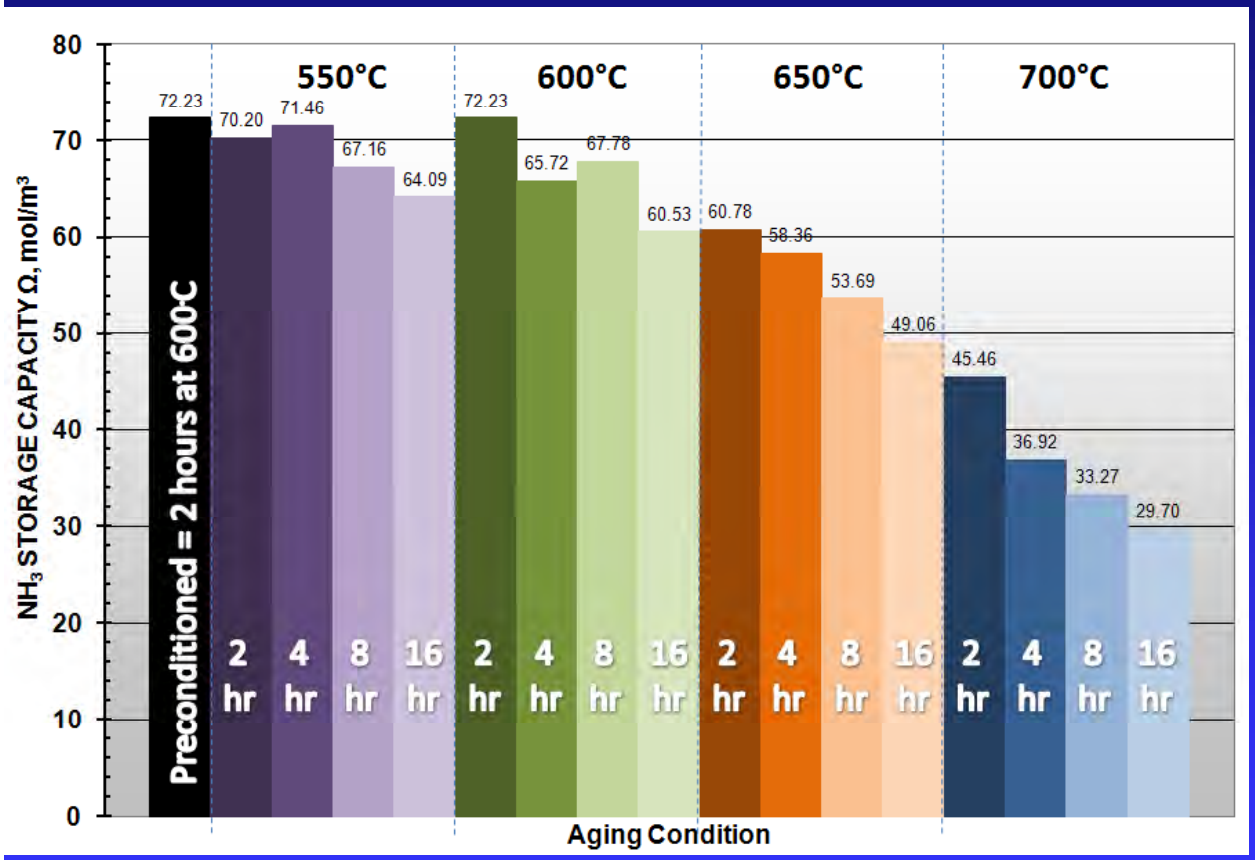
$V/W/TiO_2$
NH_3 Adsorption Test Results (1)

- Data fitted to Langmuir adsorption isotherm model by plotting the data in Langmuir coordinates
  - R2 = 0.99, therefore NH_3 adsorption obeyed a Langmuir type isotherm well



$V/W/TiO_2$
NH_3 Adsorption Test Results (2)

- NH_3 Storage Capacity Decreased with Aging Time and Temperature



- 550°C data includes some preconditioning, with deactivation at ≥ 8 hours
- 600°C data had inconsistent data points

550 and 600°C data could not readily be used for *Ed* calcs.

