Material Discovery and High Throughput Exploration of Ru based Catalysts for Low Temperature Ammonia Decomposition

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Ammonia Fuel and Energy Storage: Cracking & Fuel Cells

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Pittsburgh, Transylvania

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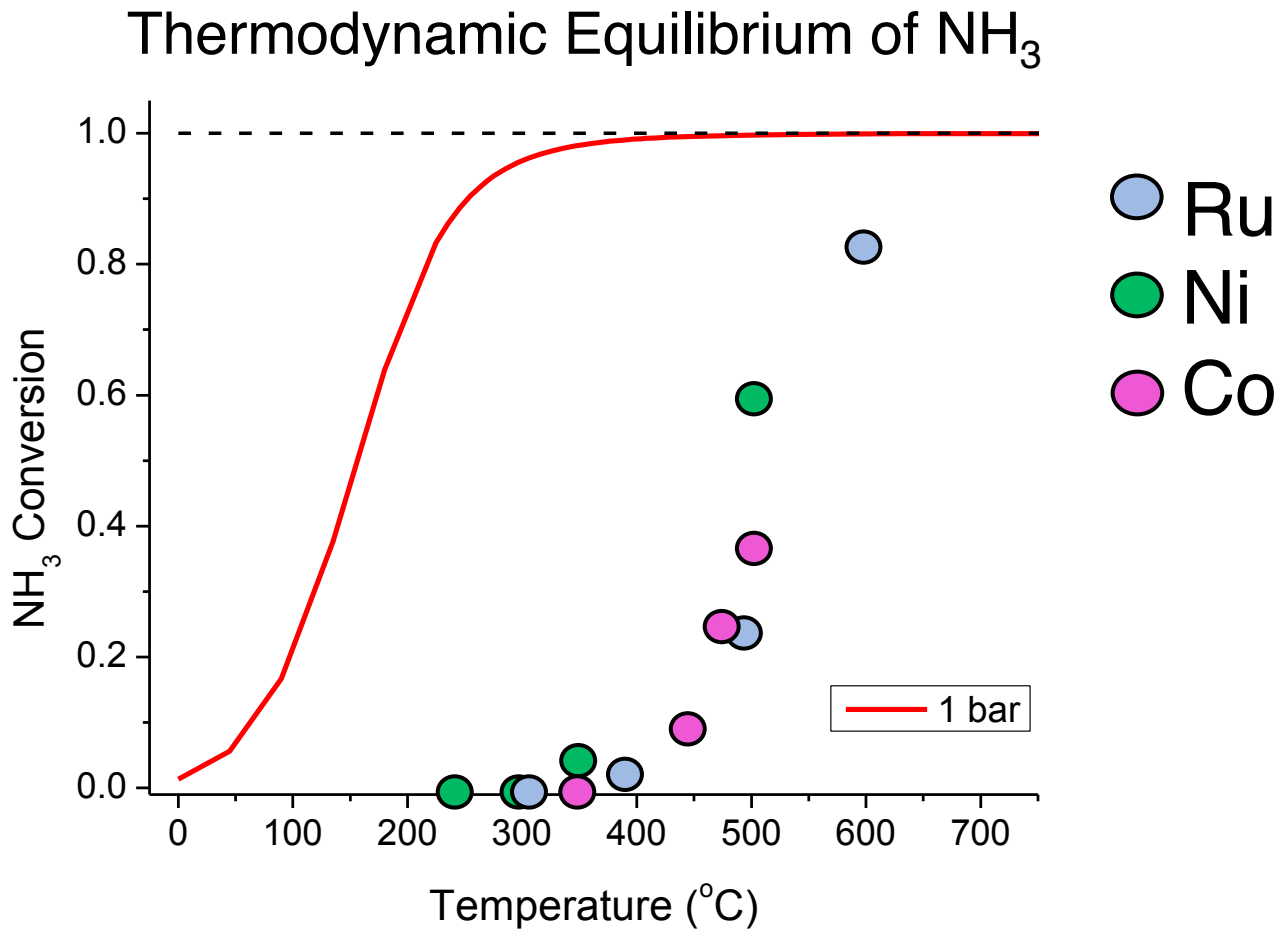
Thermocatalytic Ammonia Decomposition



Dehydrogenation

$$NH\downarrow 3 \xrightarrow{-H} NH\downarrow 2 \xrightarrow{-H} NH \xrightarrow{-H} N$$

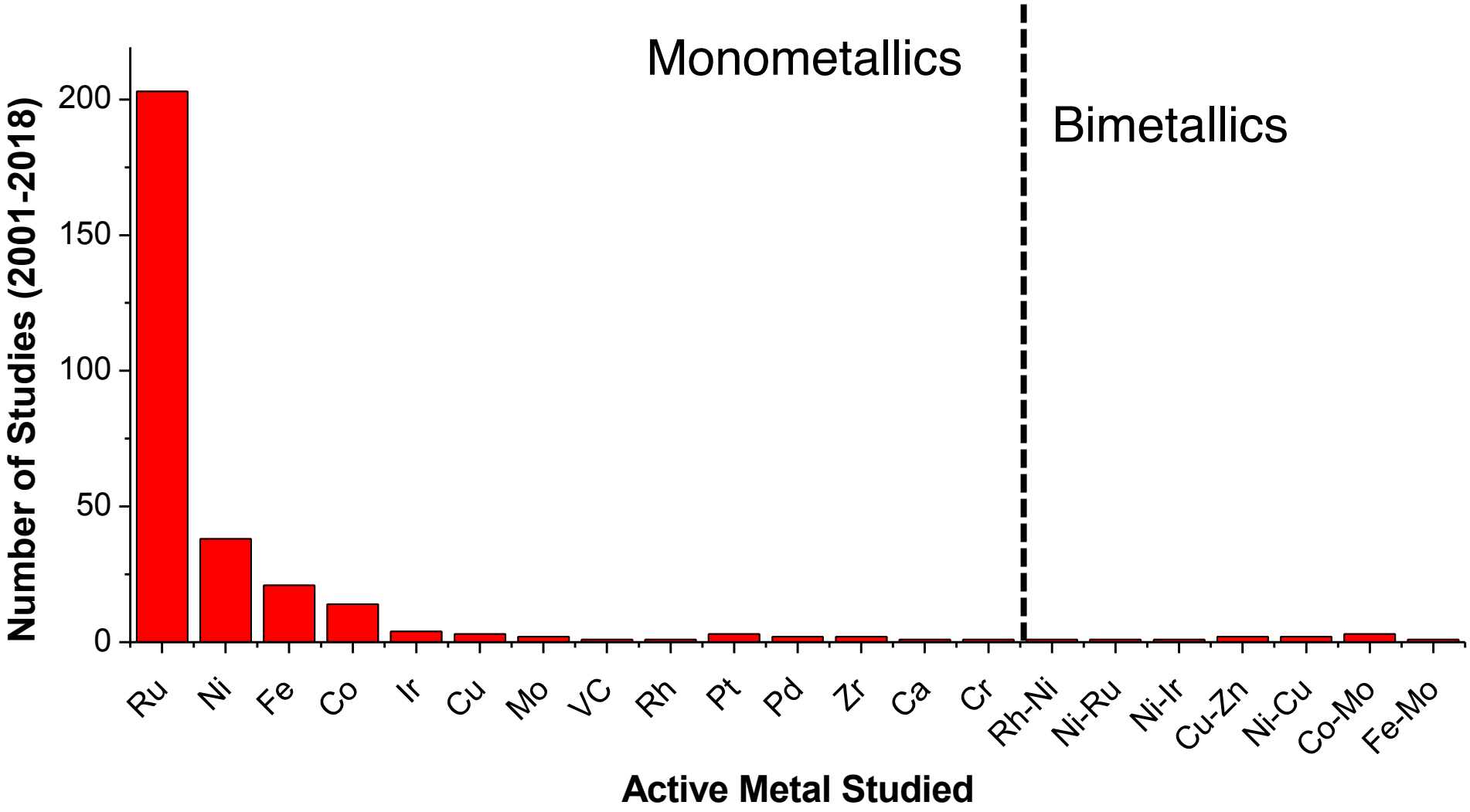
Recombination

$$N + N \rightarrow N\downarrow 2$$

$$H + H \rightarrow H\downarrow 2$$

Zheng et al., Catal Lett 119 (2007) 311-318.
Torrente-Murciano et al., Catal. Today 286 (2017) 131-140.
Mukherjee et al., App. Catal B: Environmental 226 (2018) 162-181.

