Combi and HT Application of Spectroscopic Techniques

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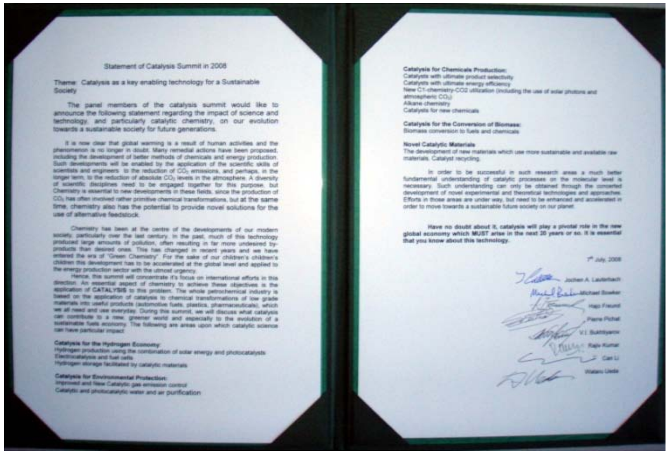
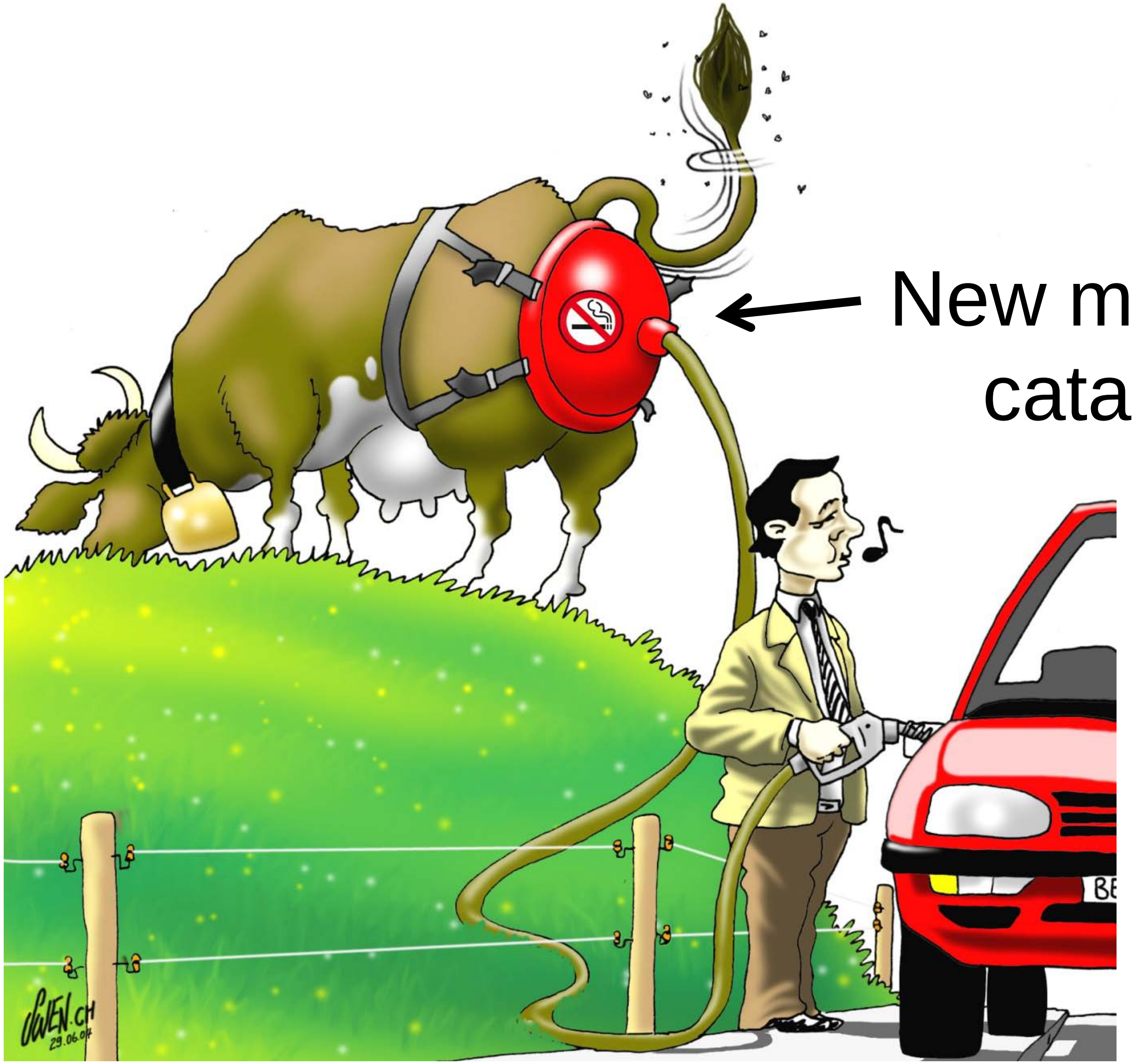
Catalysis is a key enabling technology for modern life as we know it.

In the future, it will facilitate the development of “green” and more efficient processes for the conversion of fossil and renewable or alternative energy feedstock.

Examples:

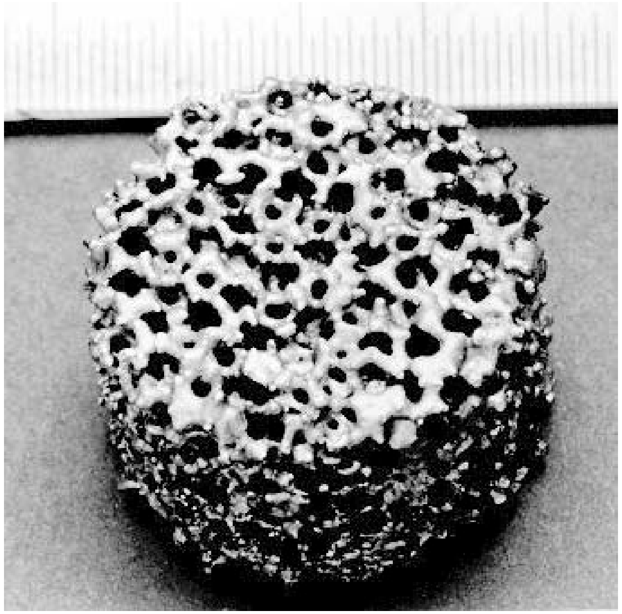
- More efficient chemical processes
- Hydrogen economy
- Pollution abatement
- Bio-derived feedstock
- ……………..

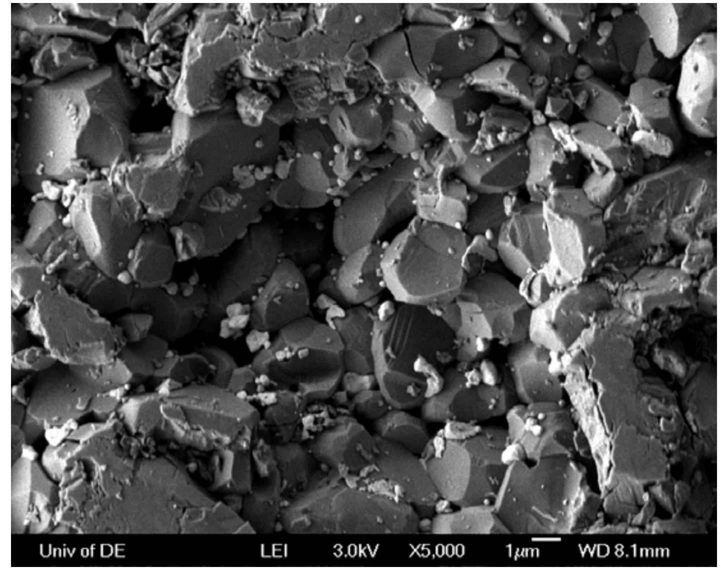


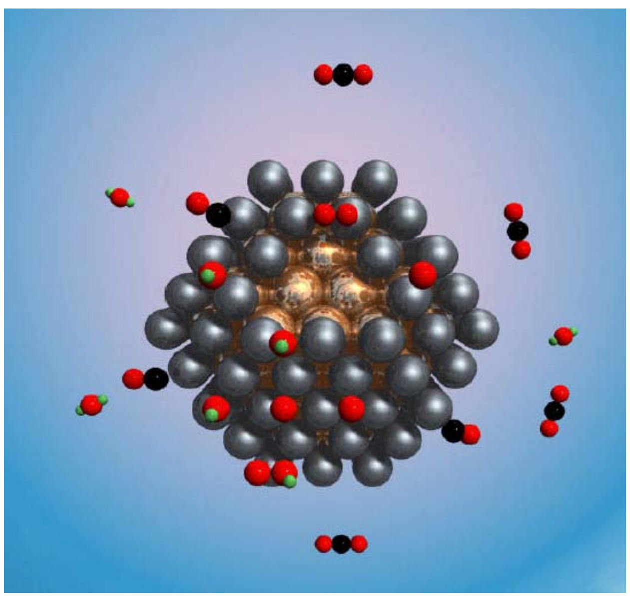


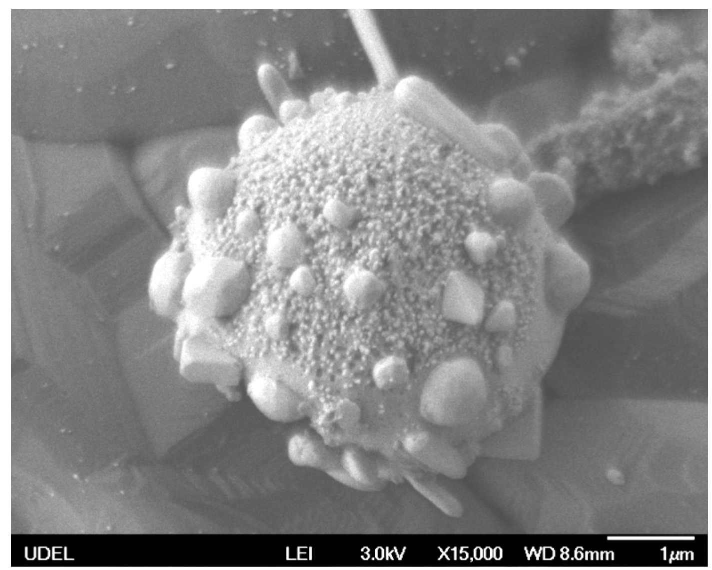
New miracle catalyst

Real Catalysts are Multiscale Systems









Real Catalysts are Complex Systems

- Multi-dimensional parameter space
- Usually we study only a small subspace
- Must reduce the number of experiments
  - Prior knowledge
  - Design of experiments
- Employ high-throughput techniques

Parameter Space

Precursor
Active metal and loading
Promoter and loading
Support
Synthesis method
Calcination time
Calcination temp
Reduction pretreatment
Temperature
Time
Pressure
Concentration
Space velocity

High-Throughput Catalysis

Traditional catalysis research studies one sample at a time

→ vary reaction conditions (e.g., kinetic experiments)

→ choose next sample → vary reaction conditions

→ ...