$V/W/TiO_2$
Deactivation Energy Determination, *Ed* (1)

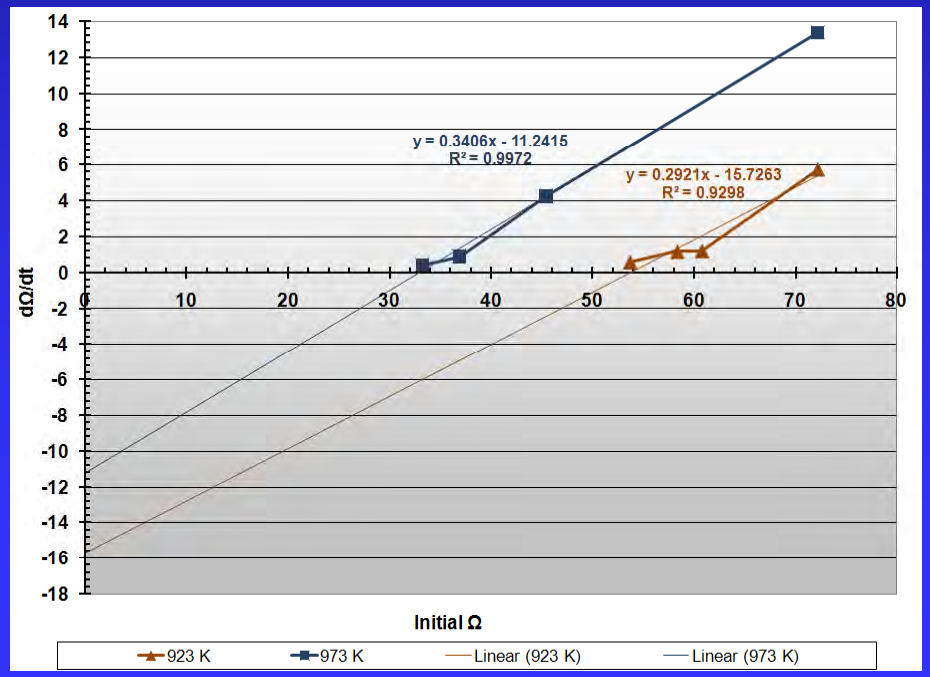
- 1st Order Rate Equation with Variable Intercepts

Rate Equation $- d\Omega/dt = k\Omega + (x - yT)$

Ω NH_3 storage capacity, mol/m^3 t time, hours k rate constant T temperature, K
x constant y constant

$k = A\, e^{-(Ed / RT)}$ Arrhenius Equation

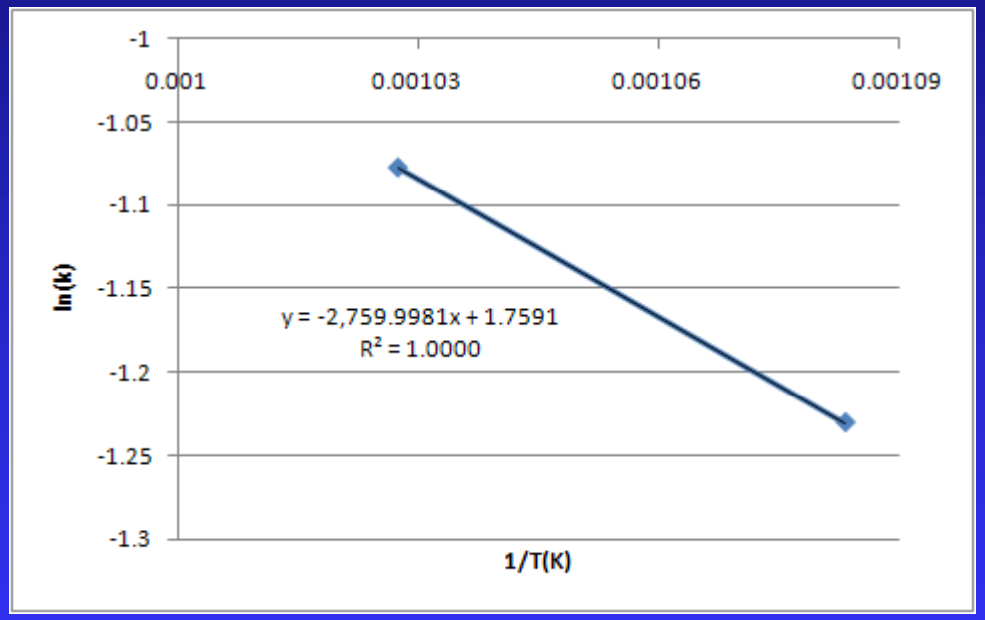
- Only 650 and 700°C data used (550°C data includes conditioning, 600°C data inconsistent)