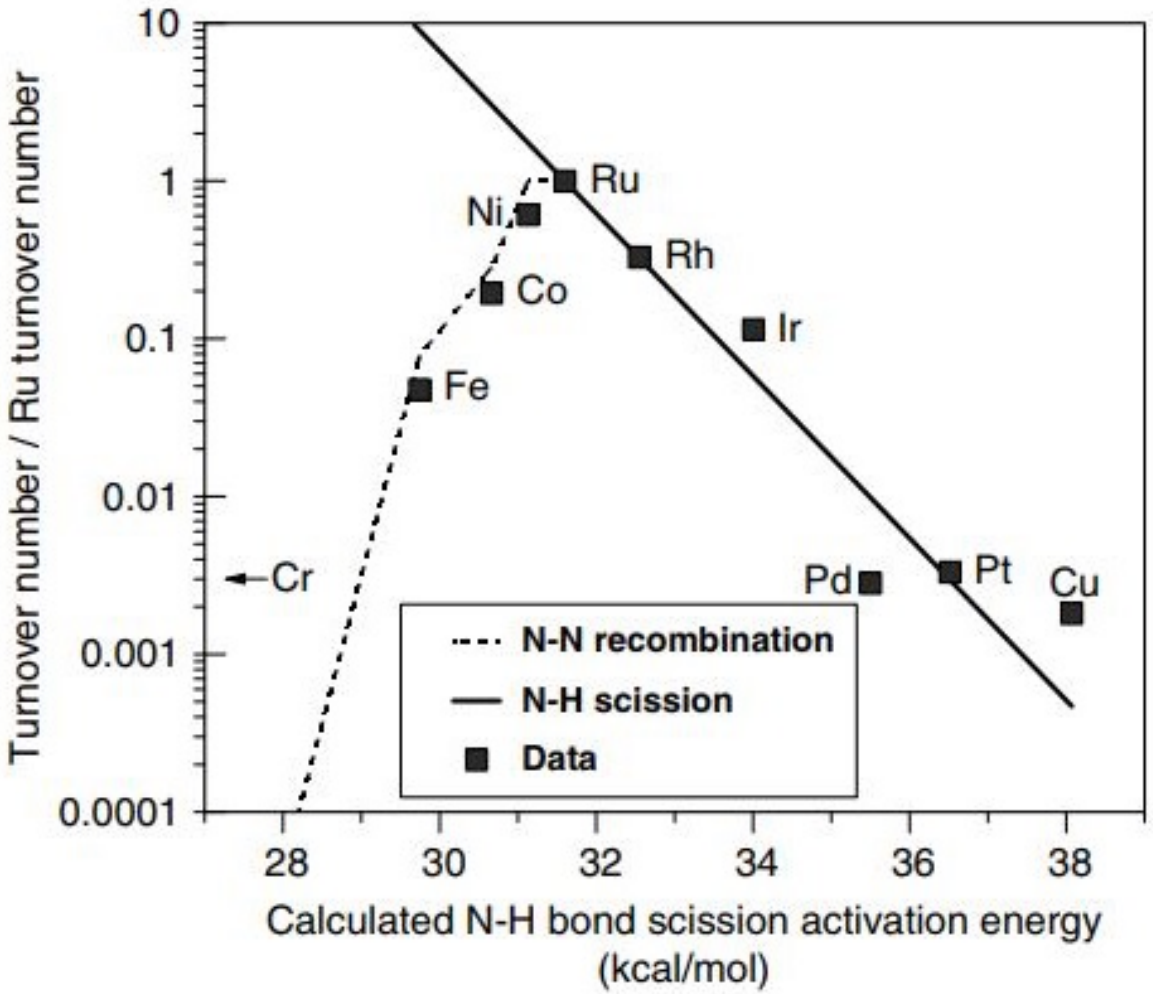
Materials for Ammonia Decomposition



Ammonia Decomposition

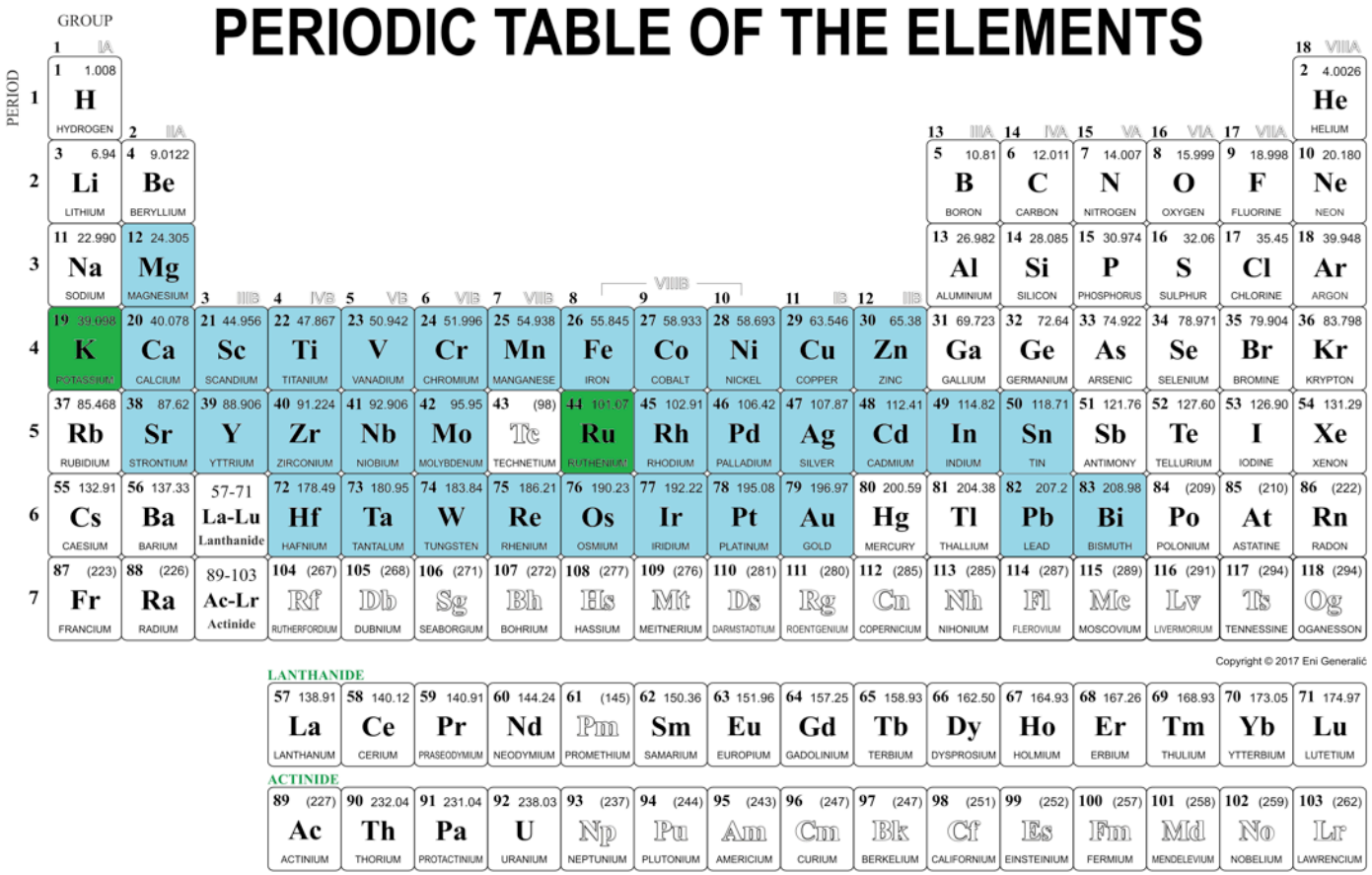
Many theoretical models exist that correlate different energies to NH_3 decomposition activity

No correlation found between 7 models and 13 metals



Ganley et al., Catalysis Letters (2004) 96:117

Design Space



Incipient Wetness Impregnation

Baseline 4wt% Ru on Al_2O_3

Total 4wt% metal

- 3wt% Ru + 1wt% M
- 2wt% Ru + 2wt% M
- 1wt% Ru + 3wt% M

+12 wt% K

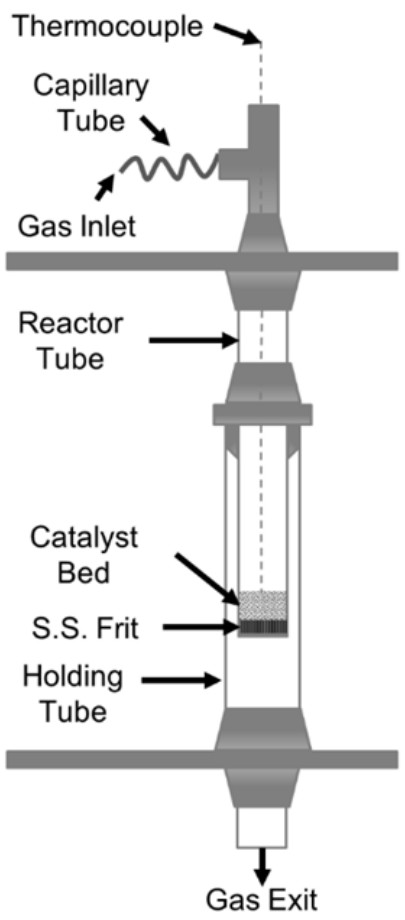
---

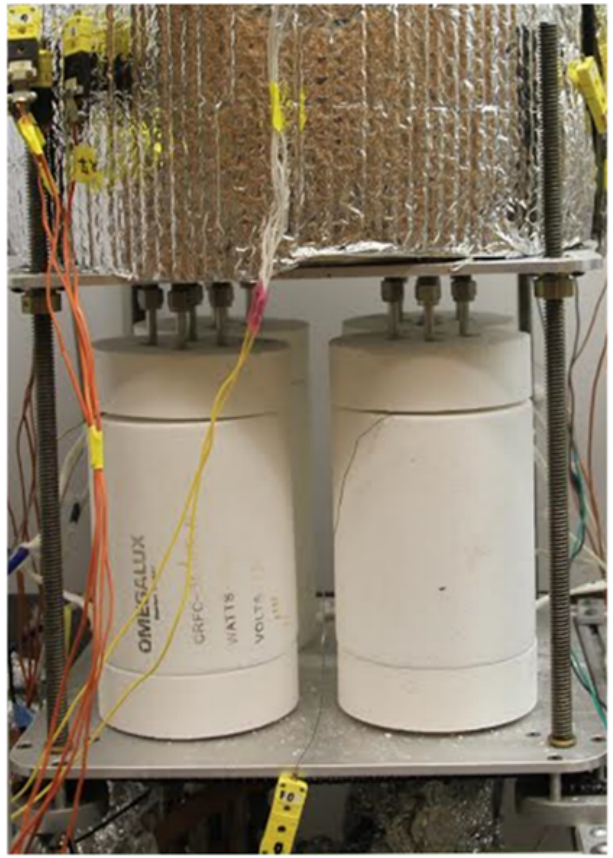
105 unique formulations + repeats

Pyrz et al.,Top Catal (2008) 50:180-191.

High-Throughput Reactor System

- 16 parallel plug flow reactors
- Capillary flow distribution system
- Individual catalyst bed thermocouples
- Four furnaces with PID control (Tmax=950°C)
- Powder catalysts: 0.05-1 g
- Atmospheric pressure
- Moving top plate and winch system for efficient loading/unloading



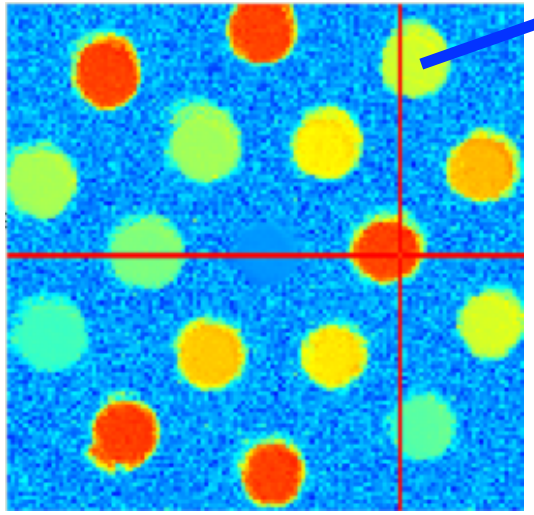


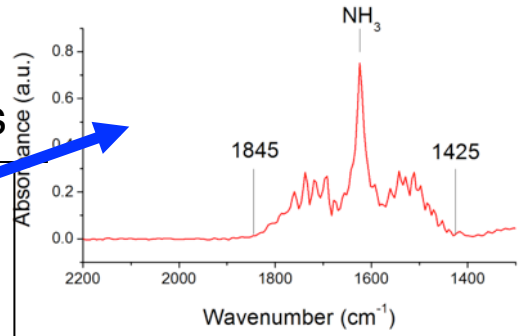
Sasmaz et al., Engineering 1(2), 2015
Hendershot et al., Appl. Catal. A 254, 107 – 120 (2003)

Effluent Gas Analysis

- **IR gas-phase spectroscopy**
  Works for any gas with IR signature

Spatially resolved IR spectra
128 x 128 = 16,384 detectors



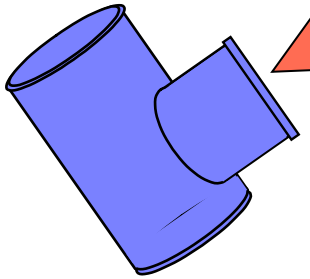


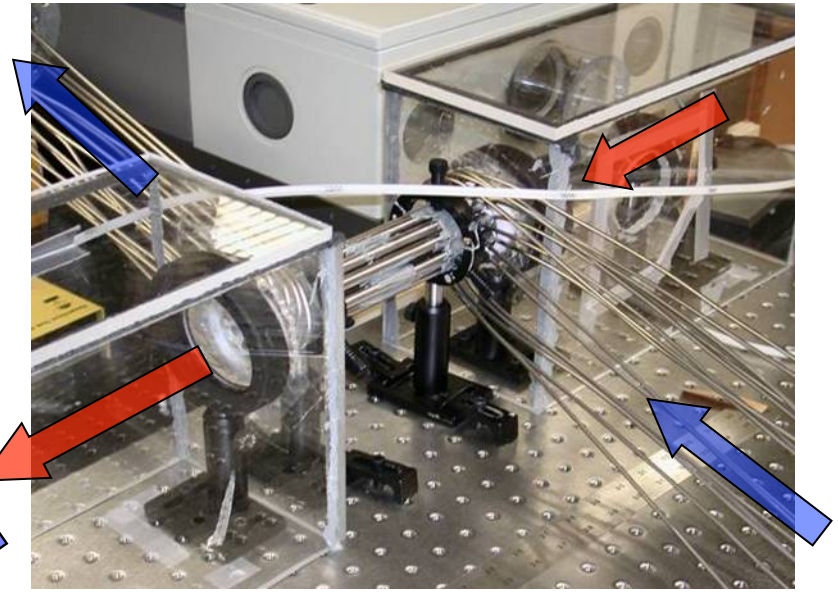
128 pixels

128 pixels

- **16-element gas-phase array**
  Analyze all 16 product streams in parallel in < 2 sec