Rate: one sample/week to one sample per PhD

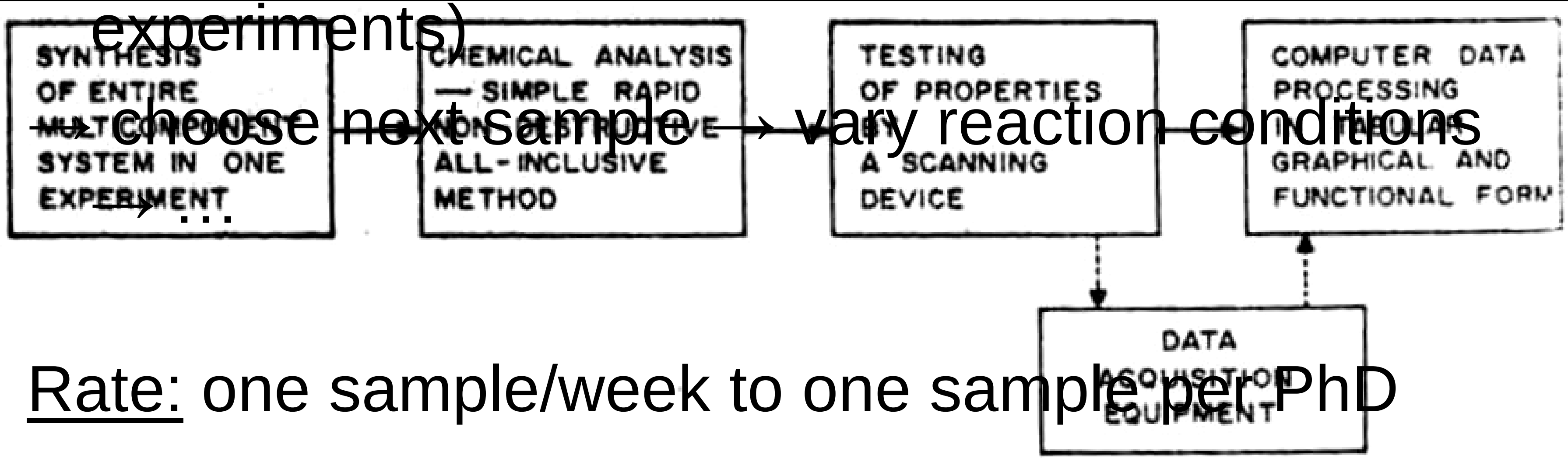
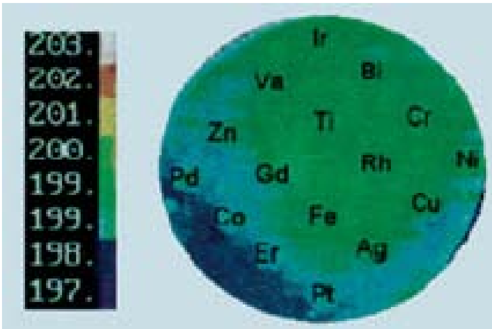


Figure 1 Flow chart of processes needed for the study of entire multicomponent systems in single steps.

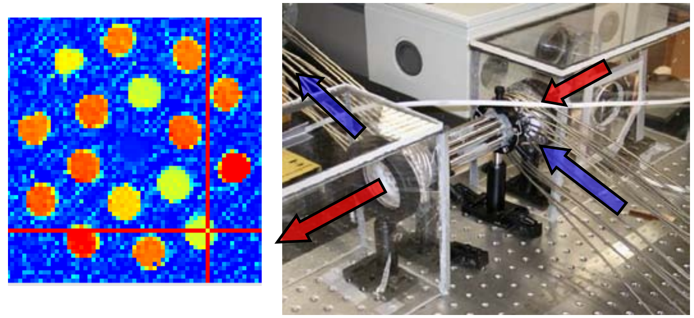
Can we speed up this process – ideally without loosing data quality?

J. J. Hanak, *Journal of Materials Science* **1970**, *5*, 964.

Types of Reactor Technologies



Stage I



Stage II

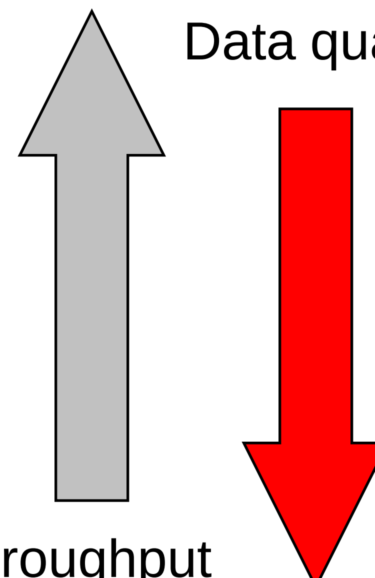
Stage III

Stage I :
- Screen large catalyst libraries (~1000 samples/week)
- Qualitative information

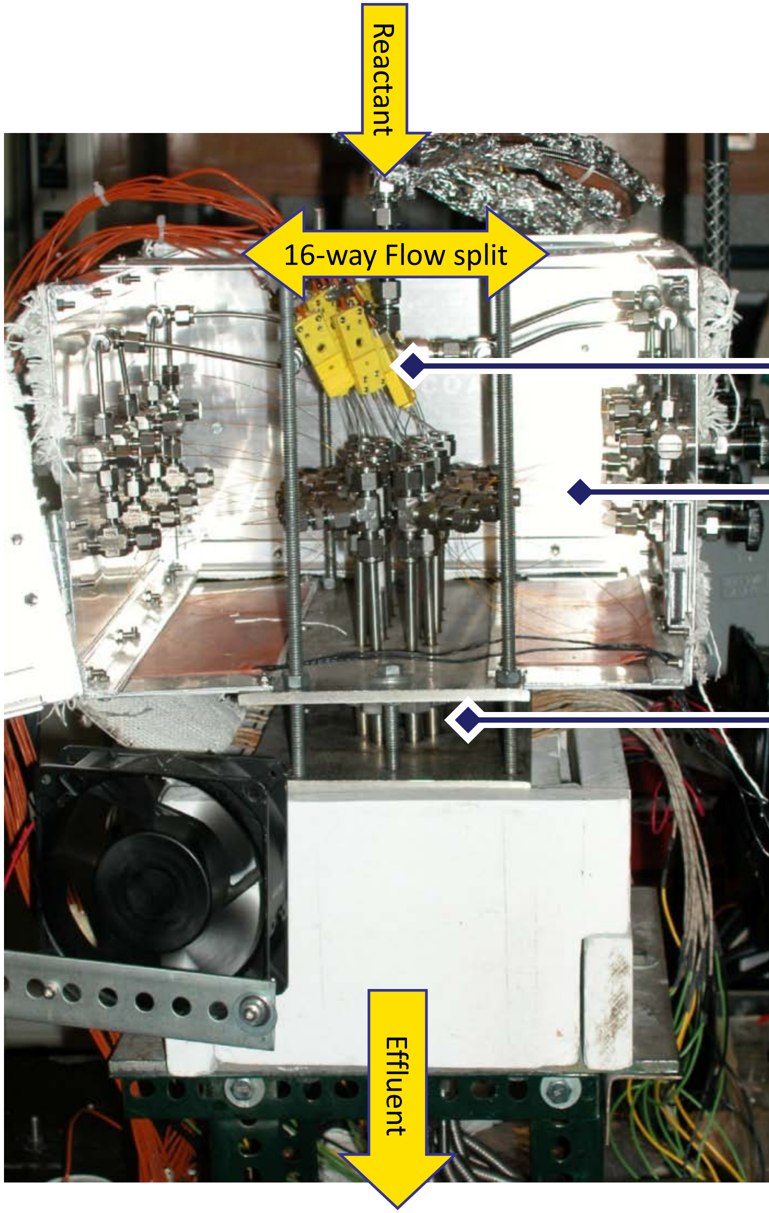
Stage II:
- Test multiple catalyst samples (~100 samples/week)
- Quantitative information

High Throughput Reactor Set Up

Stage III:
- Only one sample at a time (<1 - 10 samples/week)
- Fundamental studies and quantitative information



High Throughput Reactor



Side view of Reactor
16 sample capacity

Individual temperature monitoring

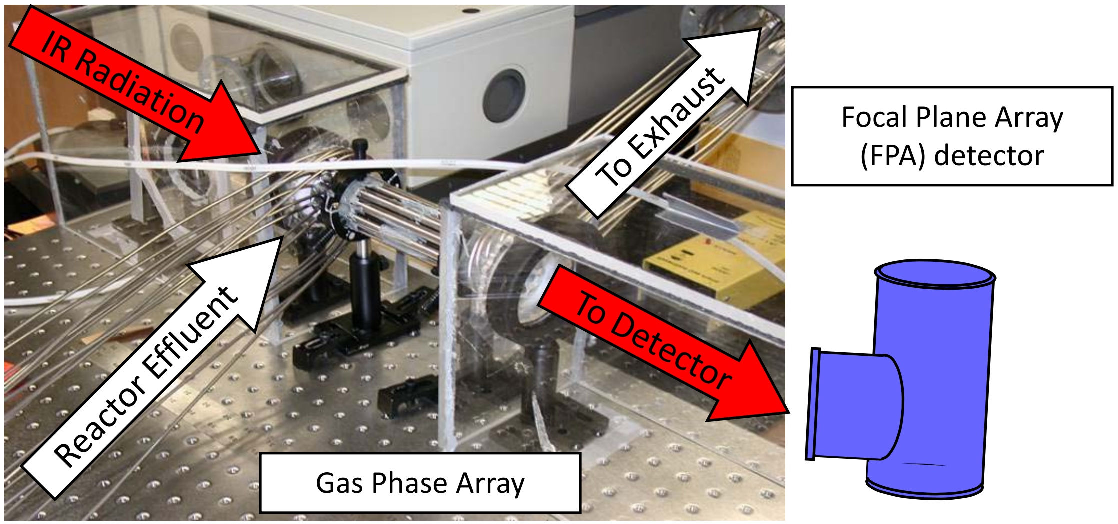
Capillaries

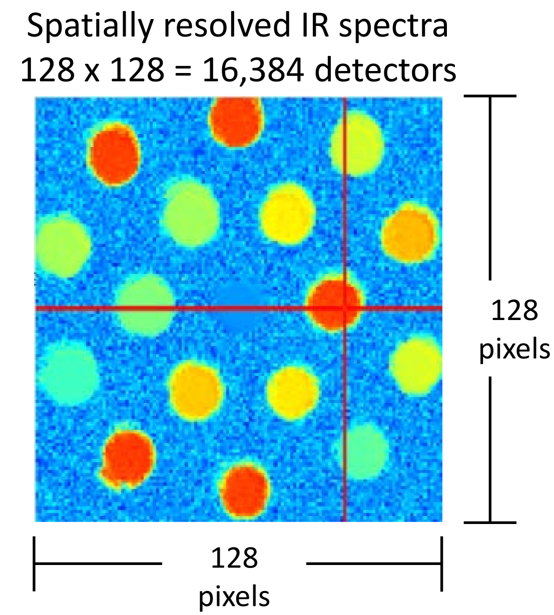
16 stainless steel reactor tubes

Reaction Conditions
- atmospheric pressure
- 200°C to 500°C, 50°C increments
- 10% v/v NH_3 / He
- GHSV= 40,000 mL/(hr*g_{cat})

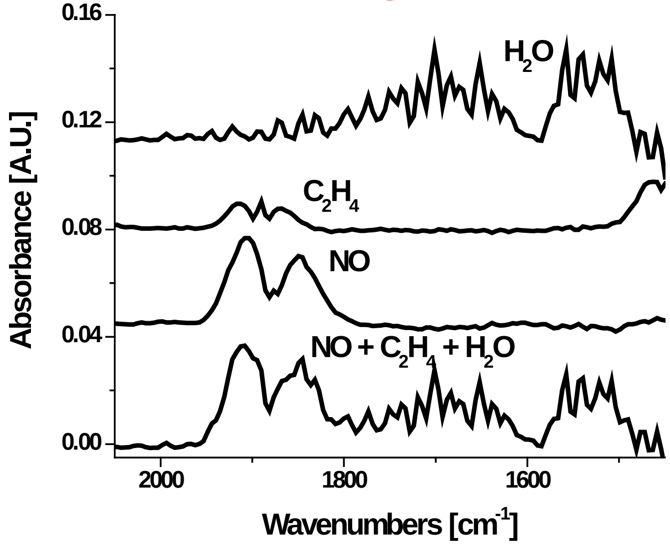
RJ Hendershot, et al, *Applied Catalysis A* (2003)