$V/W/TiO_2$
Deactivation Energy Determination, *Ed* (2)

Arrhenius Equation Plots $k = A e^{-(Ed / RT)}$

- Raw Data - *Ed* = 22.95 kJ/mol A = 5.81



Only two test points used. Therefore, repeat/verification testing highly recommended

$V/W/TiO_2$
Deactivation Energy Determination, *Ed* (3)

- MS Excel Solver Used to Obtain Best Fit Constants
- Best fit - *Ed* = 98 kJ/mol A = 71971 x = 89.10 y = 0.10701

	MEASURED Ω			
	TEMPERATURE, Kelvin			
Aging, Hrs	823.15	873.15	923.15	973.15
2	70.2	72.2	60.8	45.5
4	71.5	66.8	58.4	36.9
8	67.2	62.3	53.7	33.3
16	64.1	60.5	49.1	29.7

Test Data

	CALCULATED OMEGA 2			
	TEMPERATURE, Kelvin			
Aging, Hrs	823.15	873.15	923.15	973.15
2	64.0	66.9	62.5	46.1
4	56.6	60.3	57.6	44.3
8	42.9	52.0	49.7	28.7
16	20.2	44.3	51.2	29.7

Calculated Values using Rate Equation

- $d\Omega/dt = k\Omega_1 + (x - yT)$

and Best Fit Constants

	PERCENTAGE ERRORS			
	TEMPERATURE, Kelvin			
Aging, Hrs	823.15	873.15	923.15	973.15
2	--	--	2.78	1.40
4	--	--	1.32	19.94
8	--	--	7.47	13.78
16	--	--	4.38	0.15
	Average % error =		6.40	

Comparative Errors

$V/W/TiO_2$
Summary and Conclusions (1)

- Aging of Catalyst for 2, 4, 8 and 16 Hours at 550, 600, 650 and 700°C Generally Decreased NH_3 Storage Capacity (Ω)
- Deactivation Energy *Ed* determined to be 98 kJ/mol
- Pre-Exponential Factor A determined to be 71971
  - Only two aging temperatures used in calculations (650 and 700°C)
  - Repeat/verification testing highly recommended, but not performed in this work

$V/W/TiO_2$
Summary and Conclusions (2)

- Possible to Predict NH_3 Storage Capacity In-Field using same two equations:

$$t_c = t_{c-1} + e^{\left[-\frac{Ed}{R}\left(\frac{1}{T2}-\frac{1}{T1}\right)\right]}$$