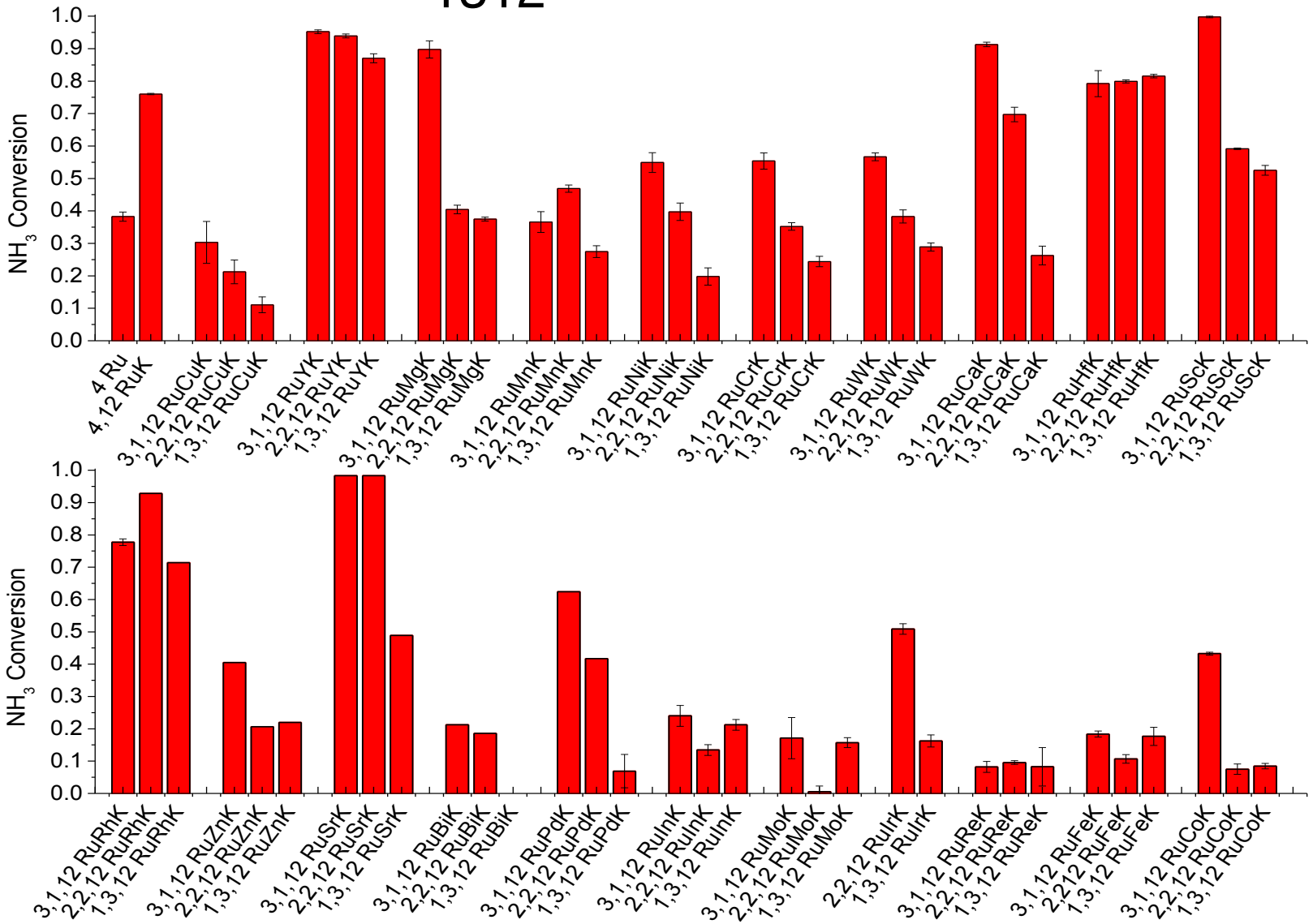
FPA





Snively, C.M. and J. Lauterbach *Applied Spectroscopy* **59**(2005)
Snively, C.M., S. Katzenberger, G. Oskarsdottir, and J. Lauterbach *Optics Letters* **24** (1999)

Groupings of 3112 2212 1312 RuMK



Reaction Conditions

Temperature = 300°C

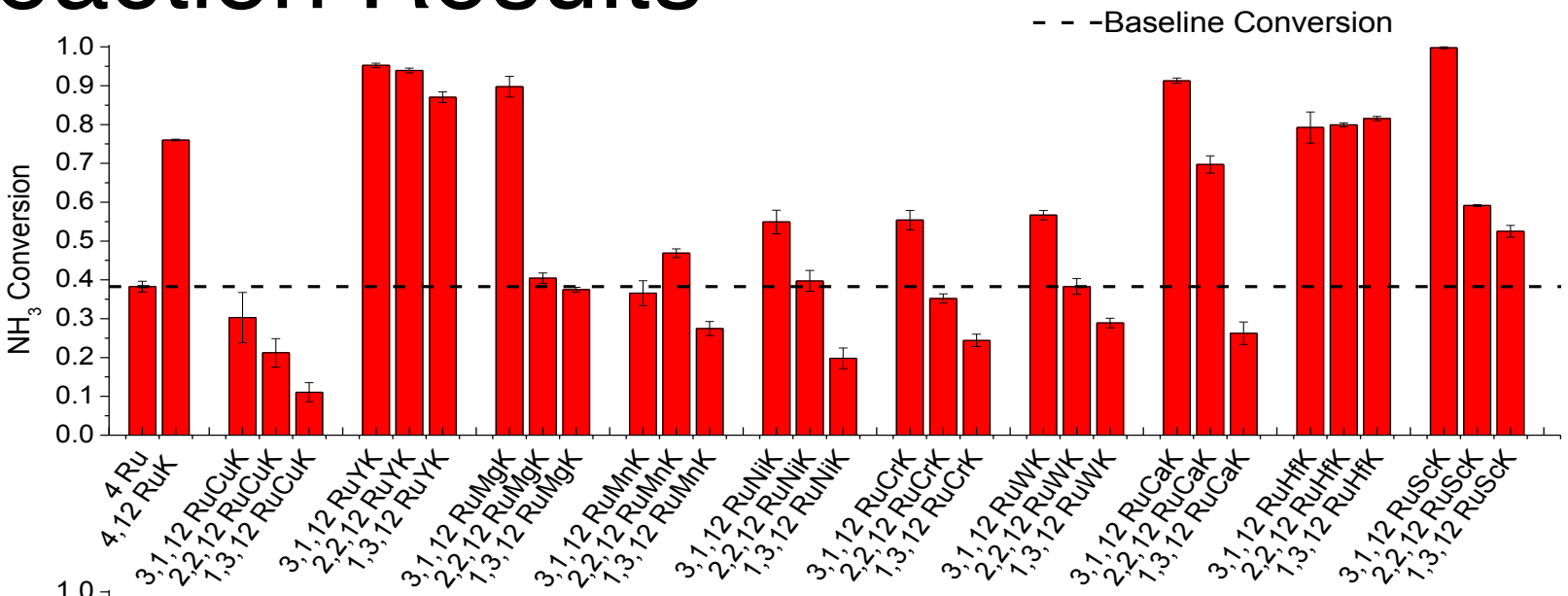
1% NH_3 in balance Ar

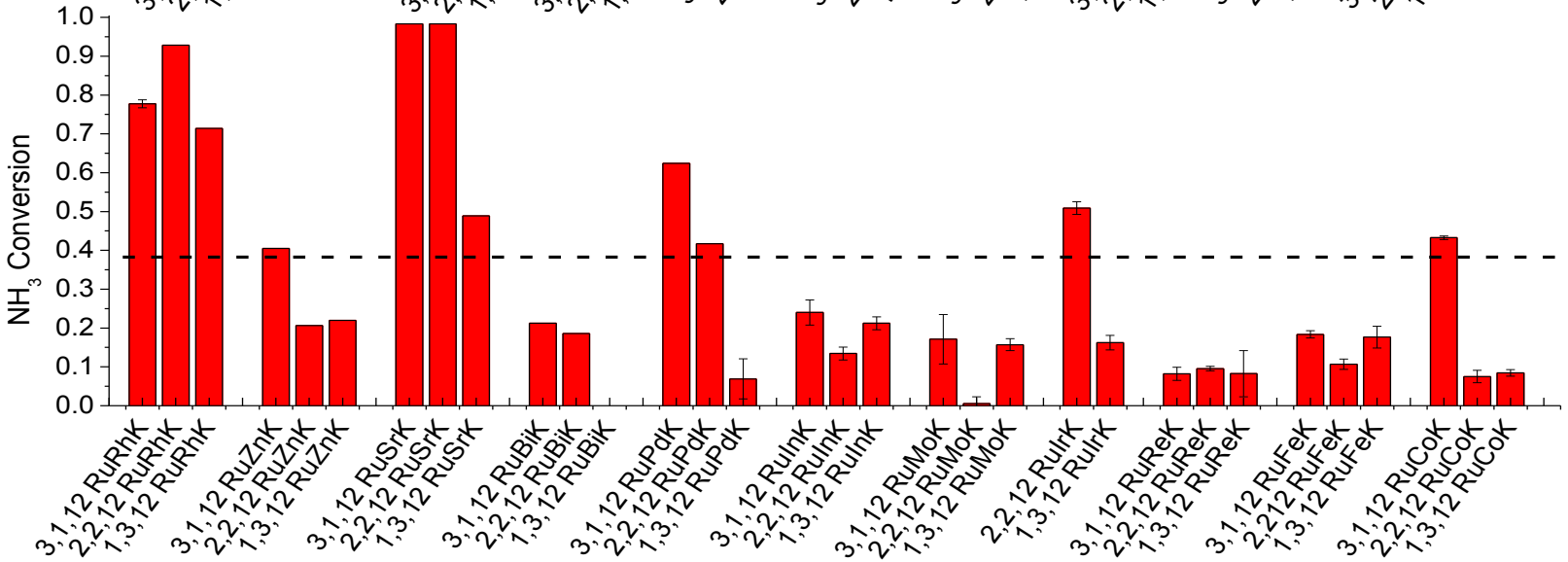
Pressure = 1.01 bar

200 mg catalyst

30,000 $\mathrm{mL/g\downarrow cat \cdot hr}$

Reaction Results





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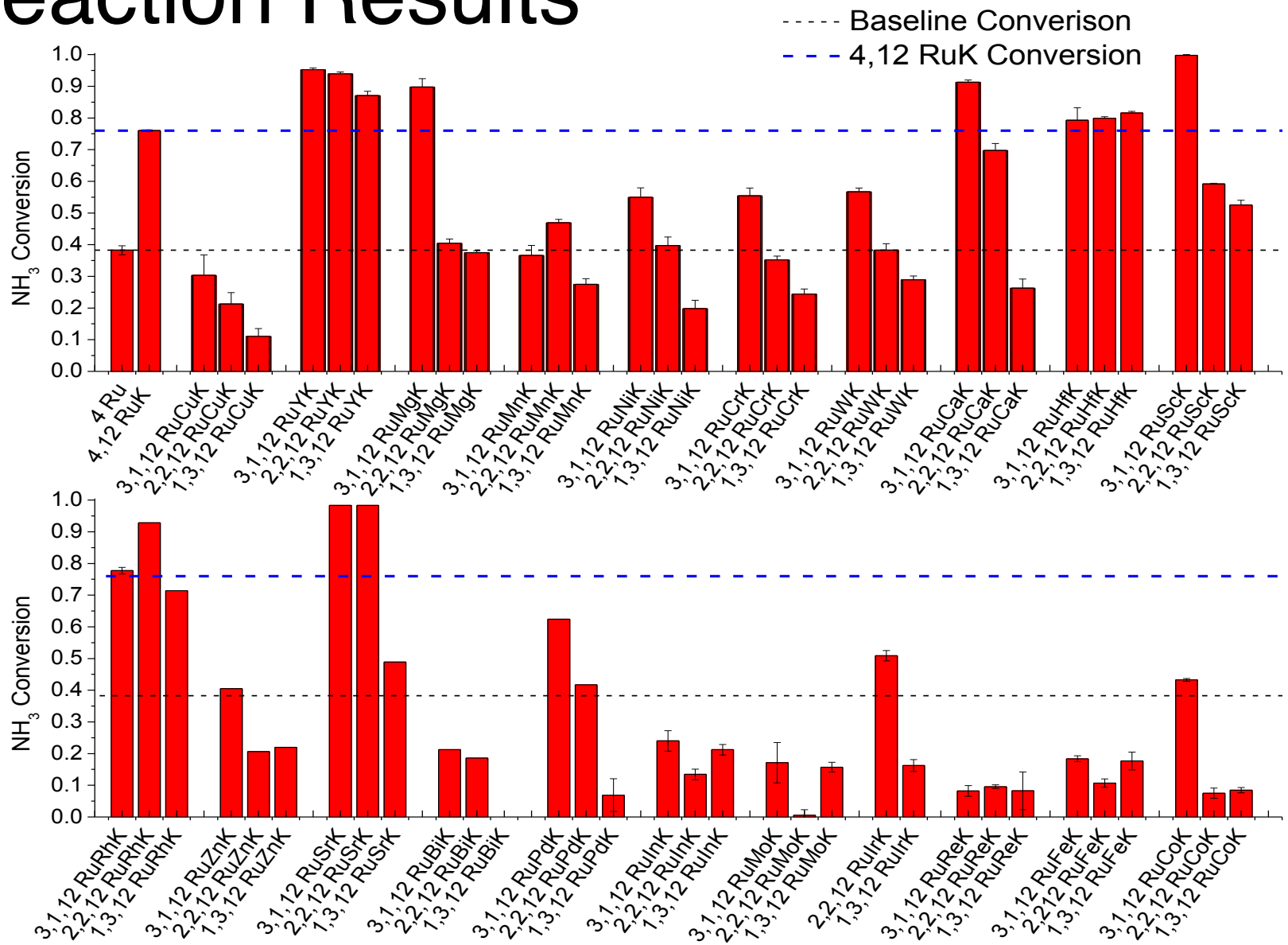
Reaction Results