FTIR Imaging for Data Collection





PARALLEL: **Screening time ~ number of samples in field of view**



Applications

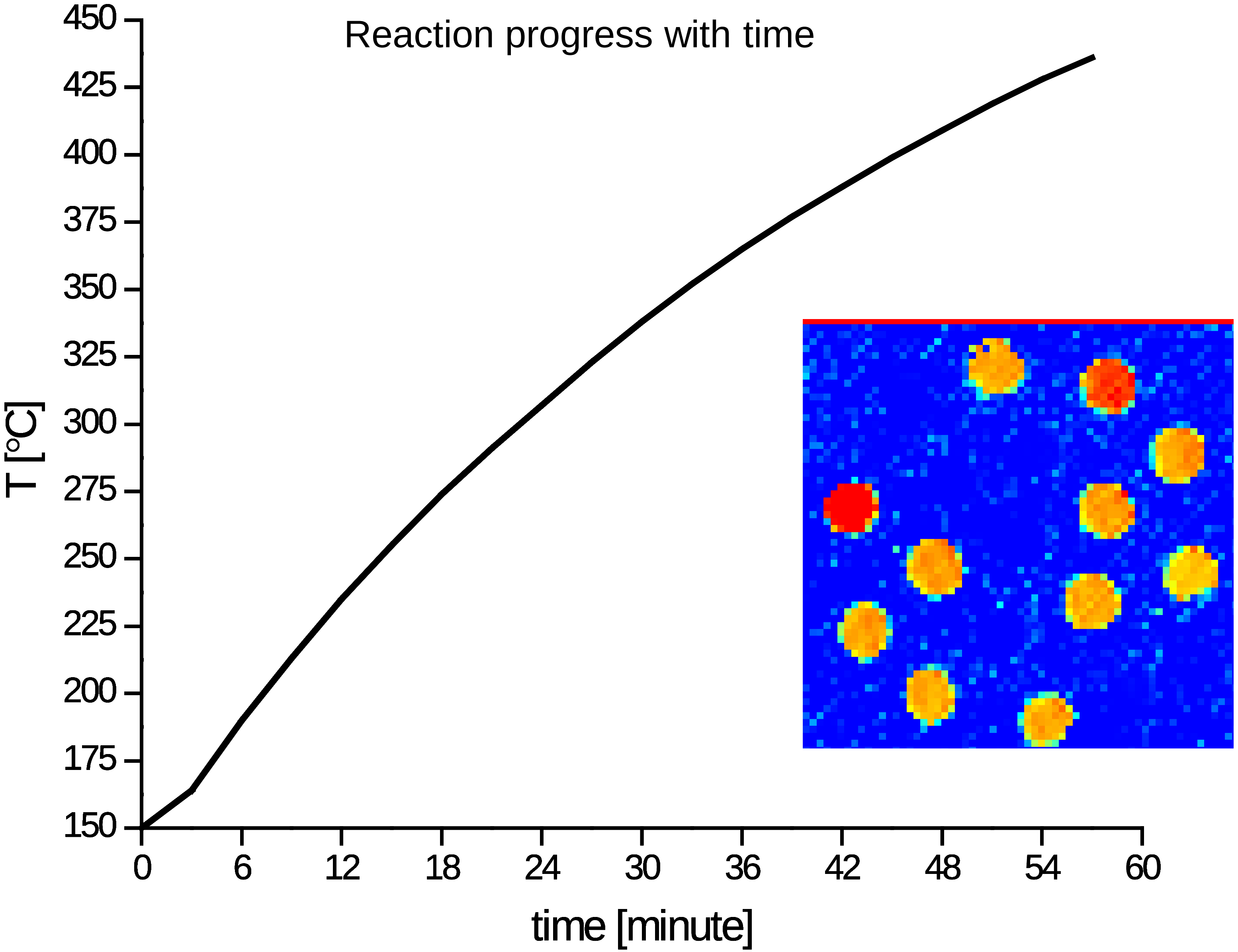
- Works for any gas with IR signature
- Chemometrics needed for complex spectra

Parallel and Fast technique

- Conversion & Selectivity of 16 catalysts collected in ~1 second

1. C. Snively, S. Katzenberger, G. Oskarsdottir, J. Lauterbach. *Optics Letters* (1999) 2. C. Snively, J. Lauterbach. *Spectroscopy* (2002)

Transient Analysis Capacity



CO-free H_2 from NH_3 decomposition

Green ***Ammonia Synthesis***

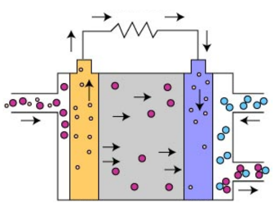
water ↓ air ↓

$$\tfrac{3}{2} H_2 + \tfrac{1}{2} N_2 \rightarrow NH_3$$

On-Board H_2 Production

$$NH_3 \rightarrow \tfrac{1}{2} N_2 + \tfrac{3}{2} H_2$$

Zero Emissions Energy Source



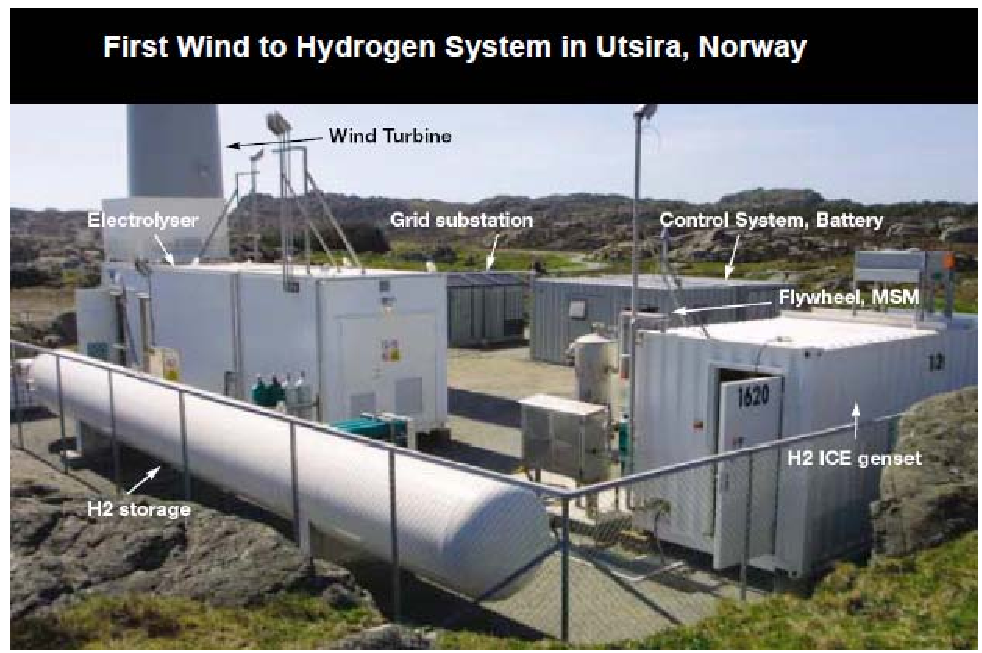
PEM Fuel Cell

Ballard Power Systems

H_2 Engine

www.bmwusa.com

Source	Energy Density (MJ/L)	H_2 Density (kg/L)	By-products	Liquid Storage Temp (°C)
Liquid H_2	9	0.070	-	-252
Methane	13	0.104	CO_x	-175
Methanol	12	0.100	CO_x	25
Ethanol	12	0.103	CO_x	25
Ammonia	**12**	**0.117**	**N_2**	**25 (8 bar)**



Project funded by US Department of Energy

NH_3 Decomposition on Ru
Resolve Competing Microkinetic Models

- Synthesis Model [1,2,3)]
  - Predicts no inhibition by either H_2 or N_2
- H-H interaction model [4)]
  - Predicts slight inhibition by N_2
  - Predicts no inhibition by H_2
- H-H & N-N interaction model [5,6)]
  - At high surface concentrations, interactions become important
  - Predicts no inhibition by N_2
  - Predicts inhibition by H_2

$$NH_3(g) + * \Leftrightarrow NH_3^*$$

$$NH_3^* + * \Leftrightarrow NH_2^* + H^*$$

$$NH_2^* + * \Leftrightarrow NH^* + H^*$$

$$NH^* + * \Leftrightarrow N^* + H^*$$

$$2H^* \Leftrightarrow H_2(g) + 2*$$

$$2N^* \Leftrightarrow N_2(g) + 2*$$

1) Yin, S.F., Xu, B.Q., Zhou, X.P., Au, C.T. *Applied Catalysis A* **277** (2004) 1

2) Bradford, M.C.J., Fanning, P.E., Vannice, M.A. *J. Catalysis* **172** (1997) 479

3) Tsai, W., Weinberg, W.H. *J. Phys. Chem.* **91** (1987) 5302

4) Hinrichsen, O. *Catalysis Today* **53** (1999) 177

5) Mhadeshwar, A.B. Kitchin, J.R., Barteau, M.A., Vlachos, D.G. *Catalysis Letters* **96** (2004) 13

6) Choudhary, V.T., Sivadinarayana, C. Goodman, D.W. *Catalysis Letters* **72** (2001) 197

Kinetic Parameters

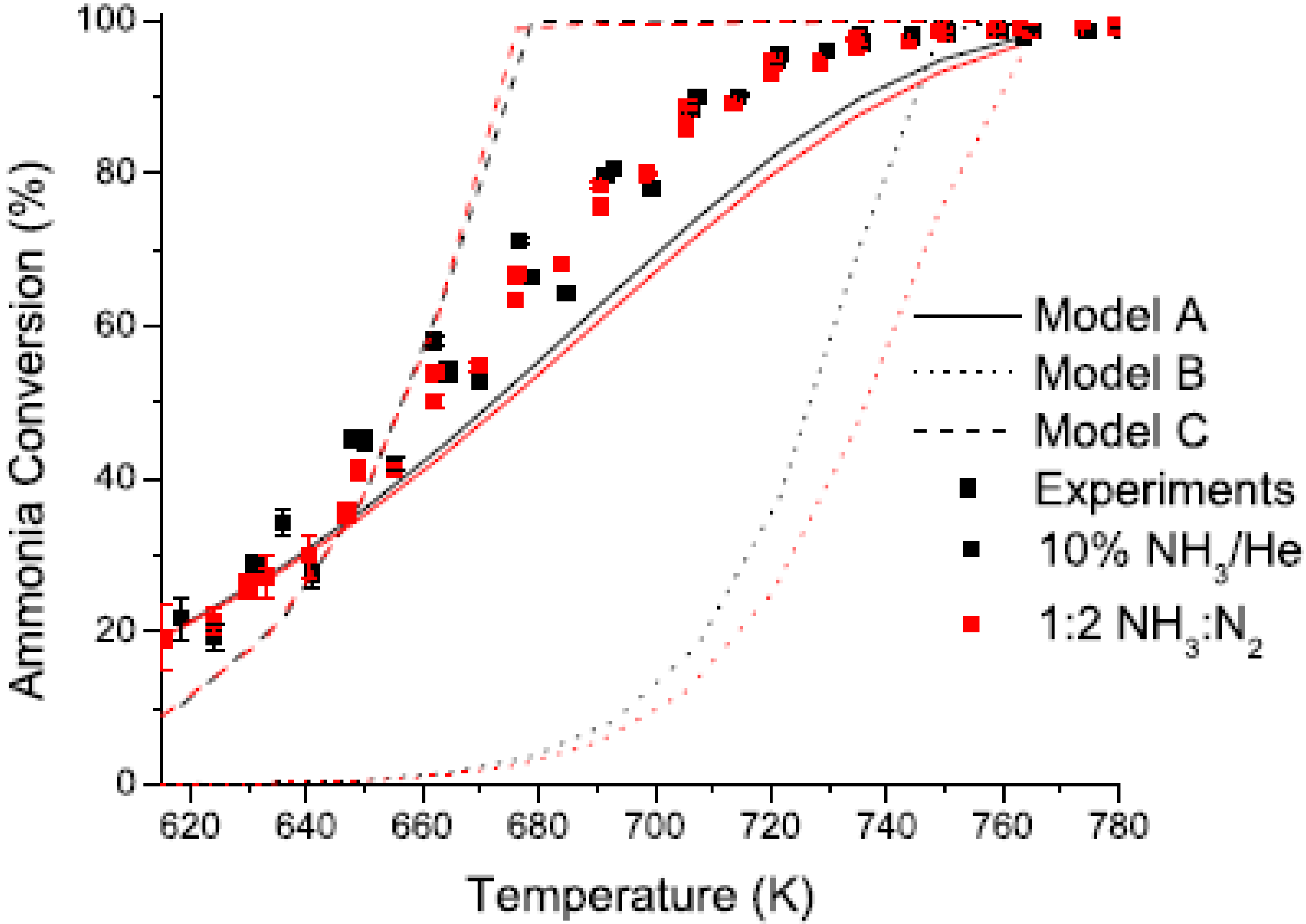
Step	A_f or s	E_f	A_r or s	E_r
$NH_3(g) \rightleftharpoons NH_3^*$	1.5×10^{-4}	0.0	8.1×10^{11}	17.7
	1.1×10^{-3}	0.0	2.4×10^{11}	17.7
	1.18×10^{13}	0.0	5.9×10^{13}	20.0
$NH_3^* \rightleftharpoons NH_2^* + H^*$	2.0×10^{12}	$18.7 + 1.3\theta_H$	3.4×10^{9}	$11.6 - 2.2\,\theta_H$
	2.0×10^{11}	$18.7 + 1.3\theta_H$	1.8×10^{10}	$11.6 - 2.2\,\theta_H$
	9.3×10^{12}	15.4	3.3×10^{13}	4.1
$NH_2^* \rightleftharpoons NH^* + H^*$	2.0×10^{12}	$20.1 + 1.2\,\theta_H$	1.4×10^{10}	$15.9 - 2.3\,\theta_H$
	4.5×10^{12}	$20.1 + 1.2\,\theta_H$	2.0×10^{12}	$15.9 - 2.3\,\theta_H$
	1.8×10^{13}	2.1	4.7×10^{13}	14.4
$NH^* \rightleftharpoons N^* + H^*$	1.9×10^{12}	$5.3+15.5\theta_N+\theta_H$	7.6×10^{9}	$37.6-19.5\theta_N-2.5\theta_H$
	3.6×10^{9}	$5.3 + \theta_H$	1.6×10^{12}	$37.6 - 2.5\,\theta_H$
	2.8×10^{14}	9.9	6.0×10^{13}	20.7
$2H^* \rightleftharpoons H_2(g)$	1.1×10^{11}	$19.6 - 7.0\,\theta_H$	8.7×10^{-1}	0.0
	2.5×10^{13}	$19.6 - 7.0\,\theta_H$	7.0×10^{-2}	0.0
	2.3×10^{13}	21.4	3.2×10^{12}	0.0
$2N^* \rightleftharpoons N_2(g)$	1.7×10^{12}	$51.0 - 43.8\,\theta_N$	2.0×10^{-1}	$7.1 + 26.3\,\theta_N$
	1.0×10^{15}	51.0	6.3×10^{-3}	7.1
	2.0×10^{10}	32.7	3.3×10^{8}	7.9