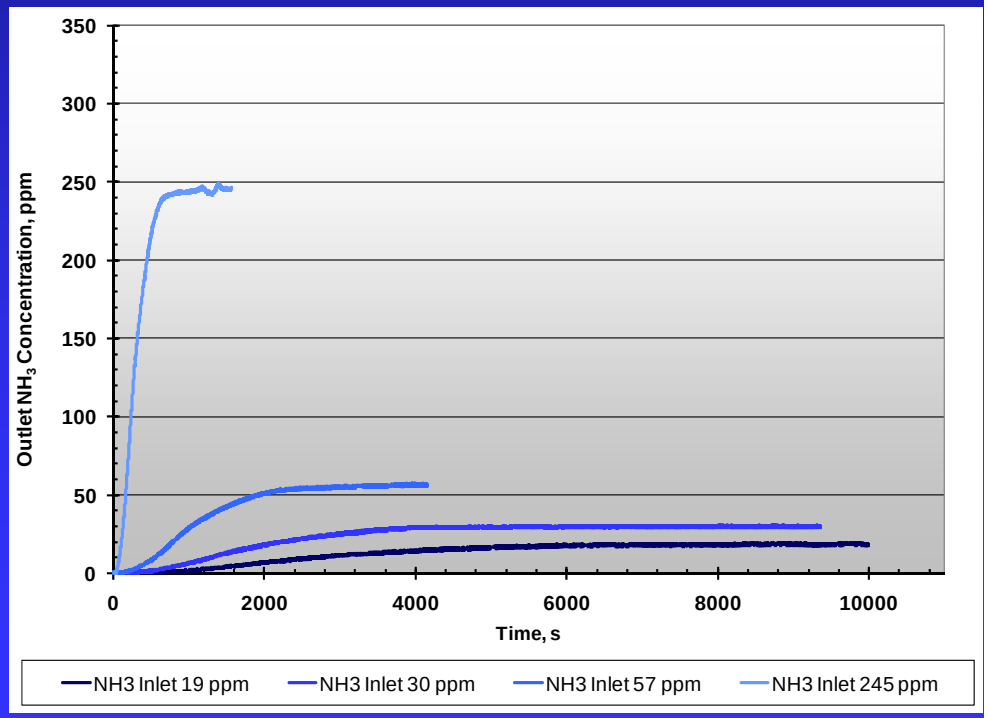
Equation 1

$$\Omega = \Omega_0 - t_c * \left[\left(A * e^{\left(\frac{Ed}{RT1}\right)}\right) * \Omega_0 + (x - yT_1)\right]$$

Equation 2

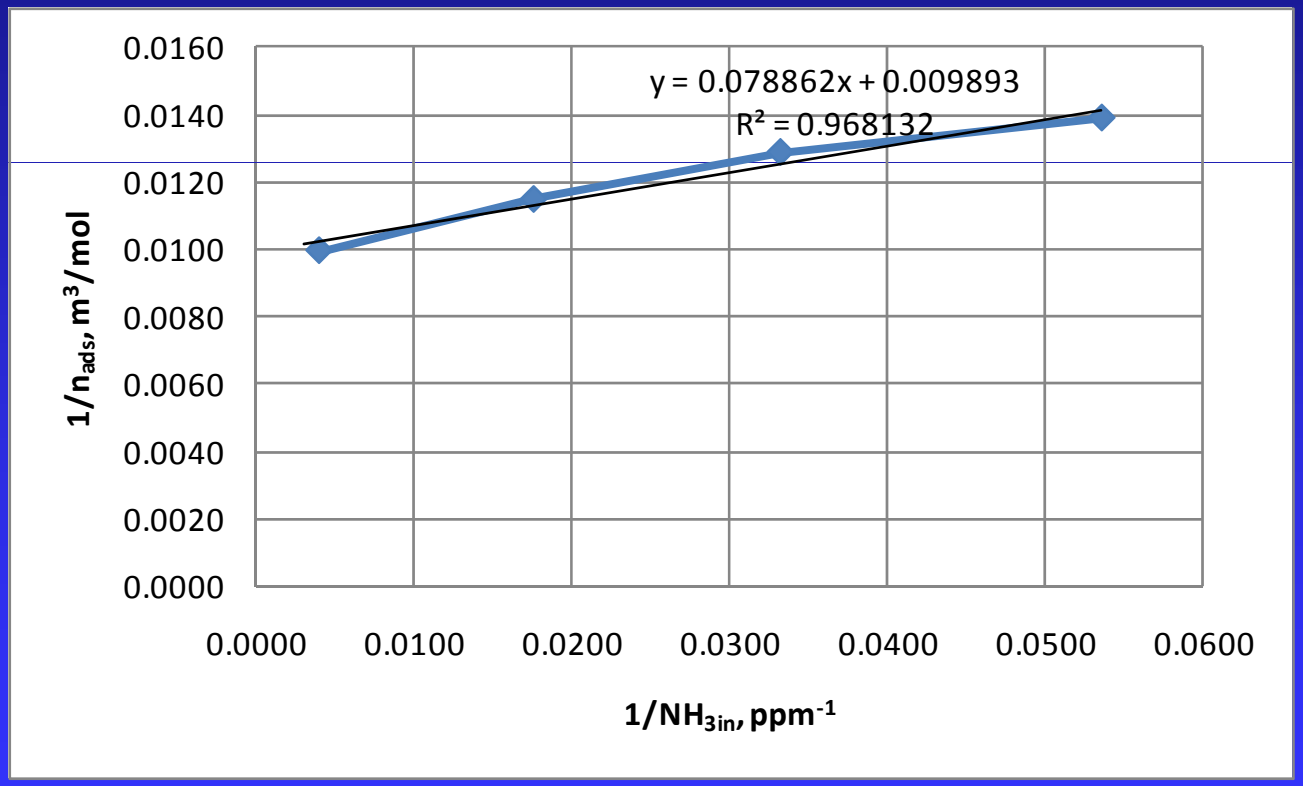
Cu-Zeolite (New Data)
NH_3 Adsorption Test Conditions