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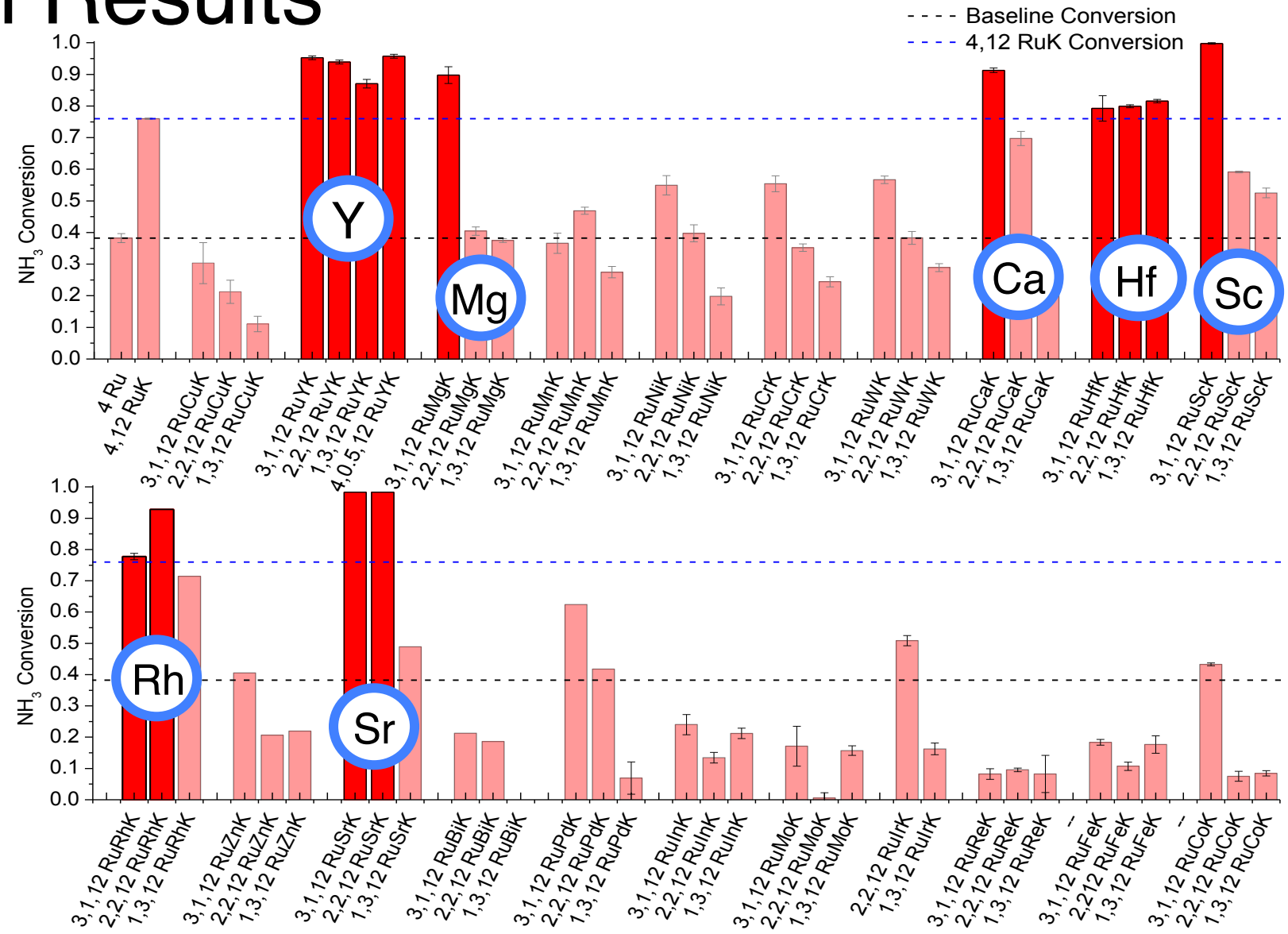
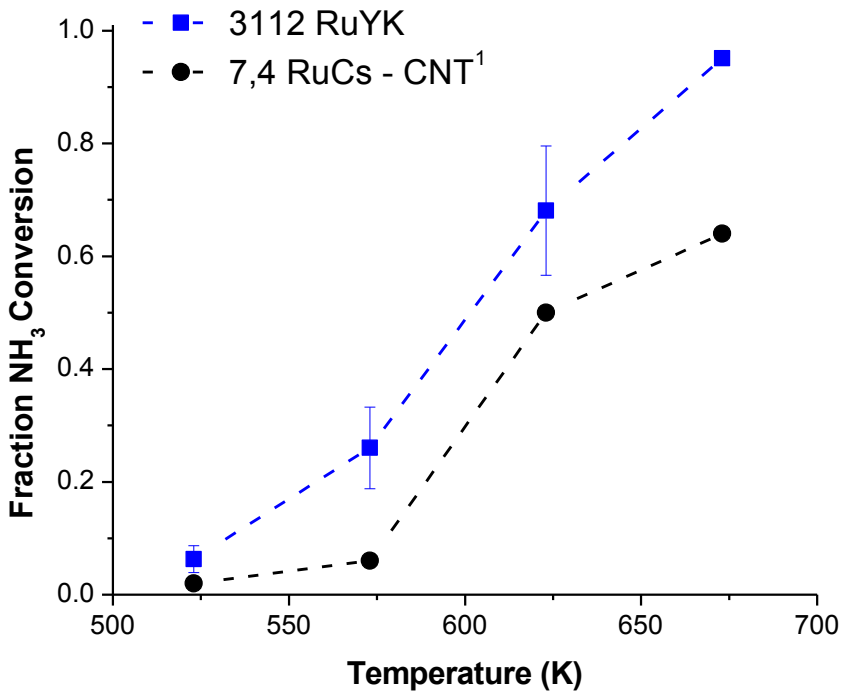
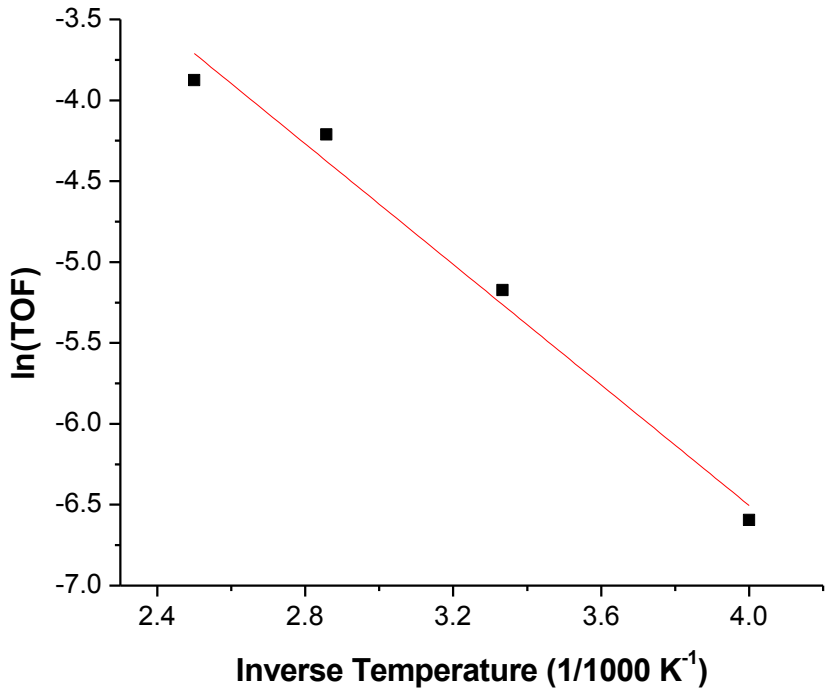
Reaction Results



Reaction Conditions: Temperature= 300°C, 1% NH_3 in balance Ar, Pressure = 1.01 bar, 200 mg catalyst, 30,000 $mL/g_{cat} \cdot hr$

3,1,12 RuYK



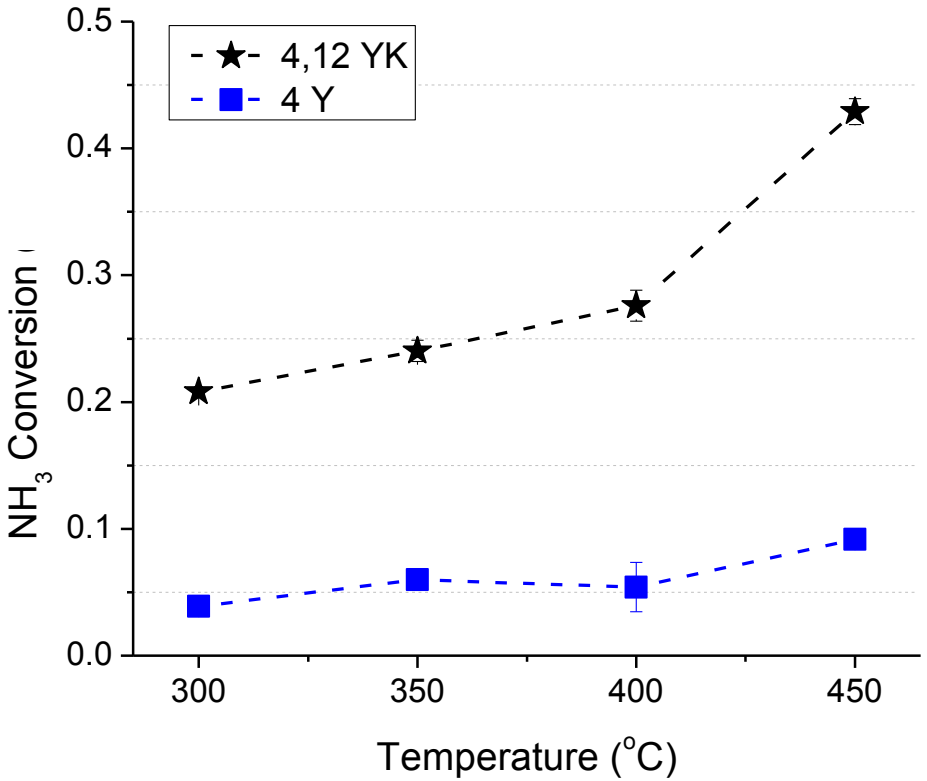


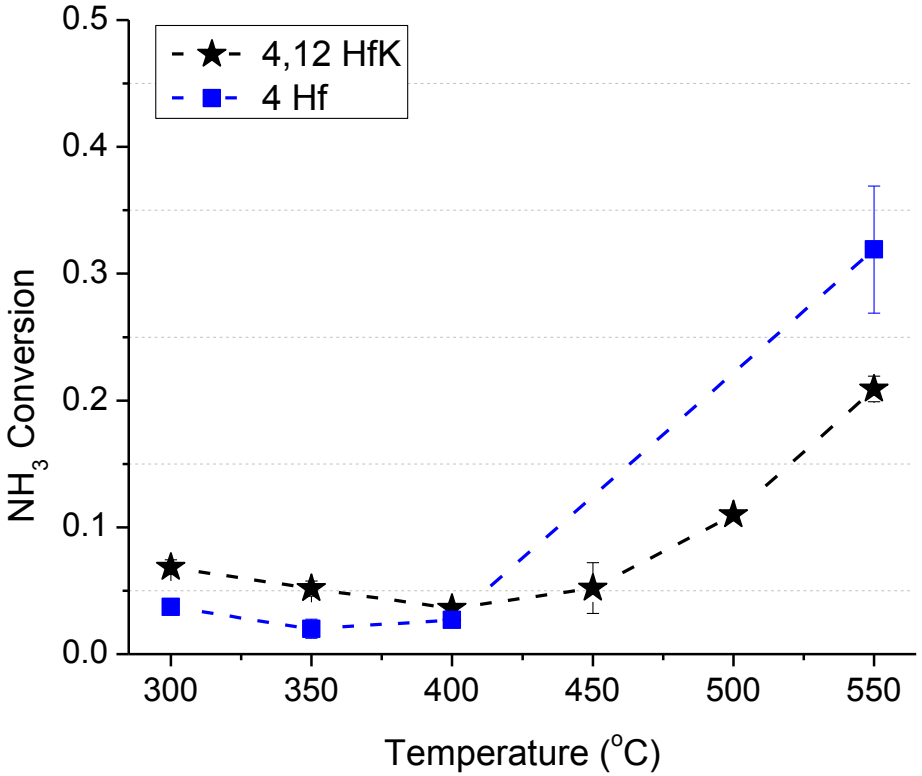
Catalytic Activity in 100% NH_3, atmospheric pressure and 52,000 mL $NH_3 \cdot (min \cdot g_{cat})^{-1}$

Catalyst	Conversion @ 673K	Activation Energy (kJ/mol)
3,1,12 RuYK – Al_2O_3	95	54.1
7,4 RuCs – CNT[1]	64	78.6

[1] Hill, Applied Catalysis B: Environmental 172–173, (2015), 129-135.
Mukherjee et al., Applied Catalysis B: Environmental 226 (2018) 162-181.
Provisional Patent Pending: *"Ammonia Decomposition Catalysts and Systems"*, US patent application 62/720,356, August 2018.