First set - heats of chemisorption modified by N-N interactions and H-H interactions - coverage dependent activation energies.

Second set - neglect N-N interactions

Third set - no interactions

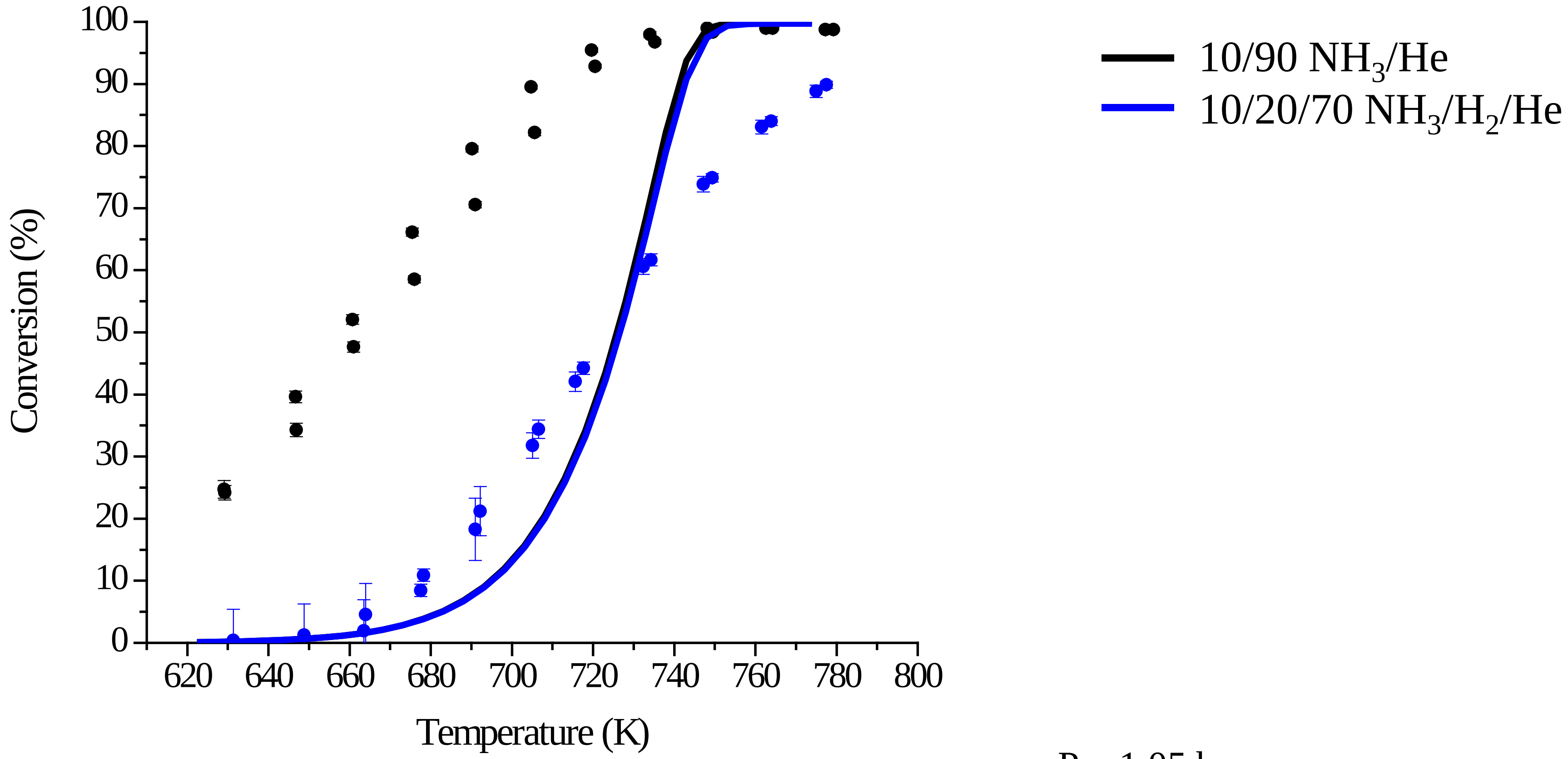
Interaction Model – Nitrogen Addition



3%(w/w) Ru / γ-Al_2O_3

P = 1.05 bar
SA/g = 1.34 m^2/g
GHSV = 30,000 $mL/h/g_{cat}$

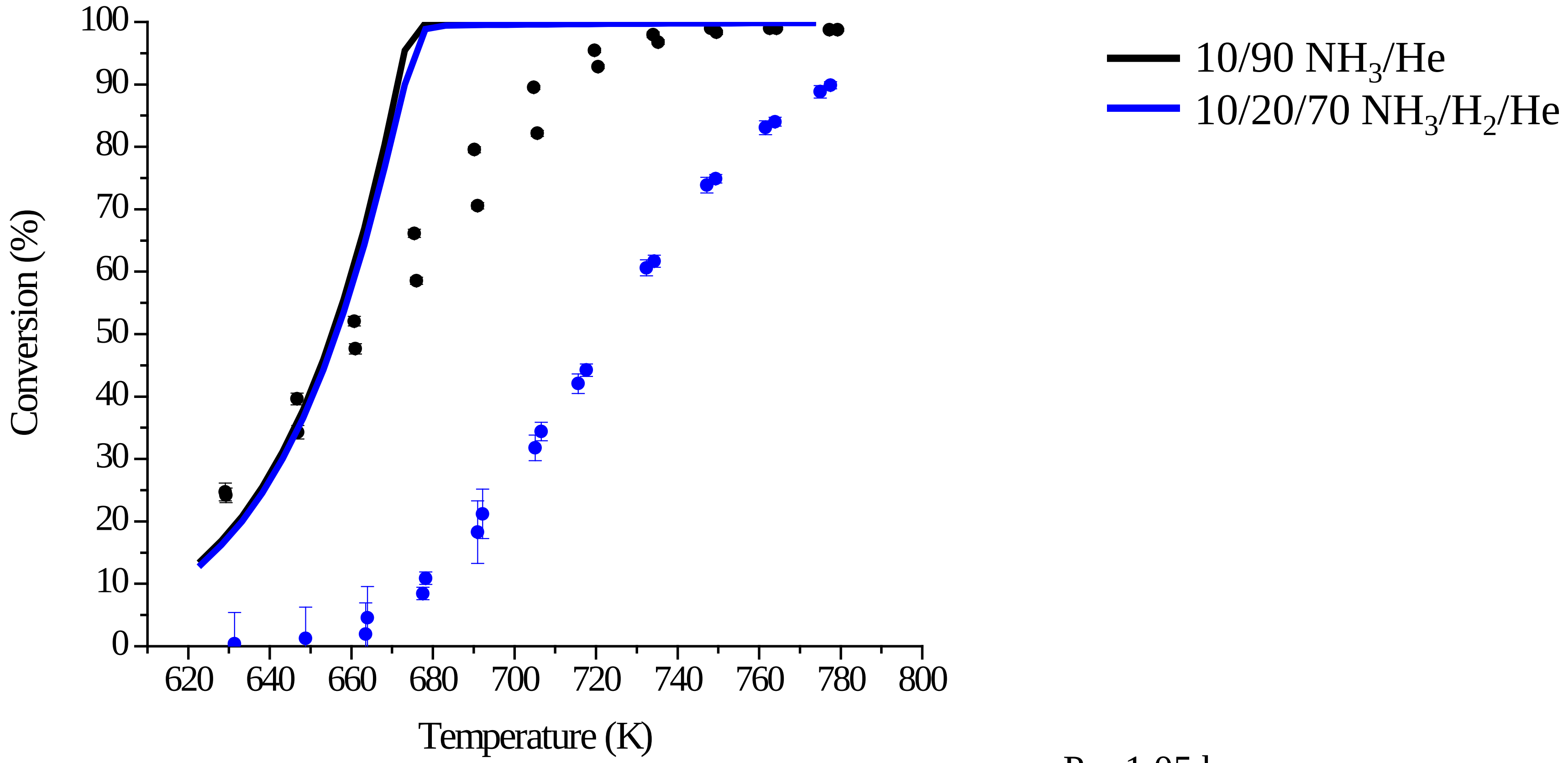
No Interaction Model - Hydrogen Addition