- Gas Mixture: 14% O_2, 5% CO_2, 5% H_2O, X ppm NH_3, balance N_2
- Test Temperature 200°C
- Space Velocity 120,000 hr^{-1}
- Catalyst 'cleaned' of NH_3 Between Tests (NO + NO_2 + NH_3 fast reaction used)
- NH_3 setpoints 20, 30, 50, 200 ppm
- Note Single Point Equilibration Times as Long as 2.8 Hours at 20 ppm NH_3 Concentration



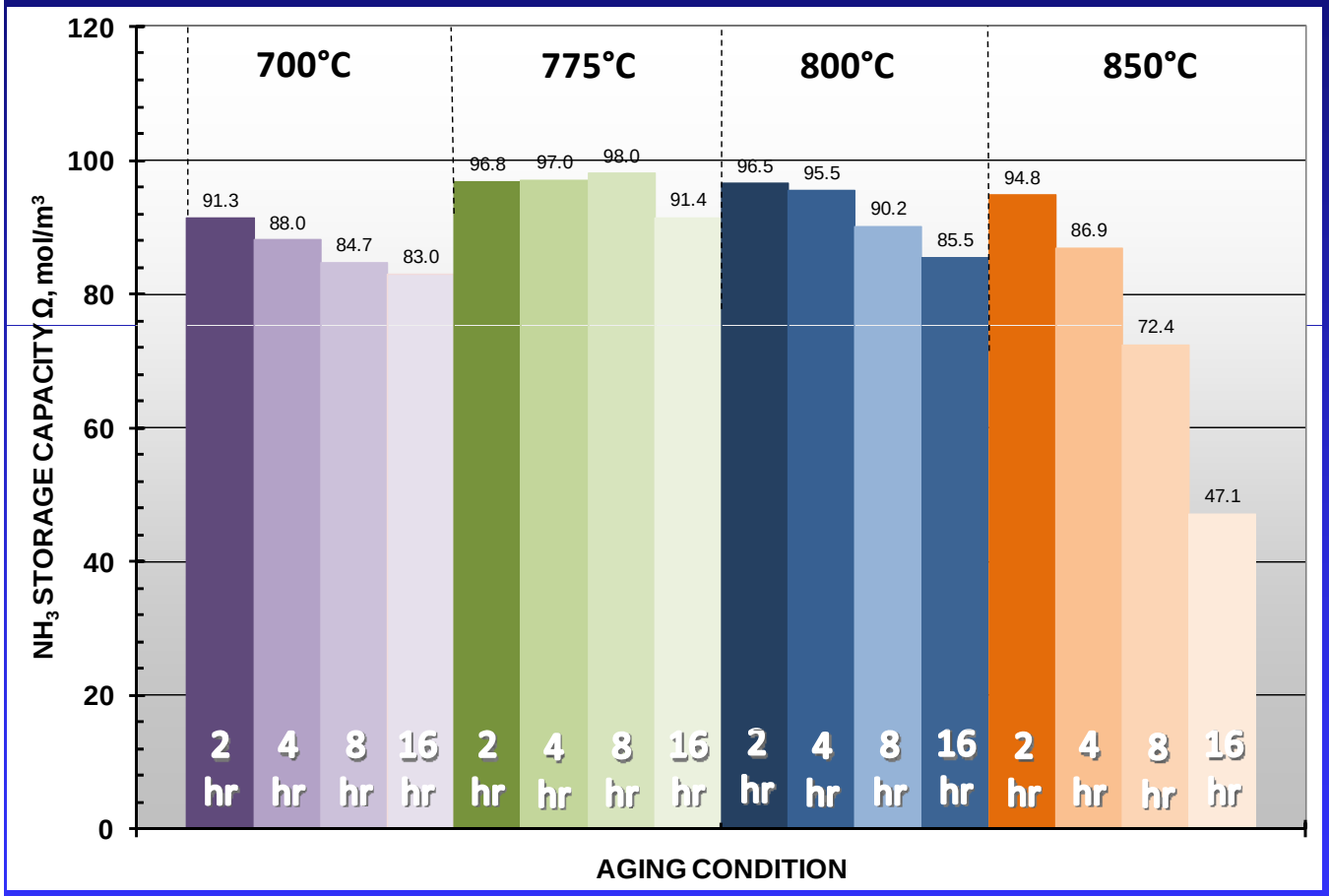
Cu-Zeolite (New Data)
NH_3 Adsorption Test Results (1)