Single Reactor Results

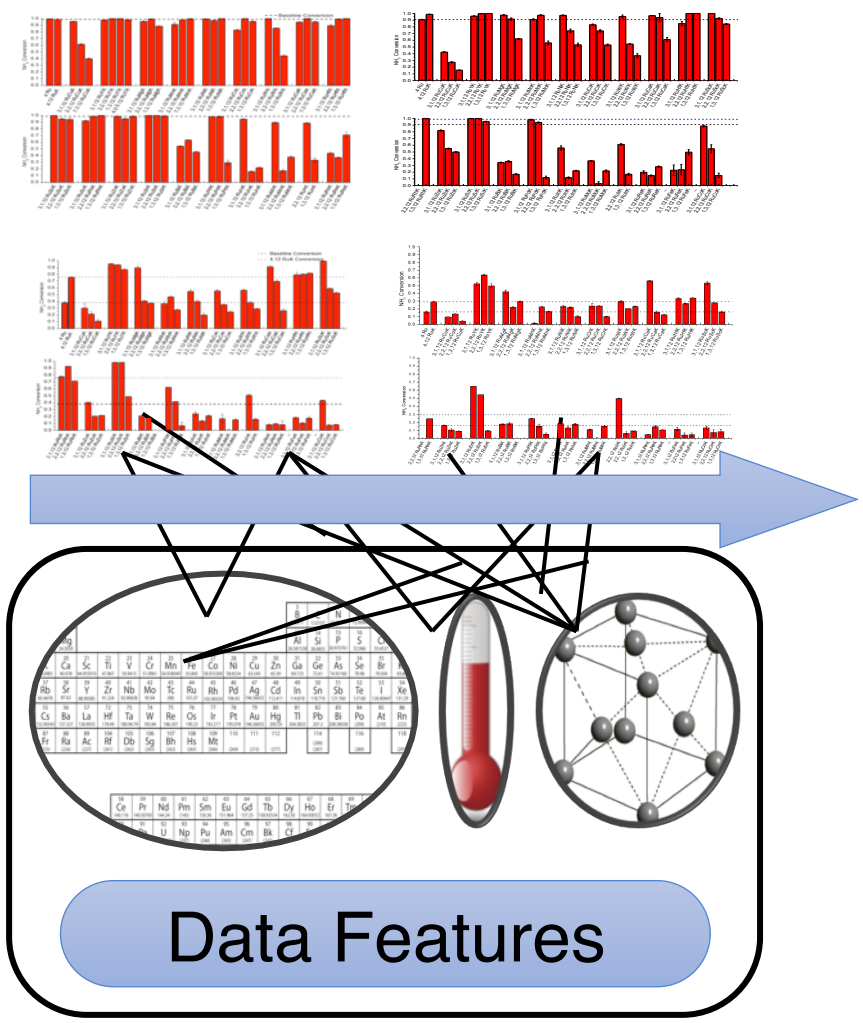




Reaction Conditions: 10% NH_3 in balance Ar, Pressure = 1.01 bar, 200 mg catalyst, 30,000 $mL/g_{cat}\cdot hr$

Provisional Patent Pending: *"Ammonia Decomposition Catalysts and Systems"*, US patent application 62/720,356, August 2018.

Application of Machine Learning in Experimental Catalysis



Machine Learning

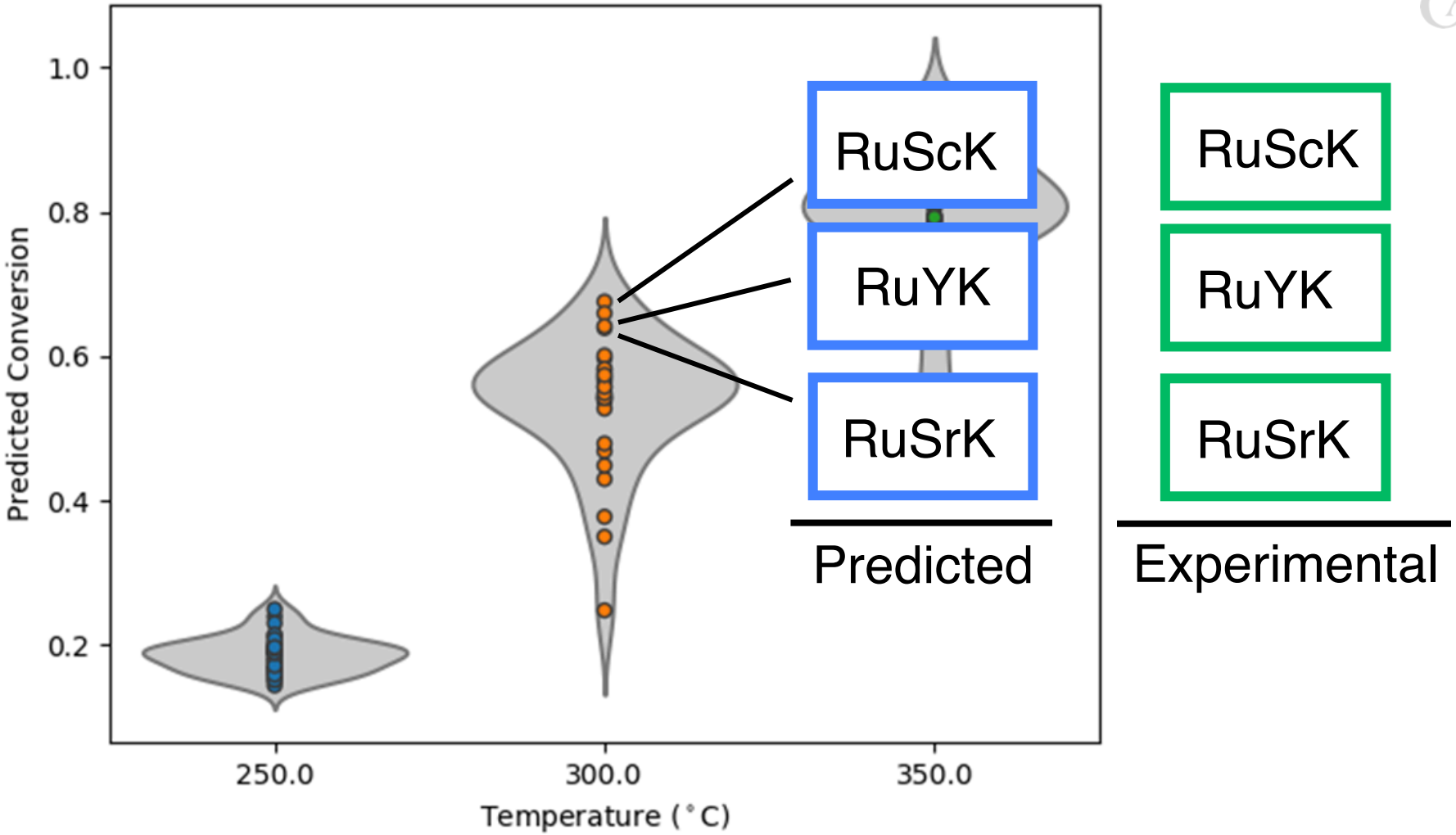
Feature Impacts

Determine which features cause better performance

Find optimally performing material faster and with less experiments

Predictions

Catalyst Predictions



Predicted NH_3 conversion using RuCaK, RuMnK, and RuInK catalysts tested at 250, 300, and 350°C as a training set

ML – Knowledge Extraction

Mean Absolute Deviation (MAD)

$$\sum_{i=1}^{n} 1/n\,(x_i - \mu)$$

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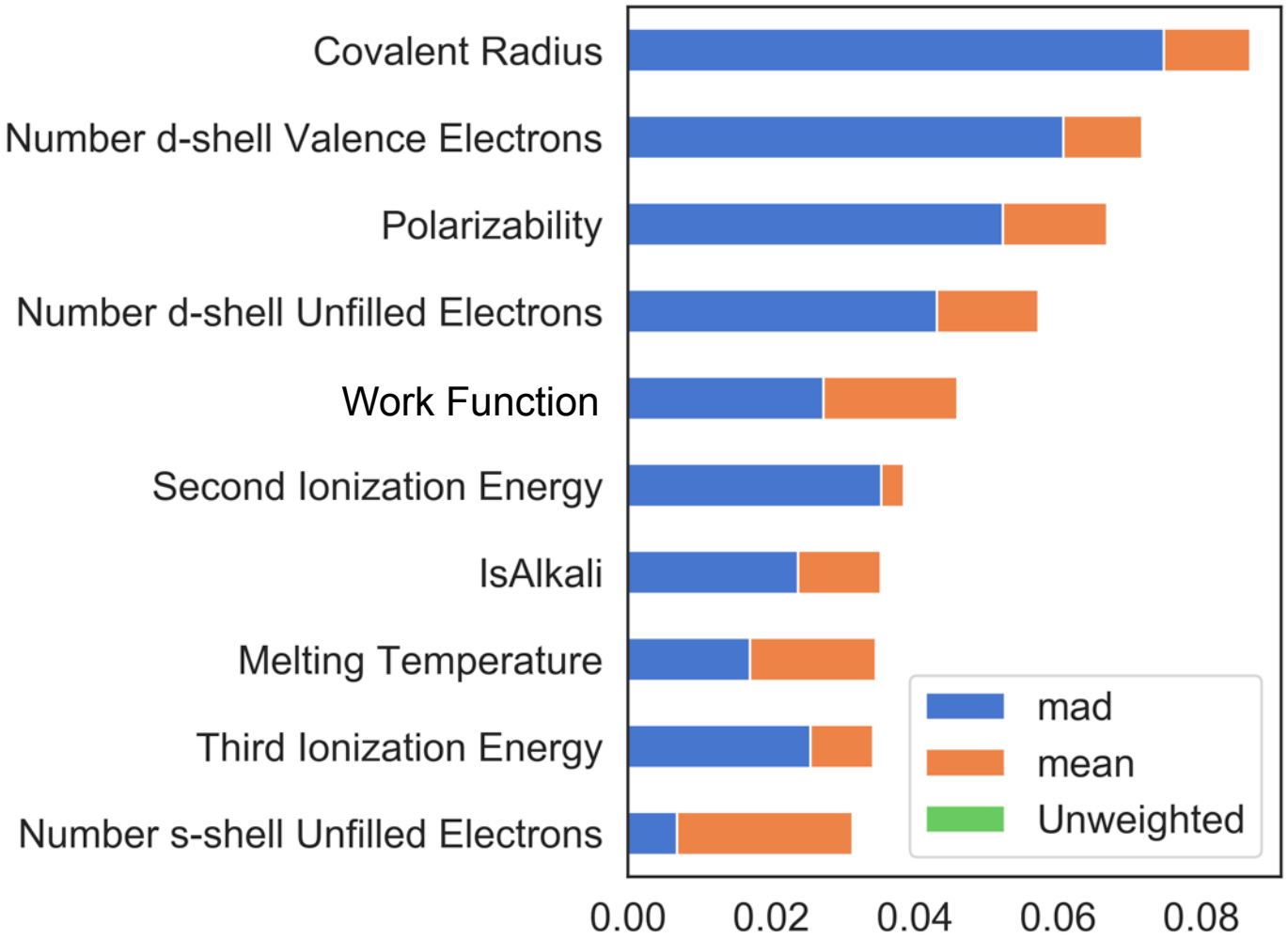
x_i = value of property
μ = average
n = number of samples