P = 1.05 bar
SA/g = 1.34 m^2/g
GHSV = 30,000 mL/h/g_{cat}

3%(w/w) Ru / γ-Al_2O_3

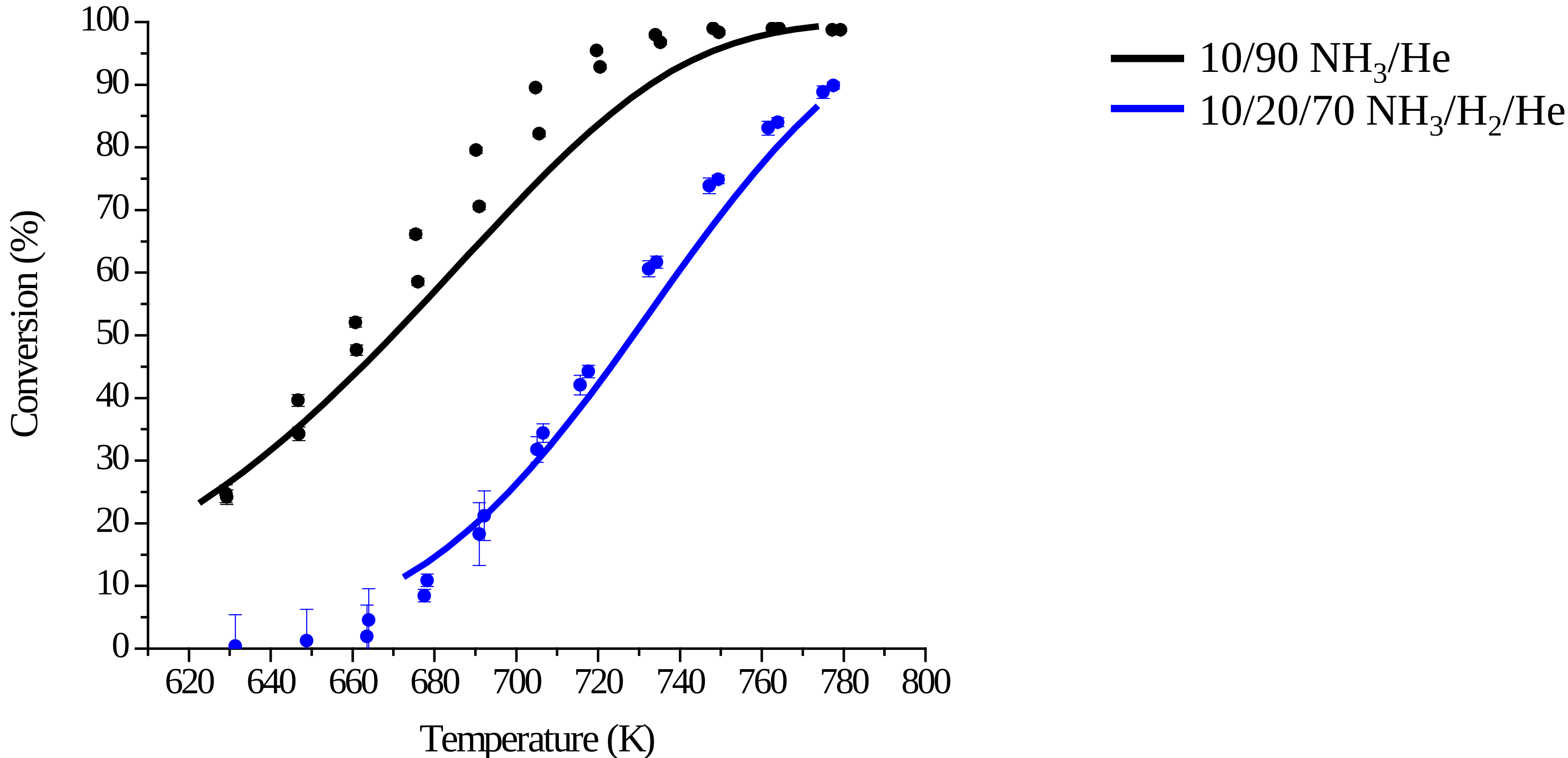
H-H Interaction Model



P = 1.05 bar
SA/g = 1.34 m^2/g
GHSV = 30,000 mL/h/g_{cat}

3%(w/w) Ru / γ-Al_2O_3

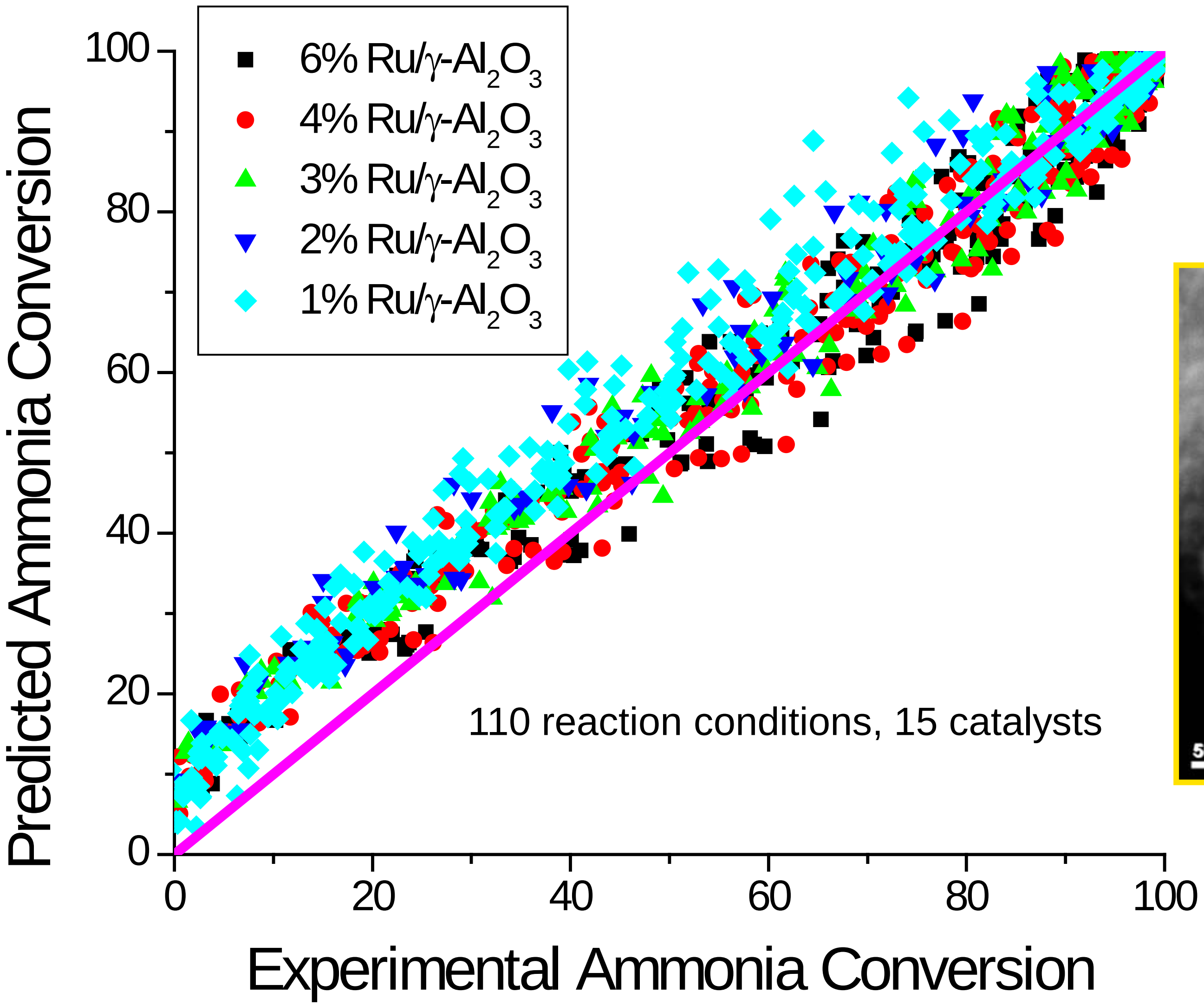
Full Interaction Model

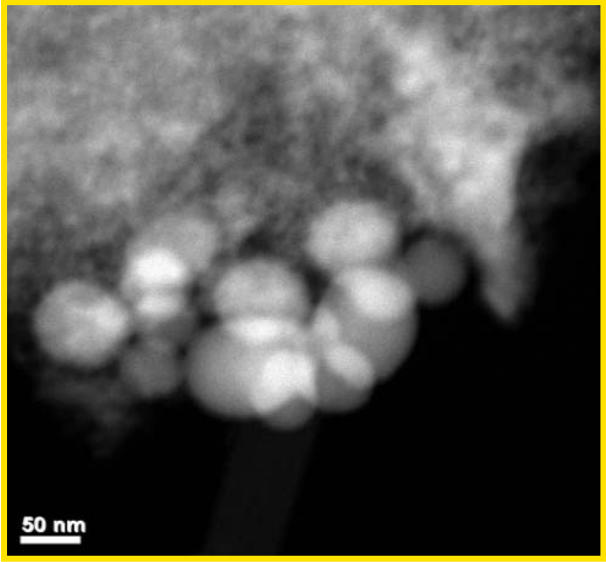


P = 1.05 bar
SA/g = 1.34 m^2/g
GHSV = 30,000 mL/h/g_{cat}

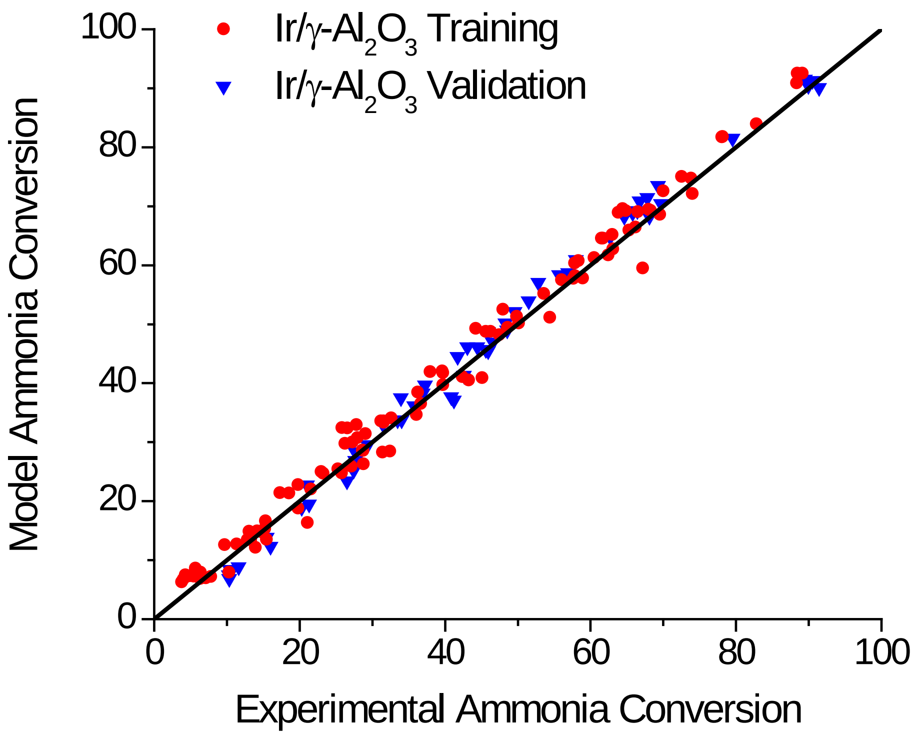
3%(w/w) Ru / γ-Al_2O_3

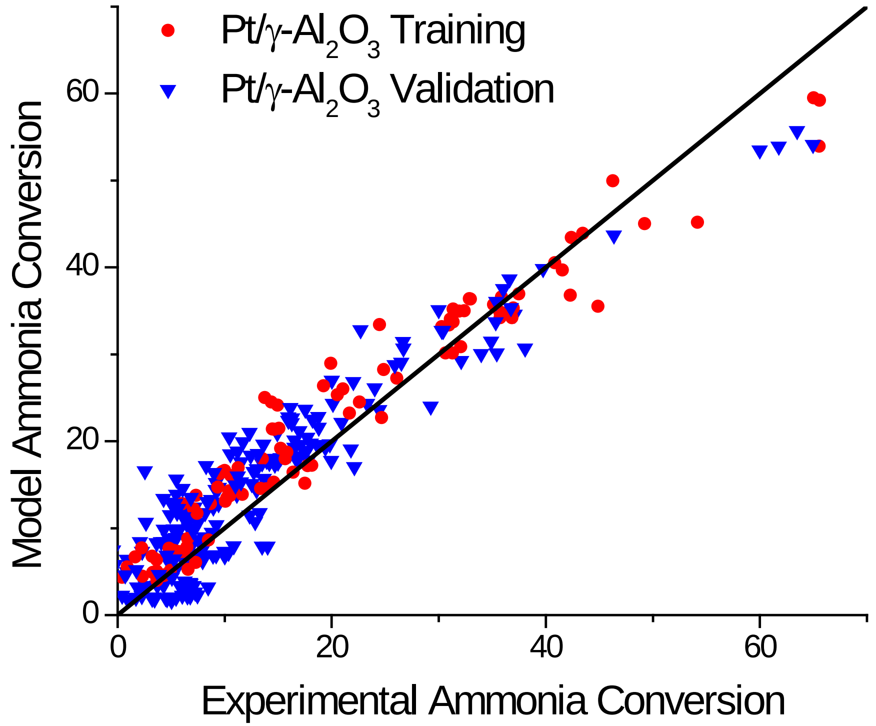
Optimized Model for Ru





Optimized Models for Ir & Pt

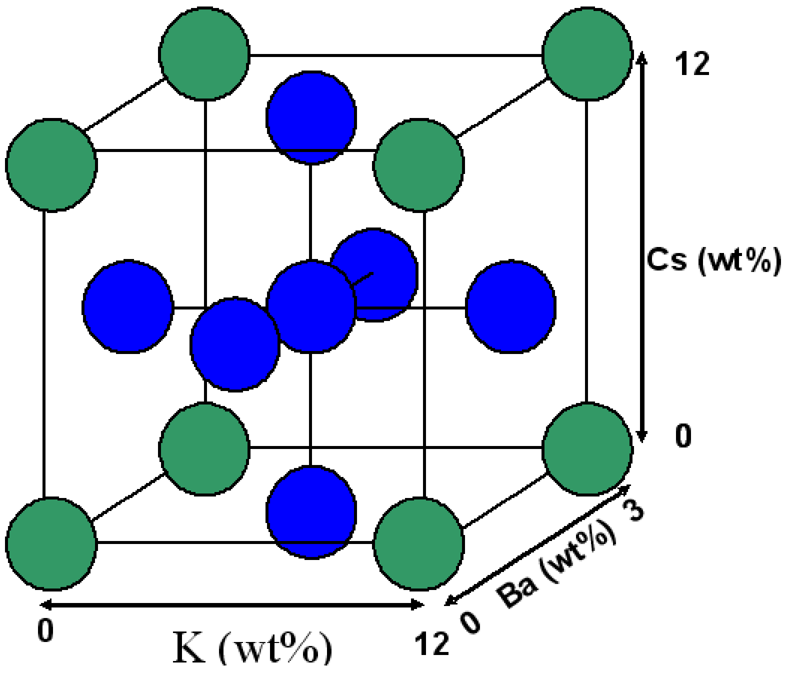


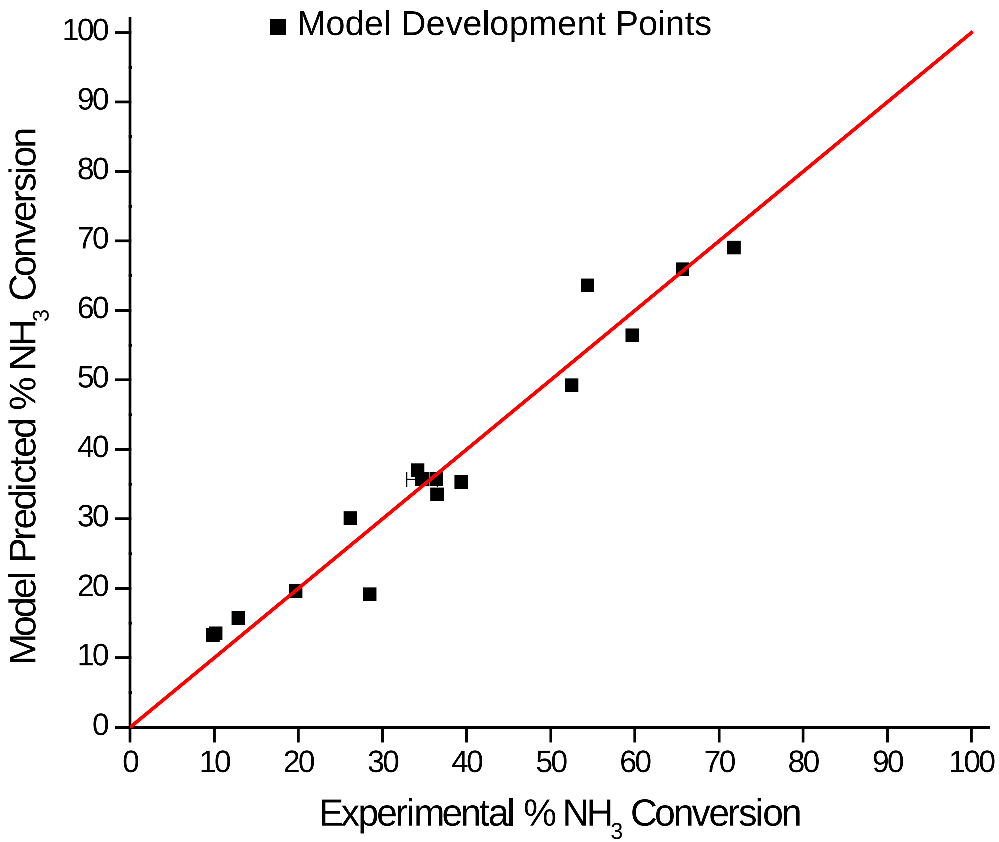


Reaction	Forward Energy	Reverse Energy
$NH_3(g) \leftrightharpoons NH_3^*$	0.0	17.1 - 8.5 θ_{NH3}
$NH_3^* \leftrightharpoons NH_2^* + H^*$	23.9 - 4.25θ_{NH3}	1.8 + 4.25θ_{NH_3}
$NH_2^* \leftrightharpoons NH^* + H^*$	20.6	11.3
$NH^* \leftrightharpoons N^* + H^*$	5.9 + 12.4θ_N	34.1 - 16.8θ_N