- Data fitted to Langmuir adsorption isotherm model by plotting the data in Langmuir coordinates
  - R2 ≤ 0.97, NH_3 adsorption obeyed Langmuir type isotherm *reasonably* well



Cu-Zeolite (New Data)
NH_3 Adsorption Test Results (2)

- NH_3 Storage Capacity Decreased with Aging Time and Temperature



Maximum Ω at 8 hours - 775°C

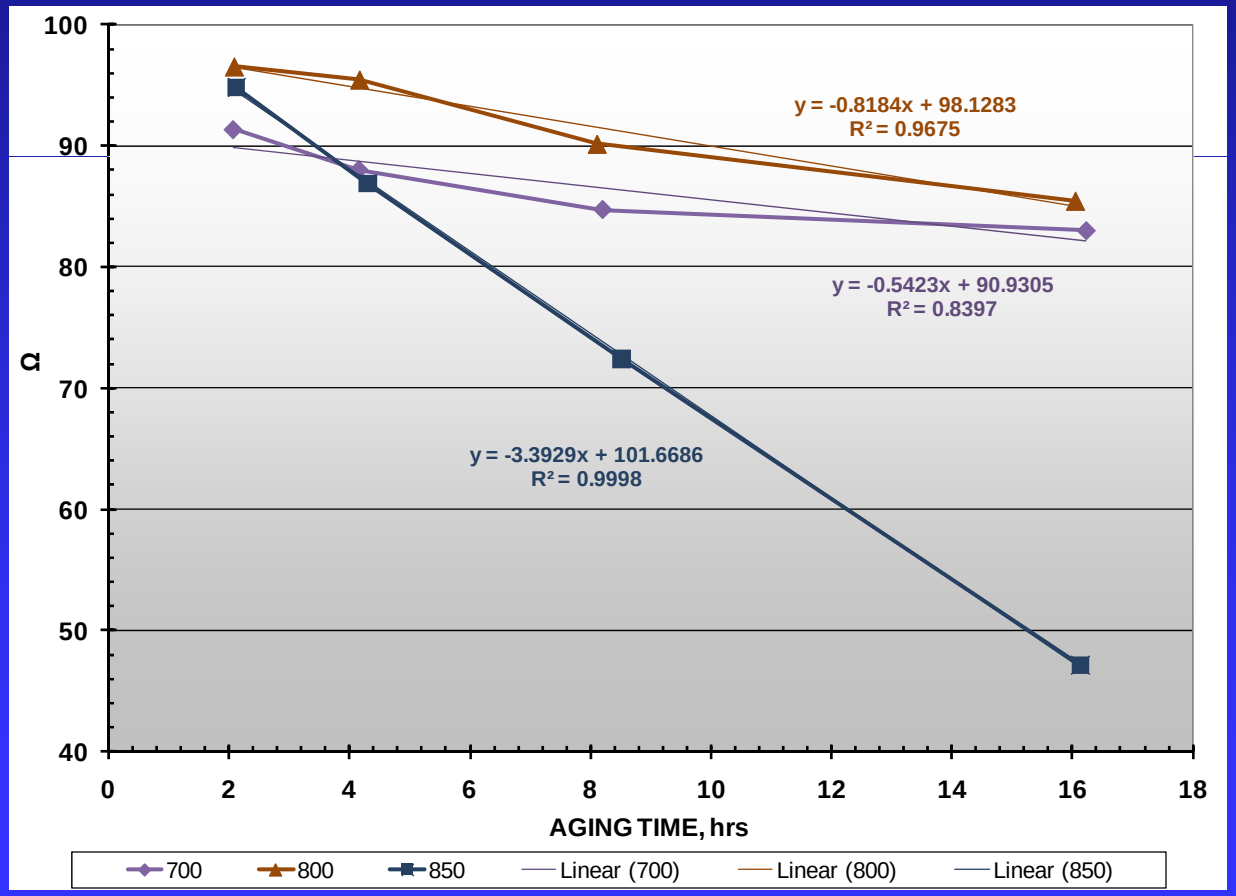
775°C data 'flat'. Not used in *Ed* calculations