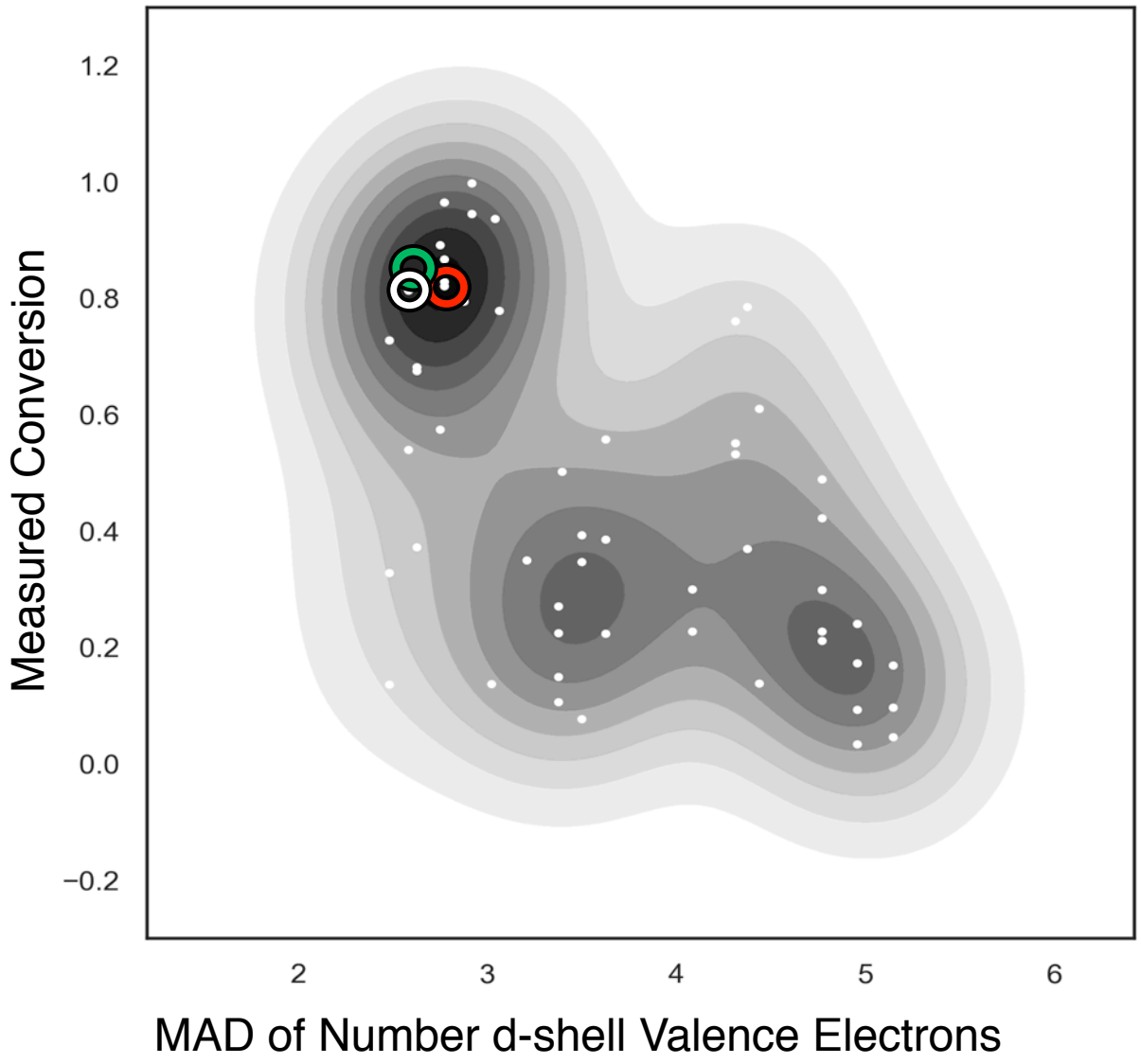
Li et al., J. Mater. Chem. A, 2017 5, 24131-24138.
Liu et al., J. Materiomics, 2017 3 (3) 159-177.

Number d-shell Valence Electrons
T = 300°C

2212 RuYK

3112 RuMgK

3112 RuHfK



Feature Interactions
T = 300°C

2212 RuYK

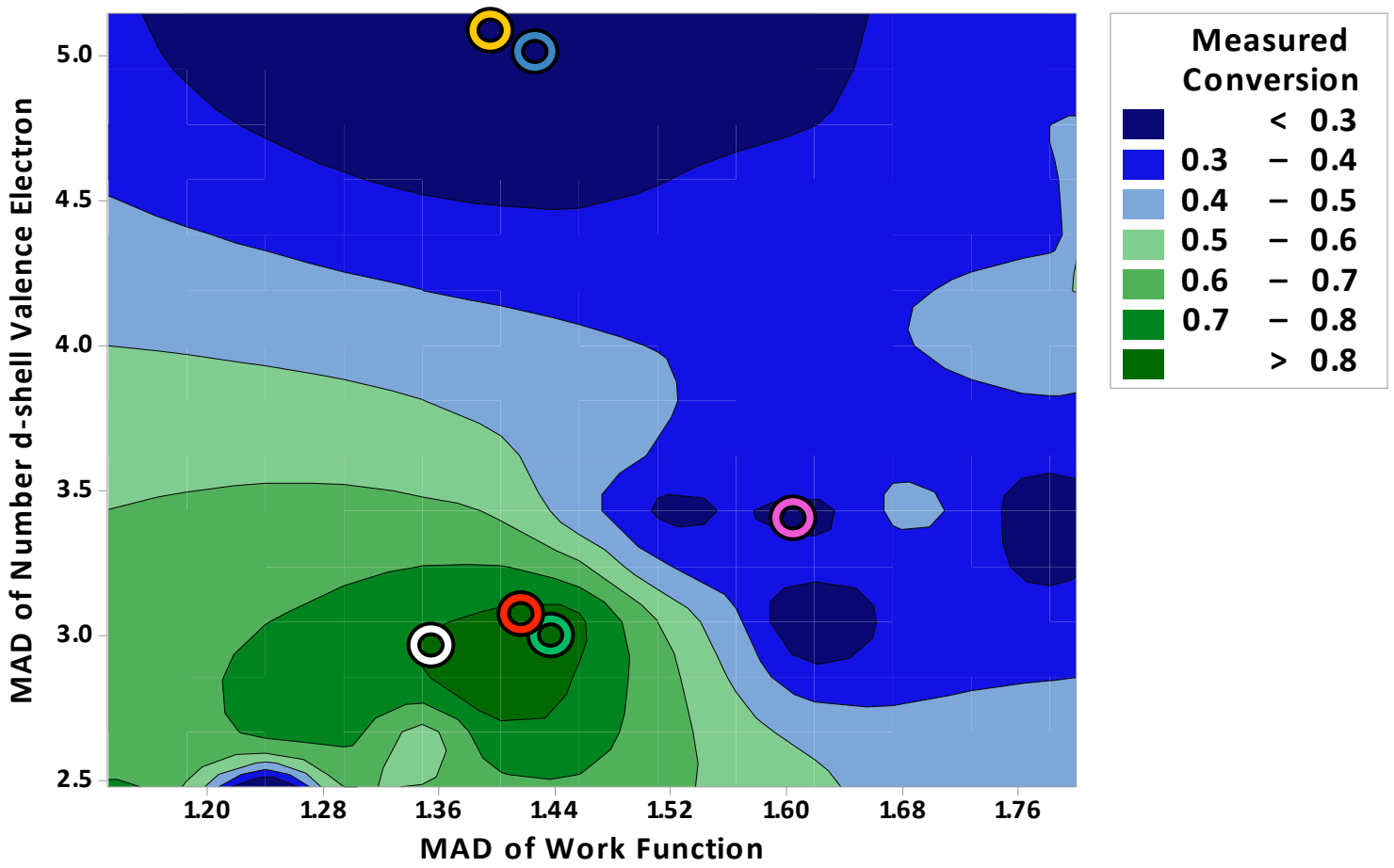
3112 RuMgK

3112 RuHfK

2212 RuInK

1312 RuZnK

3112 RuMoK



Vayenas et al., Nature 1990. 343, 625-627.
Haller, J. Catal. 216 (2003) 12-22.
Binninger et al., Phys. Rev. B. 96, 165405 (2017).

Conclusions

- HTE allows us to screen large amounts of catalysts for low temperature NH_3 decomposition
  - New catalysts formulations discovered substituting Ru with Y and Hf
  - At 300°C, we achieved 30% higher conversion than the “state of the art” catalyst, which has more than 2x Ru
- ML allows to unravel important factors and interactions from HTE data
  - Extraction of features
  - Systematic trends from feature interactions
- Guide future iterations of catalyst design

Acknowledgements

- Strategic Approach to the Generation of Electricity Center (SAGE)
- NSF IGERT DGE-1250052
- ARPA-E DE-AR0000931
- Travis Williams
  - Data Science in Catalysis
  - Nov 1 @ 12:30pm Rm 402

Supplemental Slides

Ammonia Decomposition

- Efficient method for hydrogen storage and transportation
- Liquid at 8 bar and 298K
- Less volume and weight than alternative hydrogen storage methods