$2N^* \leftrightharpoons N_2(g)$	22.5 -36.5θ_N	23.6 + 21.9θ_N
$2H^* \leftrightharpoons H_2(g)$	17.4	0.0

Reaction	Forward Energy	Reverse Energy
$NH_3(g) \leftrightharpoons NH_3^*$	0.0	26.3 - 31.2θ_{NH_3}
$NH_3^* \leftrightharpoons NH_2^* + H^*$	33.0 + 3θ_H - 17.8θ_{NH_3}	13.4θ_{NH_3}
$NH_2^* \leftrightharpoons NH^* + H^*$	21.3 + 1.1θ_H	10.2 -1.9θ_H
$NH^* \leftrightharpoons N^* + H^*$	6.4 + 0.8θ_H	32.8 - 2.2θ_H
$2N^* \leftrightharpoons N_2(g)$	23.0	24.9
$2H^* \leftrightharpoons H_2(g)$	13.6 - 6θ_H	0.0

The Next Step: Promotion of Ru/γ-Al_2O_3 Catalysts

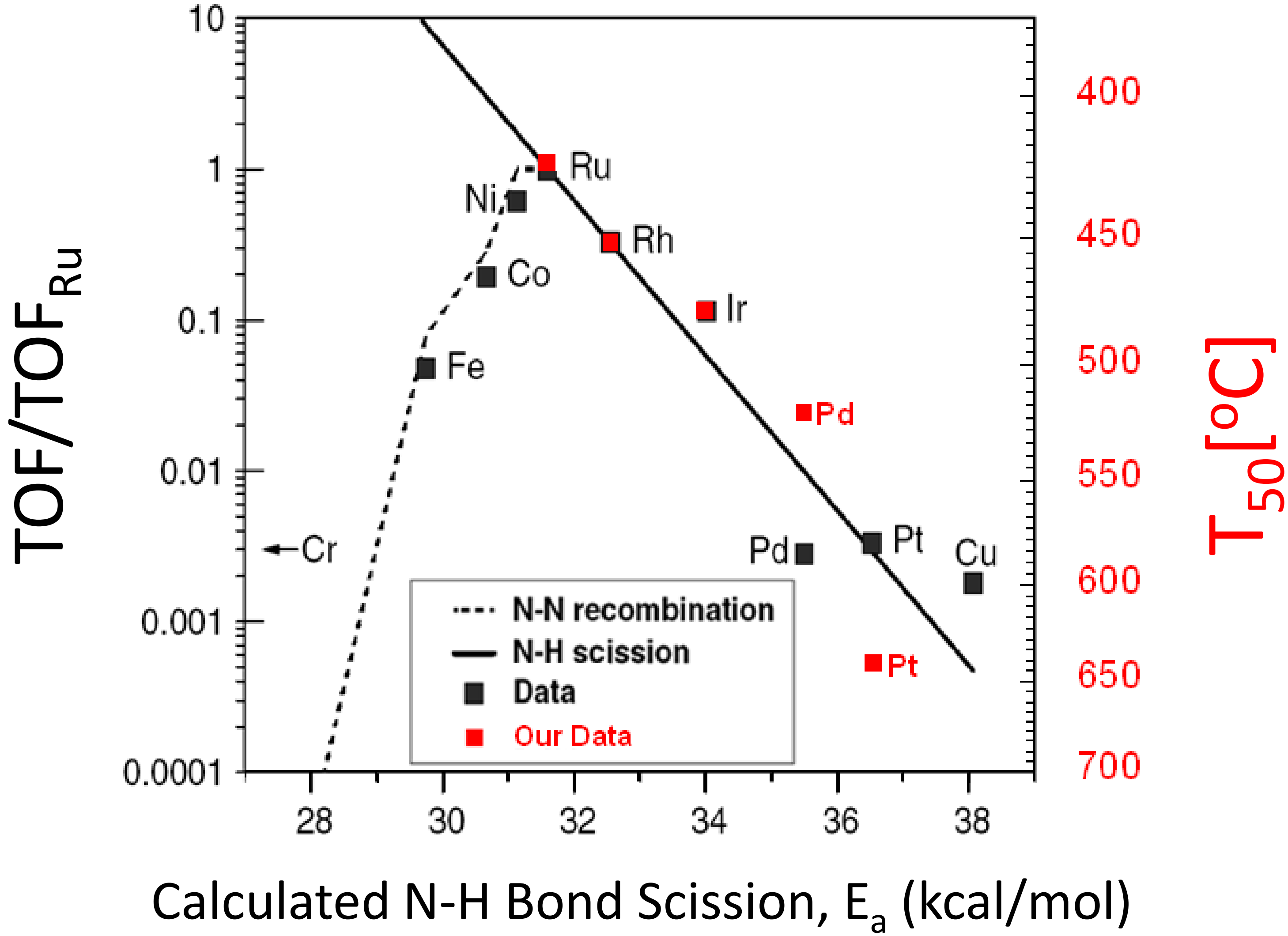




Term	Coefficients
Constant	35.7
Ba	-1.8
K	22.3
Cs	-2.6
Ba*Ba	-0.5
K*K	5.6
Cs*Cs	-3.0
Ba*K	-0.9
Ba*Cs	-1.0
K*Cs	-4.7

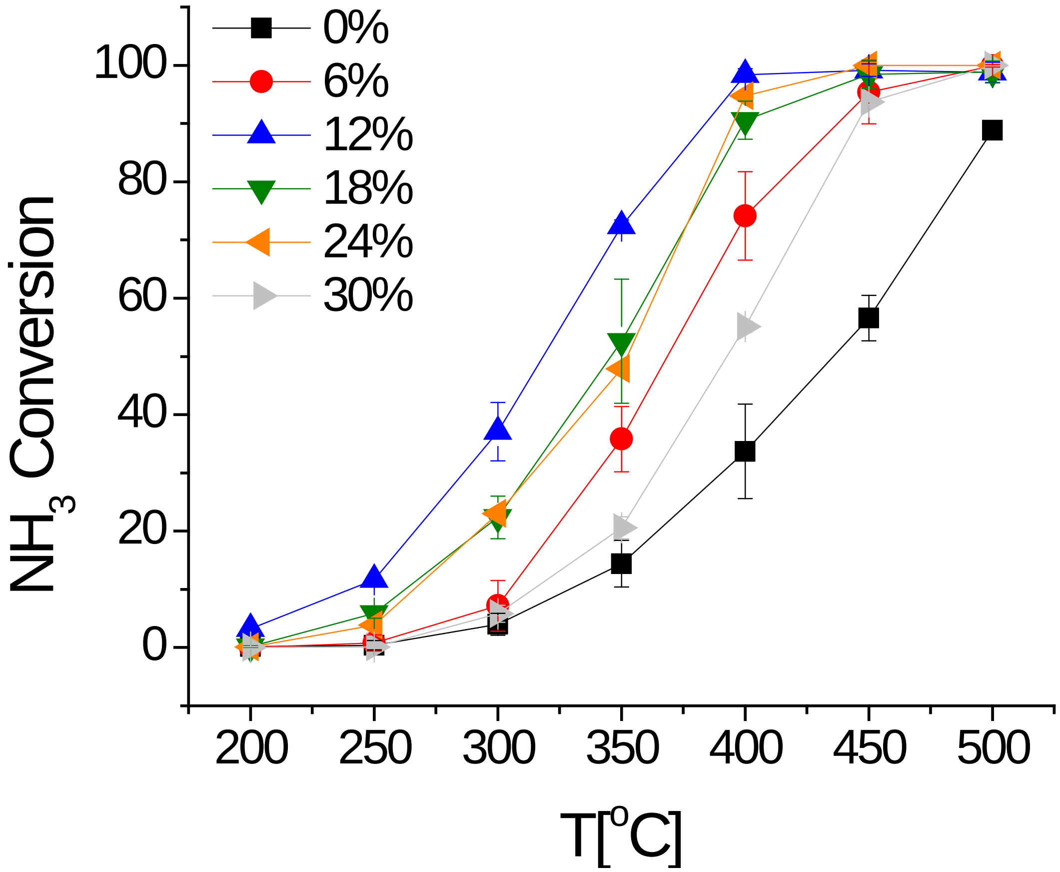
$$R = C + \alpha_1(Ba) + \alpha_2(K) + \alpha_3(Cs)\ldots\ldots + \beta_1(Ba)^2 + \beta_2(K)^2\ldots\ldots + \lambda_1(Ba*K) + \lambda_2(Ba*Cs)\ldots..$$