Cu-Zeolite (New Data)
Deactivation Energy Determination, *Ed* (1)

- A Zero Order Rate Equation Fit the Data Quite Well

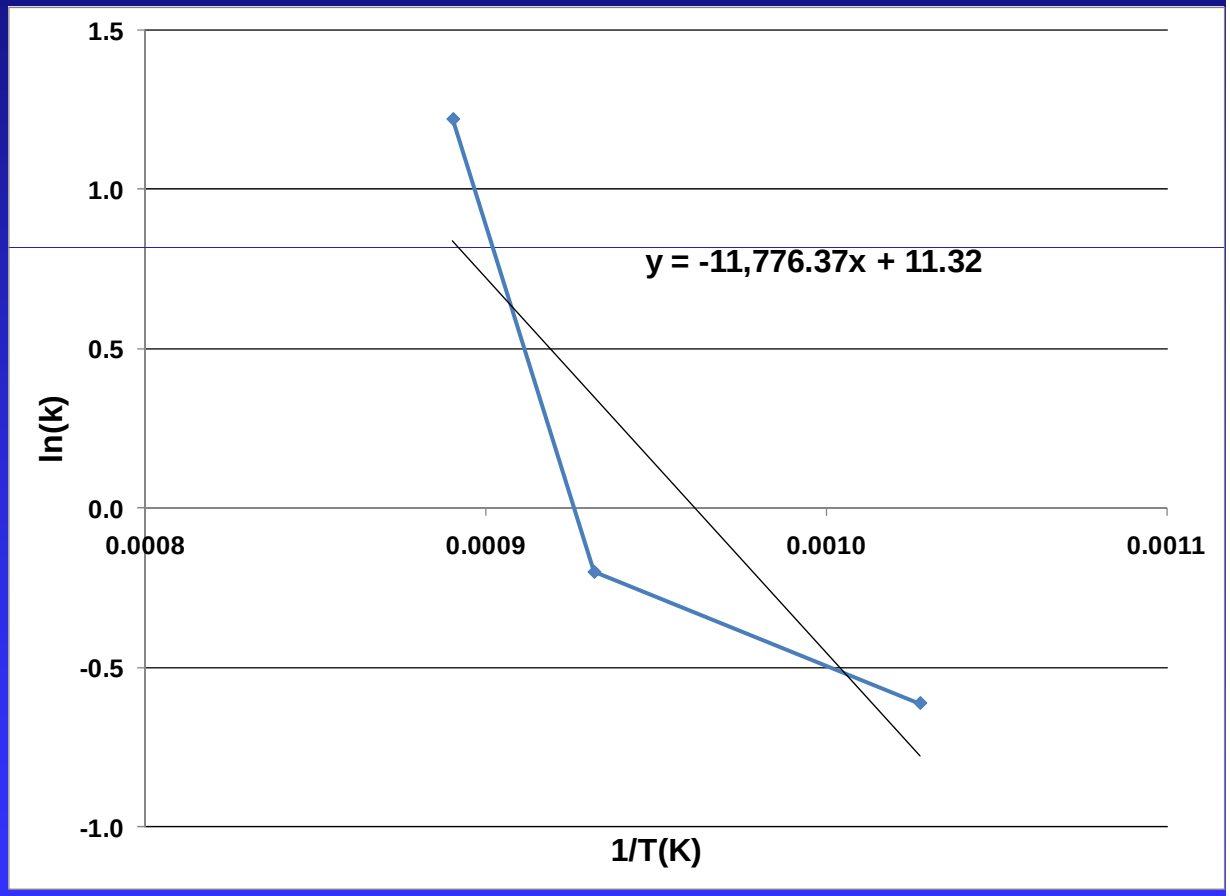
Rate Equation $-d\Omega/dt = k$

Ω NH_3 storage capacity, mol/m^3 t time, hours k rate constant



Cu-Zeolite (New Data)
Deactivation Energy Determination, *Ed* (2)

- Arrhenius Equation Plot Using Zero Order Data Returns Values of:
  - *Ed* = 98 kJ/mol
  - A = 82702



Cu-Zeolite (New Data)
Deactivation Energy Determination, *Ed* (3)

- MS Excel Solver Used to Obtain Best Fit Constants
- Best fit - *Ed* = 96 kJ/mol A = 82703

	MEASURED Ω			
	TEMPERATURE, Kelvin			
Aging, Hrs	973.15	1048.15	1073.15	1123.15
2	91.4		96.5	94.8
4	88.0		95.5	86.9
8	84.7		90.2	72.4
16	83.0		85.5	47.1

Test Data

	CALCULATED Ω			
	TEMPERATURE, Kelvin			
Aging, Hrs	973.15	1048.15	1073.15	1123.15
2	**91.3**		**96.5**	**94.8**
4	90.2		93.0	89.1
8	87.8		85.9	77.6
16	83.1		71.6	54.6

Calculated Values using Rate Equation
- $d\Omega/dt = k$
and Best Fit Constants

	PERCENTAGE ERRORS			
	TEMPERATURE, Kelvin			
Aging, Hrs	973.15	1048.15	1073.15	1123.15
2	0.0		0.0	0.0
4	2.4		2.6	2.5
8	3.6		4.8	7.1
16	0.1		16.2	15.8
Average % error =		**6.1**		