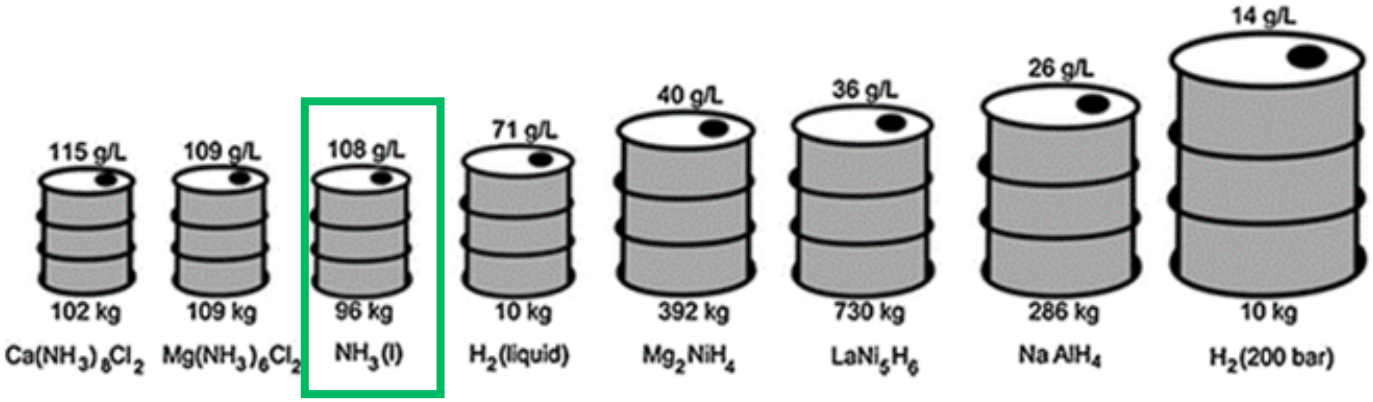
Dehydrogenation

$$NH_3 \xrightarrow{-H} NH_2 \xrightarrow{-H} NH \xrightarrow{-H} N$$

Recombination

$$N + N \rightarrow N_2$$

$$H + H \rightarrow H_2$$

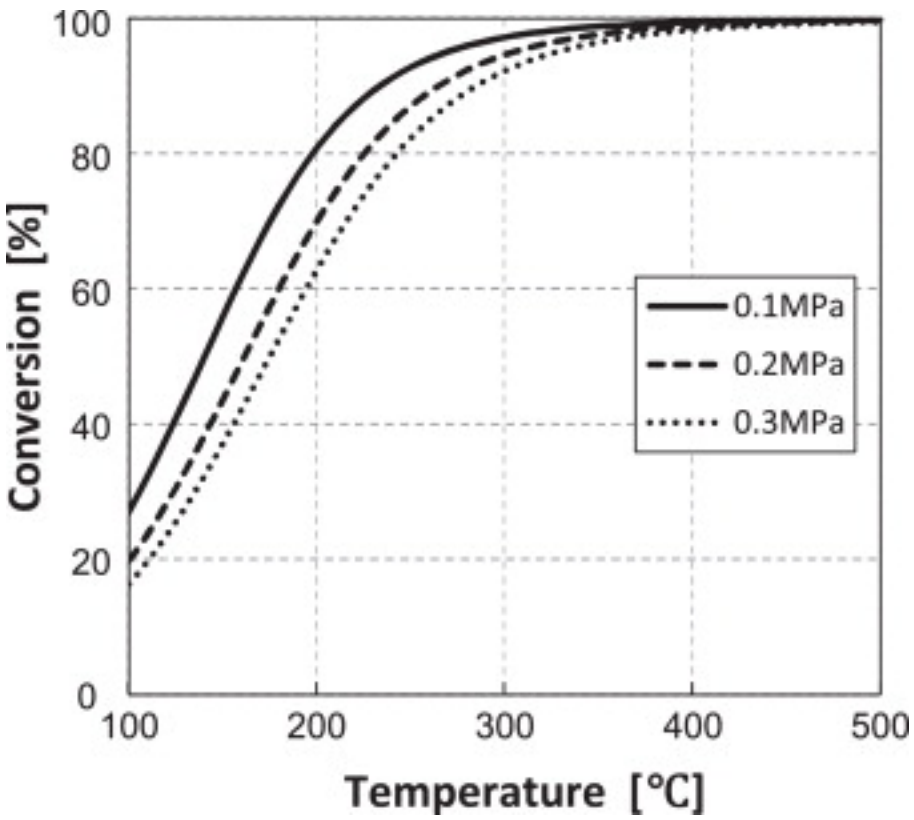


Comparison of equivalent mass and volume of 10 kg of hydrogen stored in different materials

Sakintuna et al., Internation Journal of Hydrogen Energy. (2007). 32:1121-1140.
Mukherjee et al., Applied Catalysis B: Environmental 226 (2018) 162-181.

Ammonia Decomposition

Ru supported catalysts

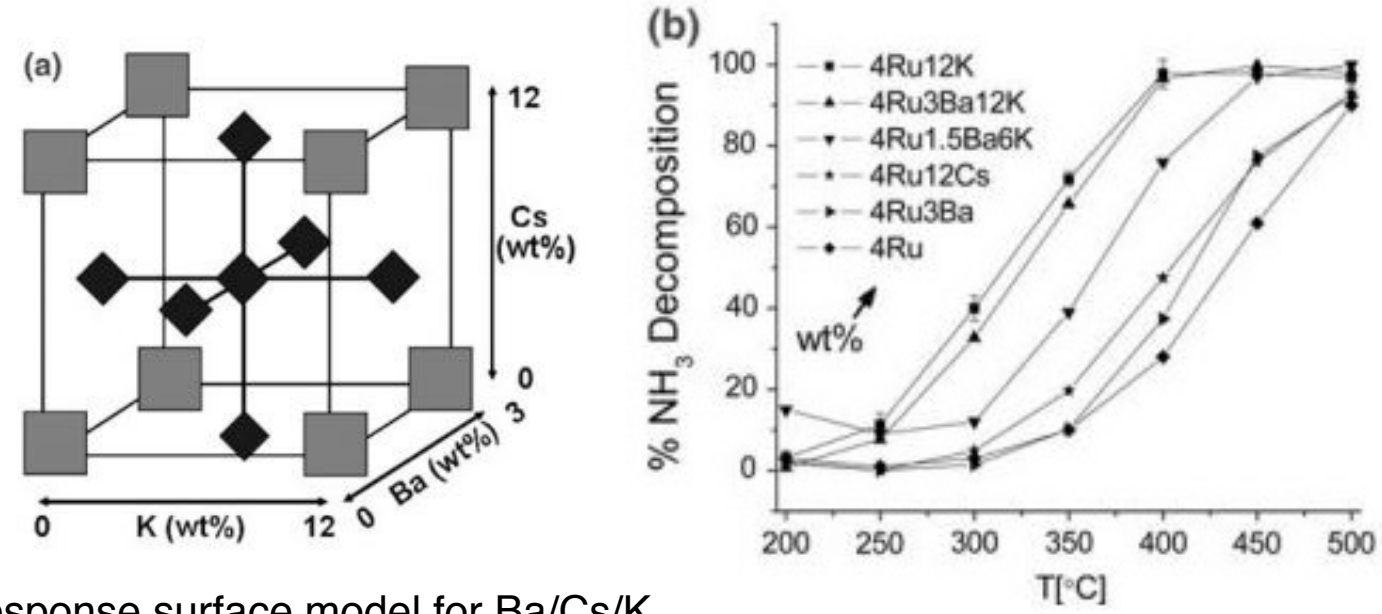


- 100% conversion at 823K (550°C)
- >95% conversion at low temperatures to avoid degradation of fuel cell

Zheng et al., Catal Lett (2007) 119:311-318.
Itoh, Catal. Today (2014)236:70-76.

Ammonia Decomposition
Promoters

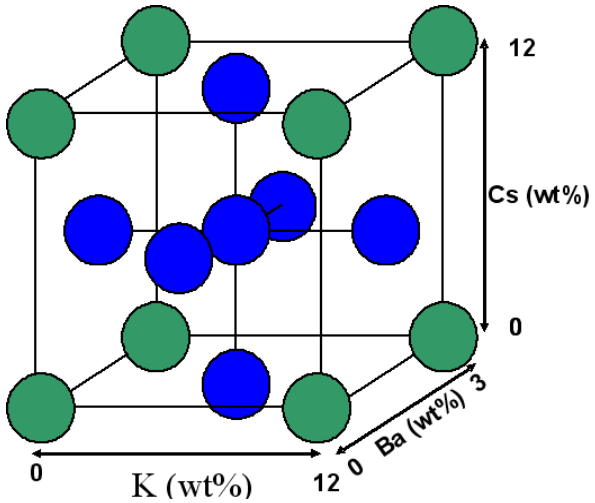
- Tested K, Cs, Ba, Sr, Rb, Ca, Na and Li
- K, Cs and Ba loadings optimized through a surface response study
- Developed response surface model as a function of promoters
- Promotional effects completely dominated by K

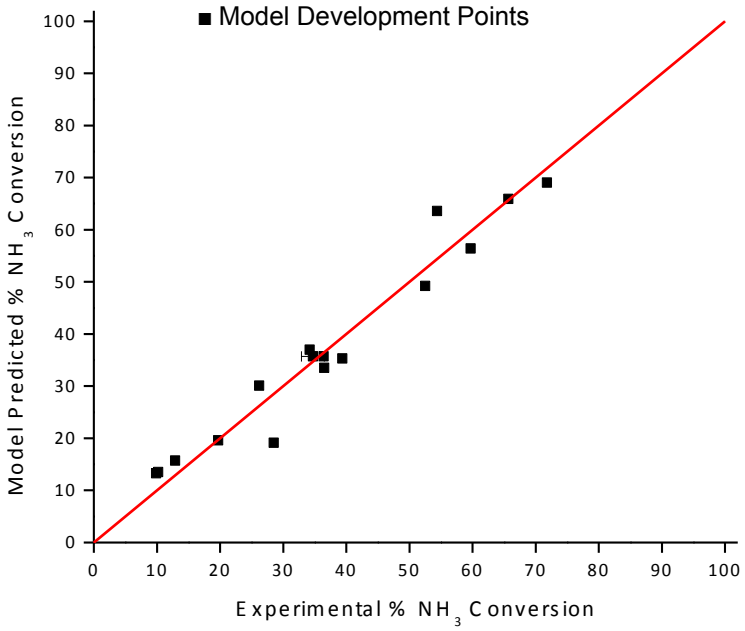


Response surface model for Ba/Cs/K promoters on 4wt%Ru on Al_2O_3

Pyrz. Top Catal (2008) 50:180-191.

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

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

Carbon Free Hydrogen Storage and Generation materials

Metal Hydrides

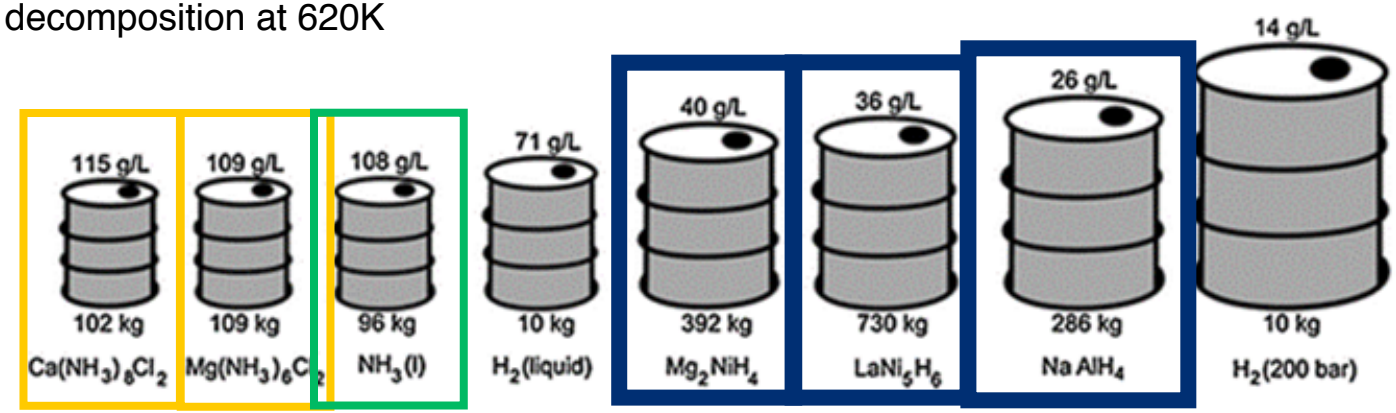
- $NaAlH_4$ - 5.6% H_2 but needs 10-40MPa to dehydrogenate
- LaN_5H_6 - 1.37% H_2
- $MgNiH_4$ - 3.59% H_2

Ammonia

- 17.4 wt% H_2
- Liquefied at RT and 8 bar
- Established transportation infrastructure and safety precautions