Prior Knowledge



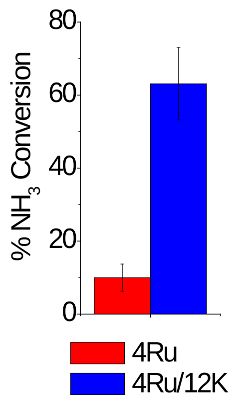
J.C. Ganley, et al. *Catalysis Letters* (2004)

Reactor Results

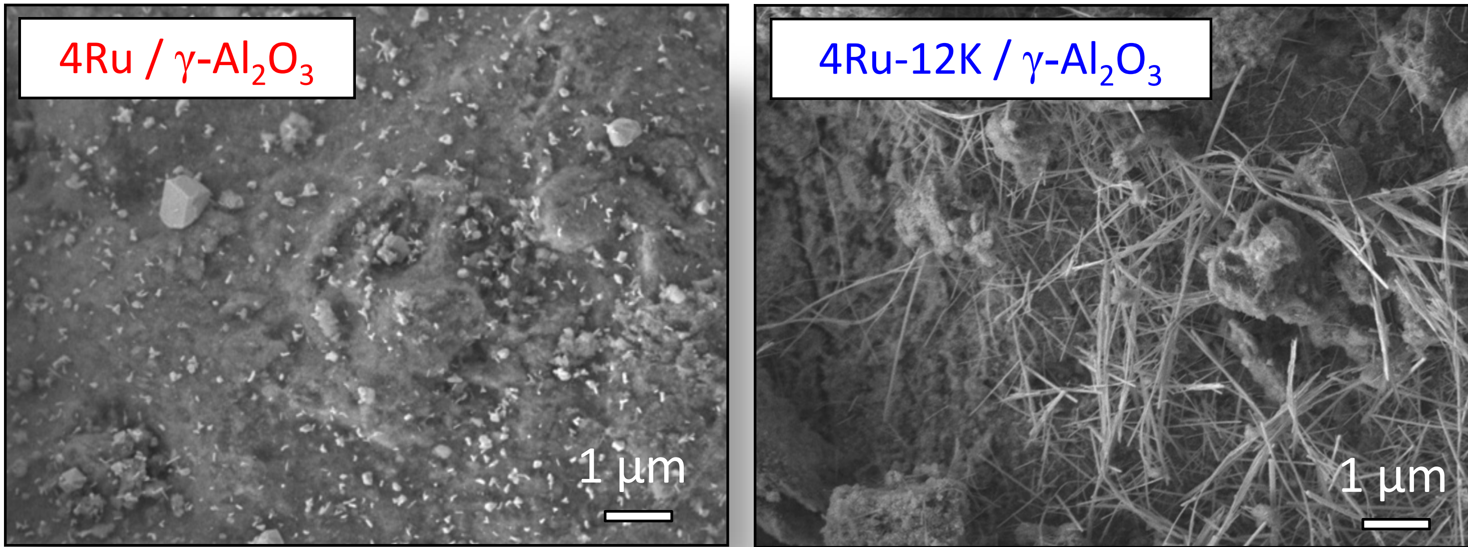


- SV_{NH3}=4000 mL/(g_{cat}*hr)
- P=1atm
- 12% is the optimal K loading for the 4% Ru catalyst.
- Error bars based on 3 runs for each catalyst. Stability tests have not yet been completed (long time on stream for one given T)

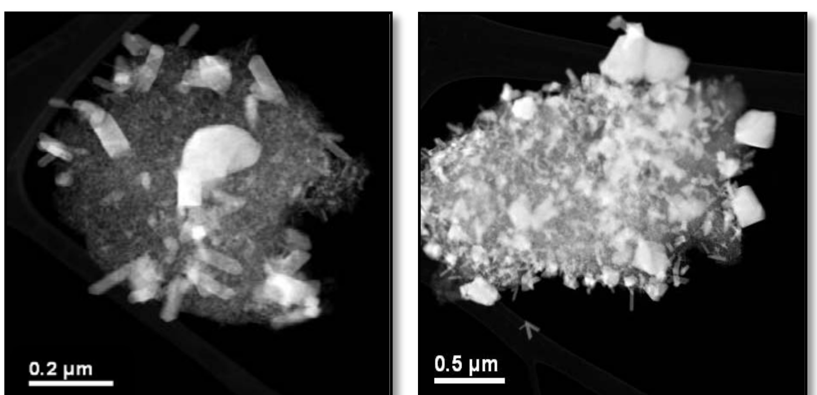
K-Promotion: Effect on Morphology



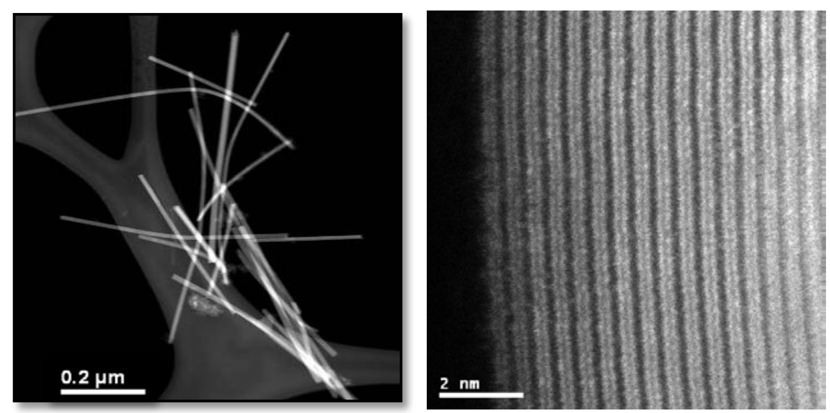
T = 350°C



Microscopy images taken by W. Pyrz



Ru catalyst is a mixture of nanoparticles and large agglomerates

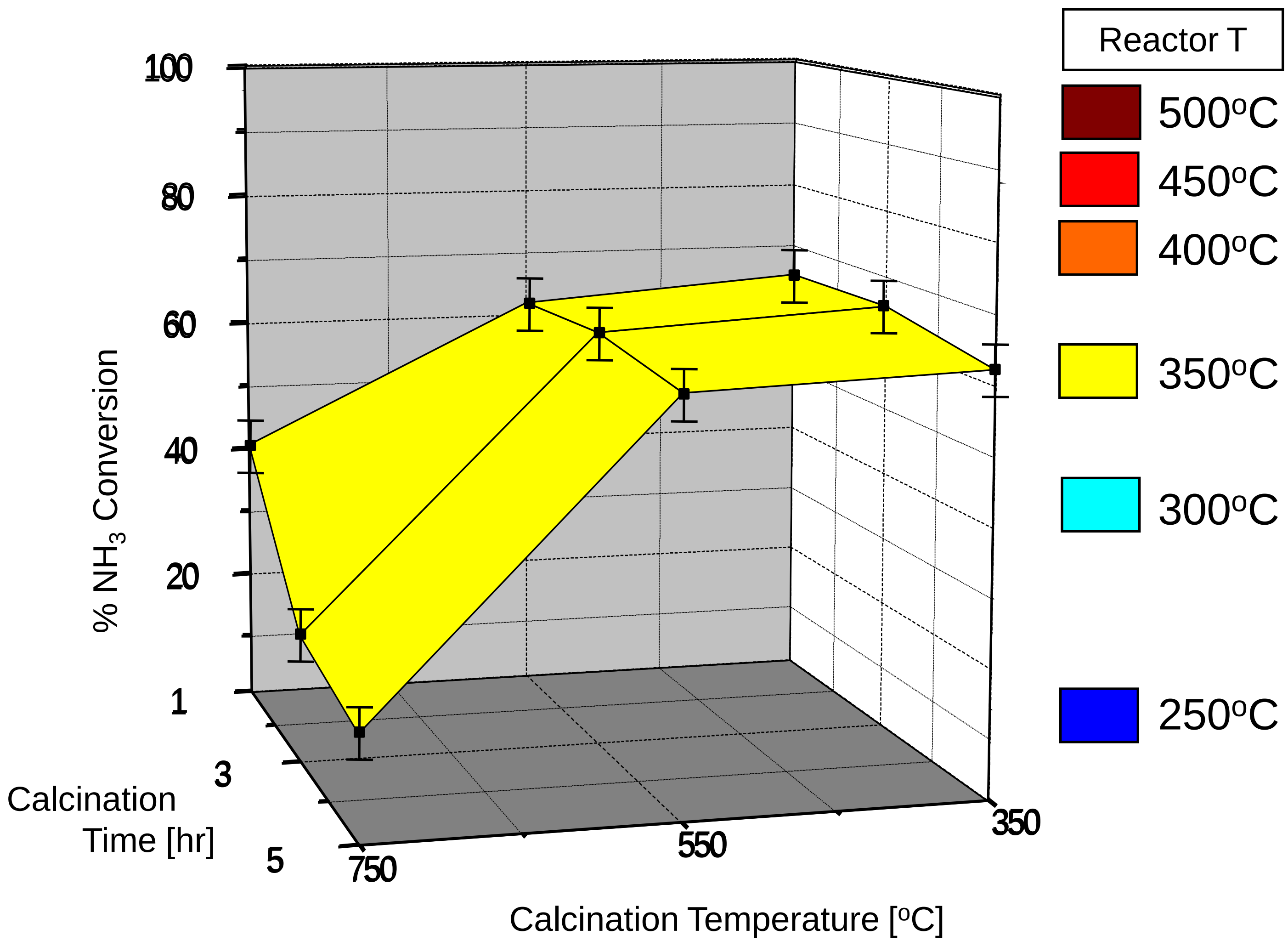


Addition of K promotes the growth of nanowhiskers

"nano-whiskers" identified as Hollandite crystal: KRu_4O_8

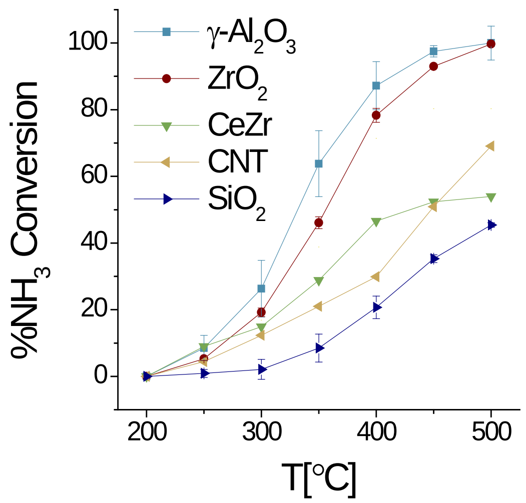
W. Pyrz, R. Vijay, J. Binz, J. Lauterbach, and D. Buttrey, *Topics in Catalysis* (2008) 50:180–191