Comparative Errors

Cu-Zeolite
Summary and Conclusions (1)

- Aging of Catalyst for 2, 4, 8 and 16 Hours at 700, 775, 800 and 850°C Generally Decreased NH_3 Storage Capacity (Ω)
- Deactivation Energy *Ed* determined to be 96 kJ/mol
- Pre-Exponential Factor A determined to be 82703

Cu-Zeolite
Summary and Conclusions (2)

- Possible to Predict NH_3 Storage Capacity In-Field using equations:

$$t_c = t_{c-1} + e^{\left[-\frac{Ed}{R}\left(\frac{1}{T2}-\frac{1}{T1}\right)\right]}$$

Equation 1

$$\Omega = \Omega_0 - t_c * \left[\left(A * e^{\left(\frac{Ed}{RT1}\right)}\right)\right]$$

Equation 3

Summary and Conclusions

SCR Formulation	Maximum NH_3 Storage Capacity Ω, mol/m^3	Deactivation Energy *Ed*, kJ/mol
Fe-Zeolite	51	43
V/W/TiO_2	72	98
Cu-Zeolite	97	96

- For SCR Catalysts, In-Use NH_3 Storage Capacity can be Calculated in Real Time using Only Operating Time and Temperature Measurements
  - Model-based controllers that rely on Ω can utilize this methodology

Acknowledgements

- SwRI Advisory Committee for Research - Funding
- Johnson Matthey – V/W/TiO_2 Catalyst
- BASF – Cu/Zeolite and Fe/Zeolite Catalysts
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- SwRI - Jason Miwa