Preparation: Calcination Temperature and Time

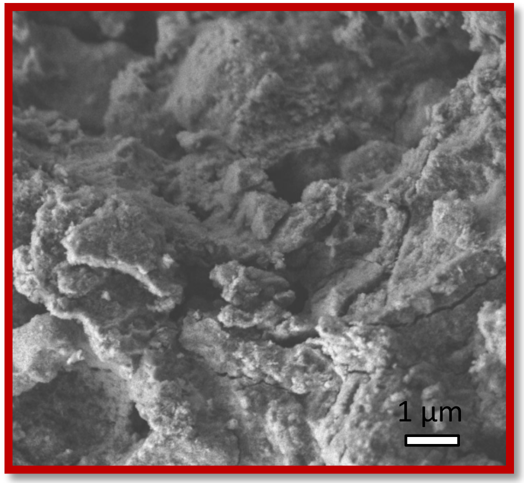


Catalyst: 4Ru /12K on γ-Al_2O_3

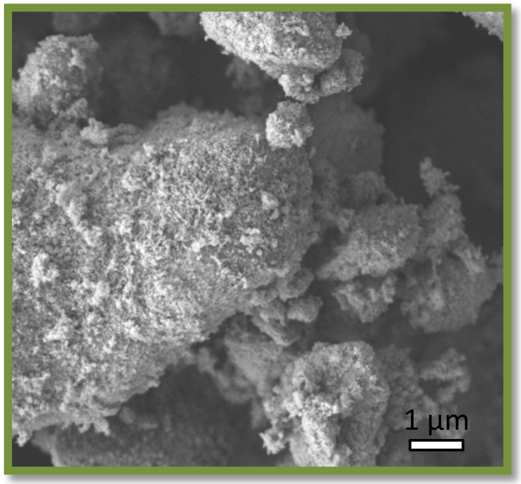
Support Material: Effect on Morphology



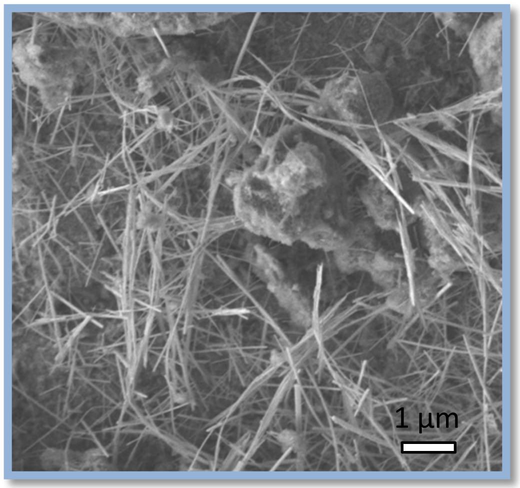
ZrO_2



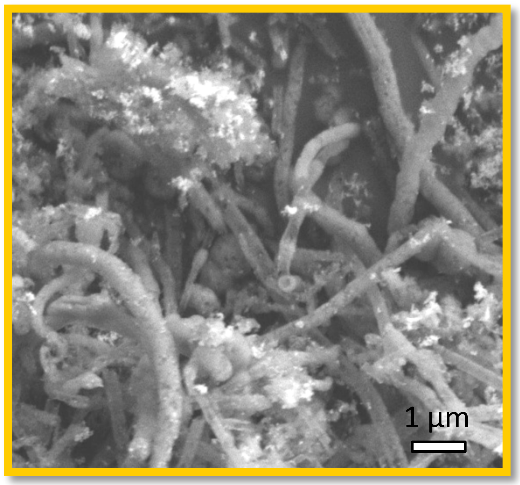
CeZr



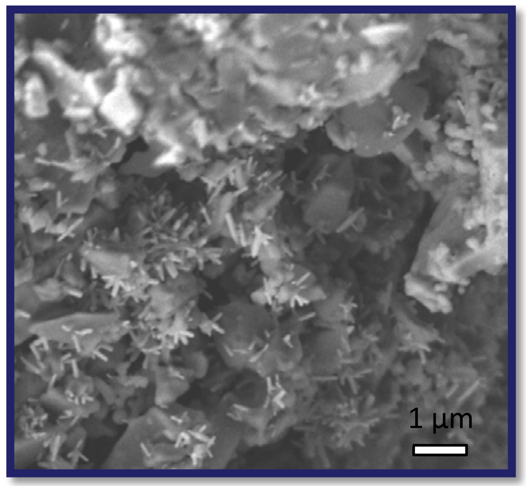
γ-Al_2O_3



CNTs



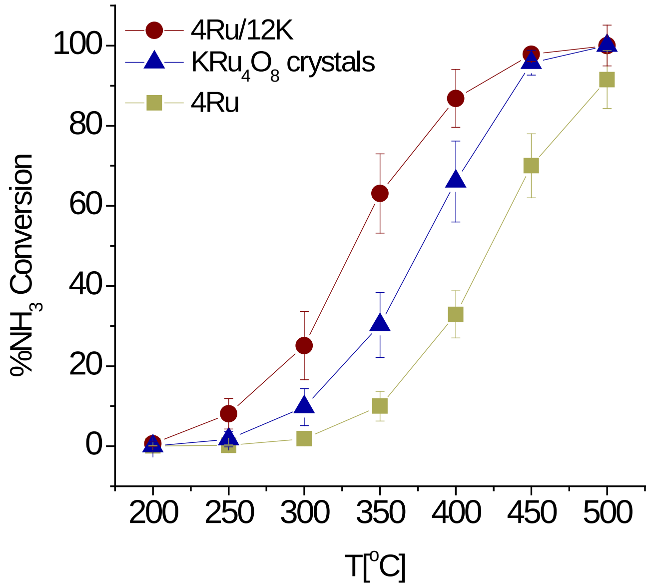
SiO_2



Whiskers only form on γ-Al_2O_3 support.

4Ru /12K on various supports

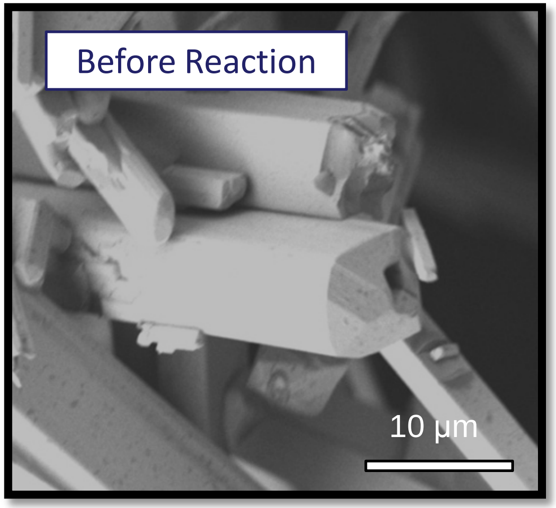
Synthesis and Activity of KRu_4O_8

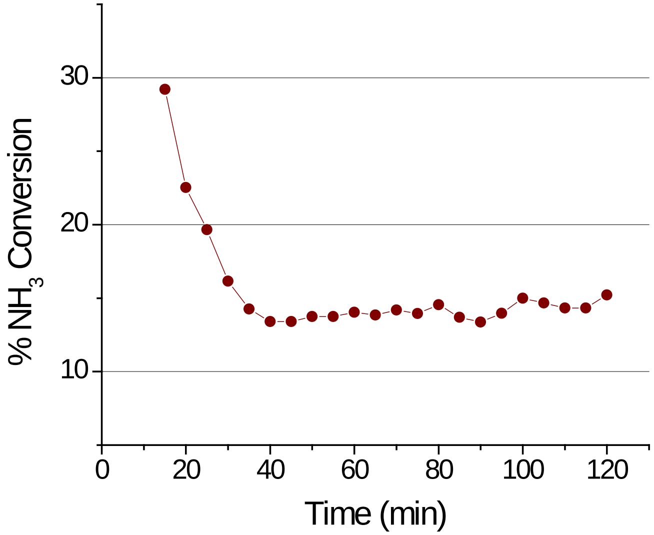


$$K_2CO_3 + RuO_2 \xrightarrow{1000^o C, 16 hours} KRu_4O_8$$

M. Foo, et al. *Mat Res Bulletin* (2004)

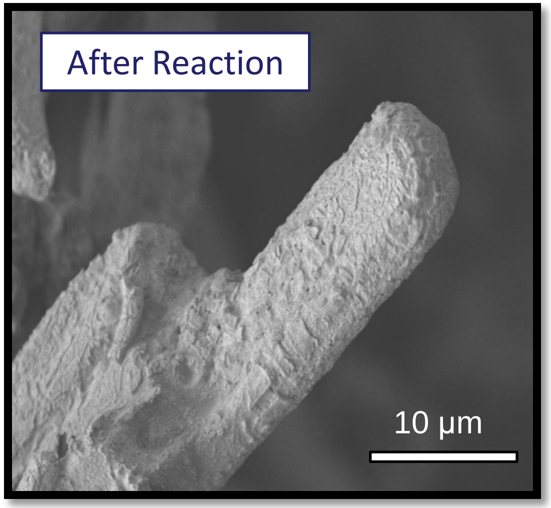
After Hollandite is synthesized, it is exposed to reduction then tested for activity





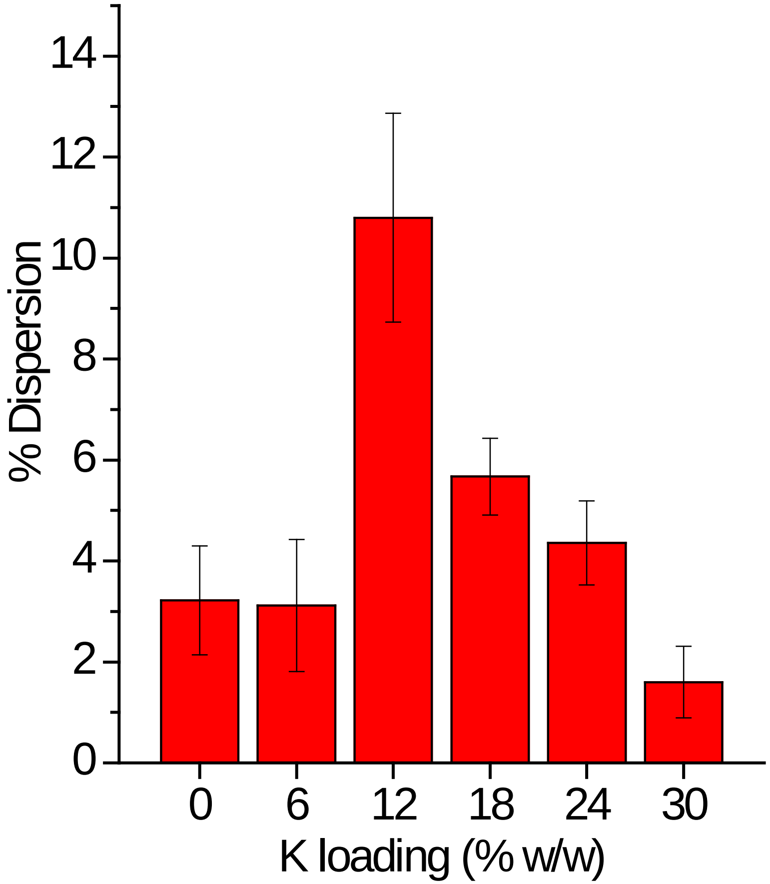
However, we find that the crystal oxide is not stable in H_2 reducing conditions

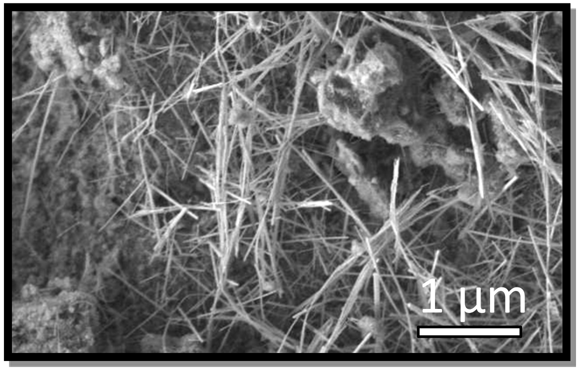
The hollandite is not the active phase



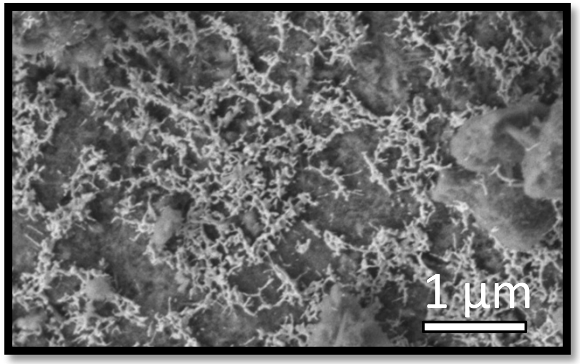
Observations

- K loadings of 6, 24, and 30 % w/w K grow no whiskers.
- Whiskers degrade during reaction.





4Ru/12K catalyst, as synthesized.



4Ru/12K catalyst, after reaction

Summary and Conclusions

- HTE: allows efficient identification of kinetic models
- HTE: identified promising leads for NH_3 decomposition
  - Ru promoted by K is highly active, forms KRu_4O_8 Hollandite
- KRu_4O_8 crystals degrade in NH_3
  - Crystals-only sample undergoes large conversion decrease
- Hollandite presence indicates high activity
  - Support: γ-Al_2O_3
  - Evidence that hollandite leads to an efficient way to disperse Ru

HTE + characterization = discovery of new morphology that leads to active catalysts

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