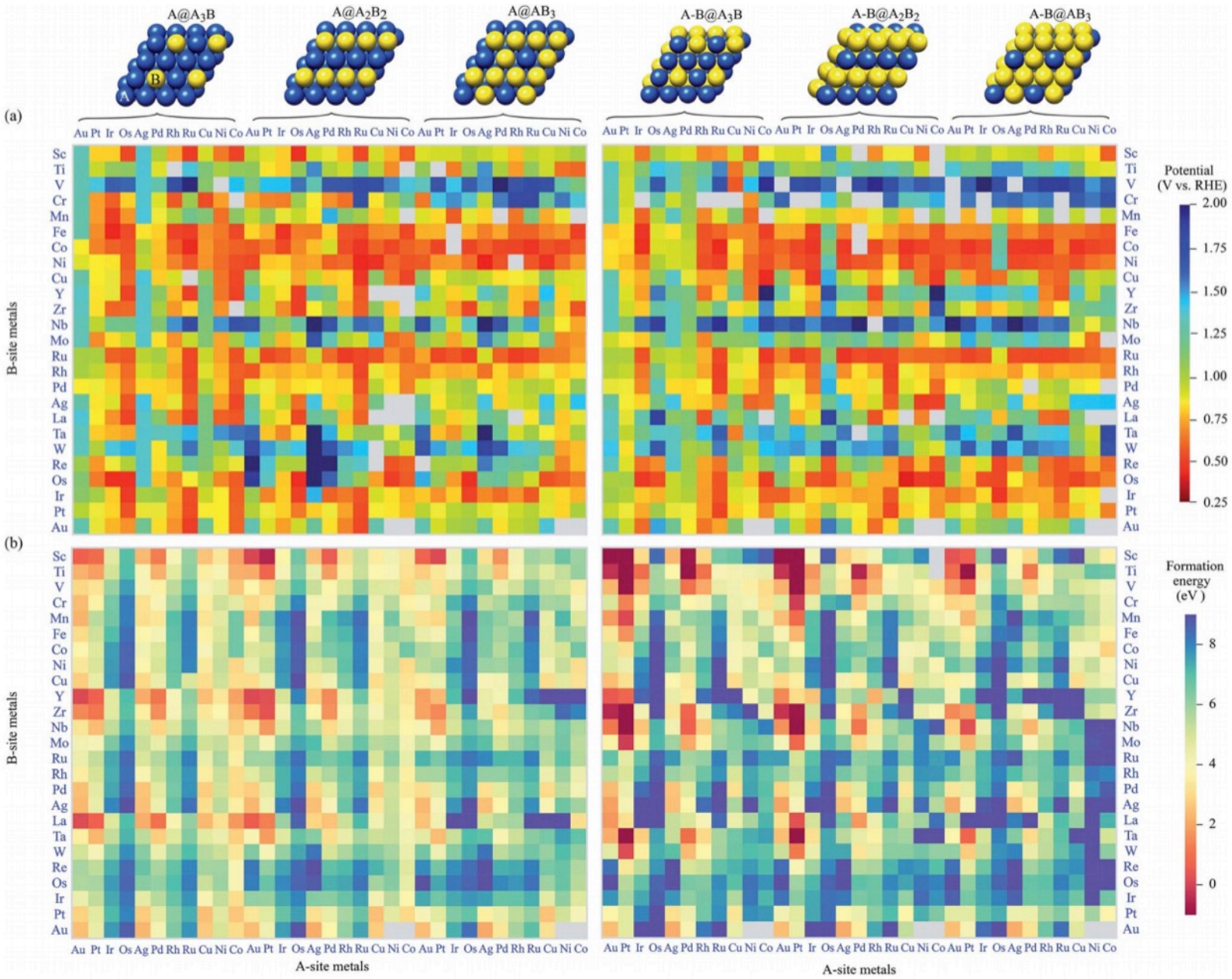
Metal Amines

- Metal chlorides easily complex with amines
- $Mg(NH3)_6Cl_2$
- Complete decomposition at 620K



Comparison of equivalent mass and volume of 10 kg of hydrogen stored in different materials

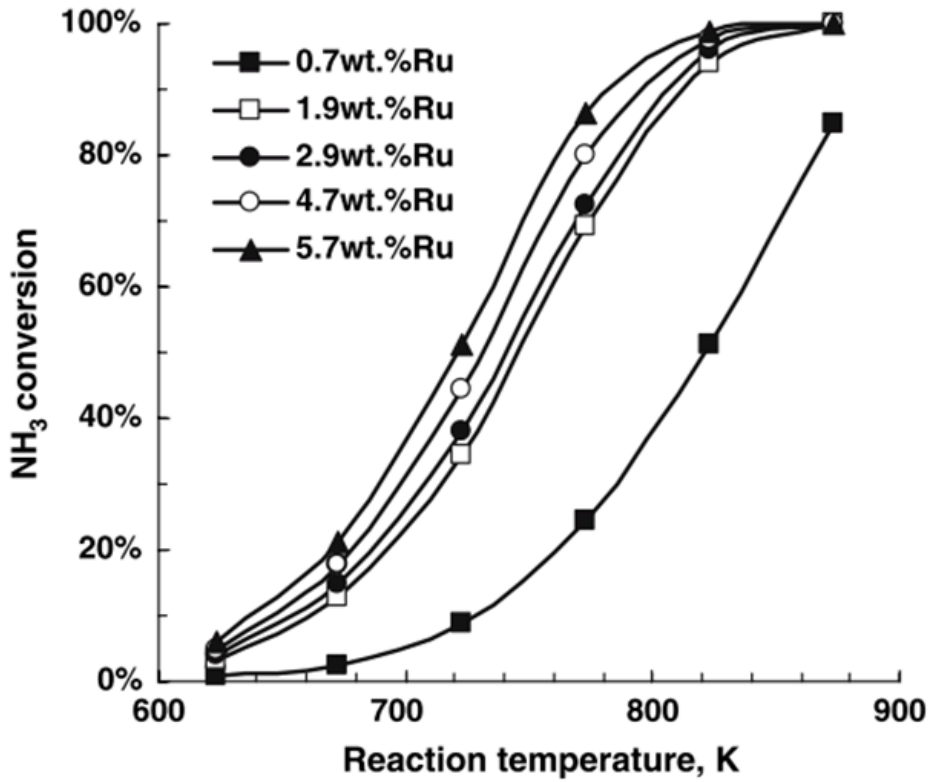
Sakintuna B., Internation Journal of Hydrogen Energy. (2007). 32:1121-1140.
Christensen et al., Journal of Materials Chemistry. (2005) 15:4106-4107.
Mukherjee et al., Applied Catalysis B: Environmental 226 (2018) 162-181.



Li et al., J. Mater. Chem. A, 2017 5, 24131-24138.

Ammonia Decomposition

Particle Size and Morphology

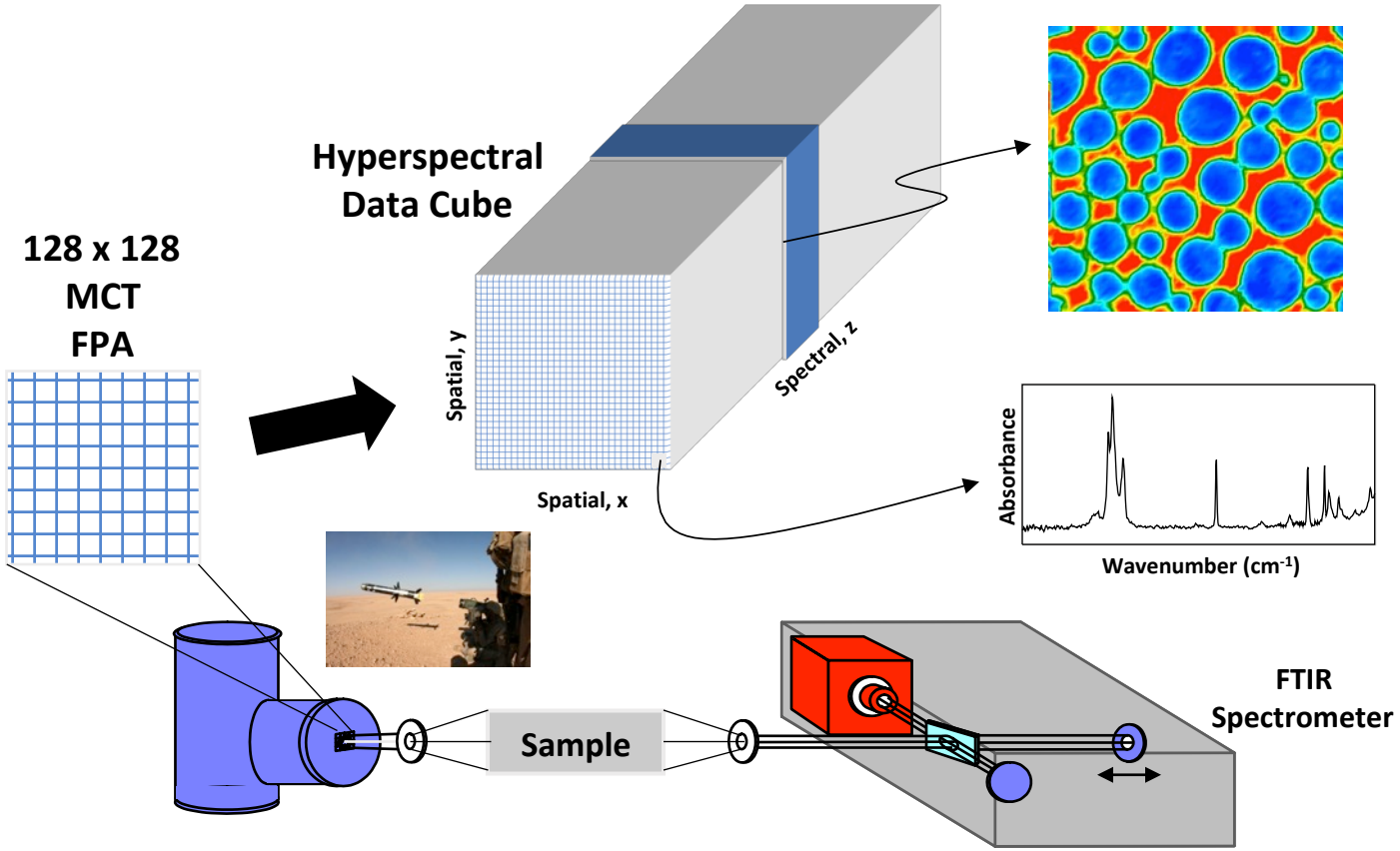


Ru wt%	0.7	1.9	2.9	4.7	5.7
Mean particle size (TEM)	1.9	2.2	2.9	3.5	4.2

Zheng et al., Catal Lett (2007) 119:311-318.

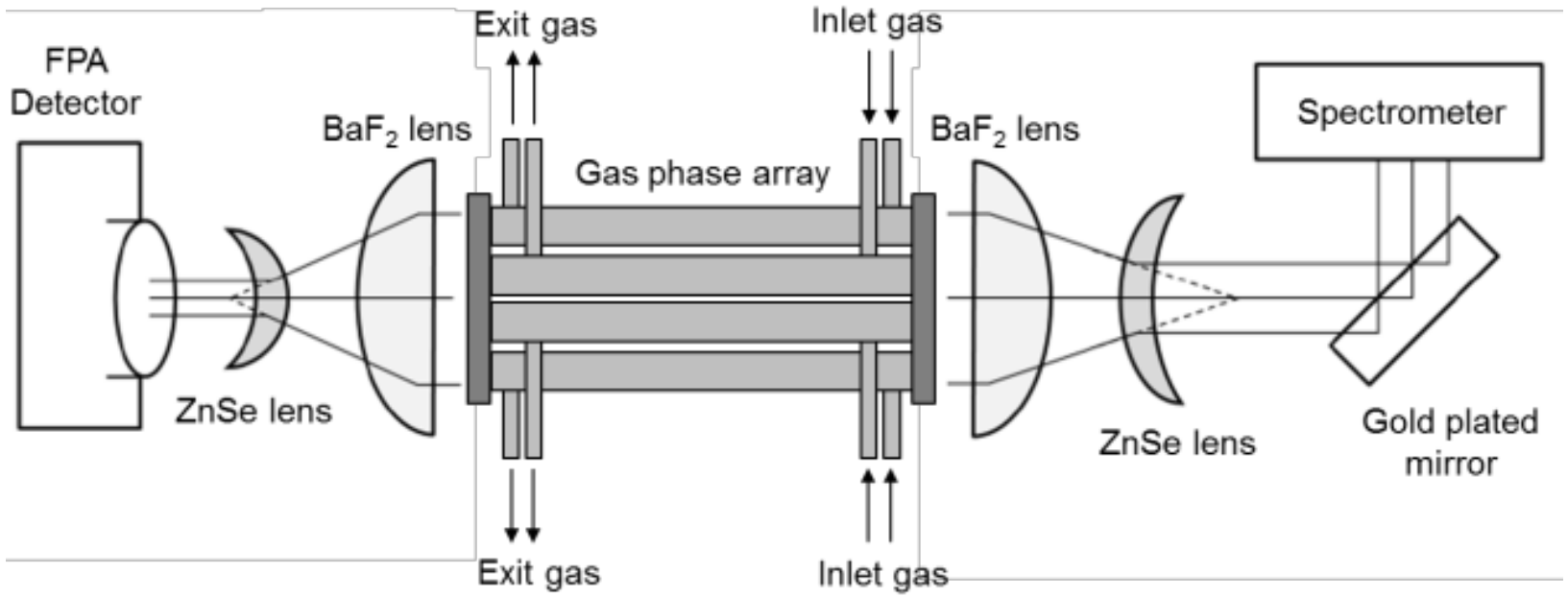
100 mg cat, 30,000 $mL/\mathrm{hr{\cdot}g{\downarrow}cat}$,
100% NH_3

FTIR Imaging



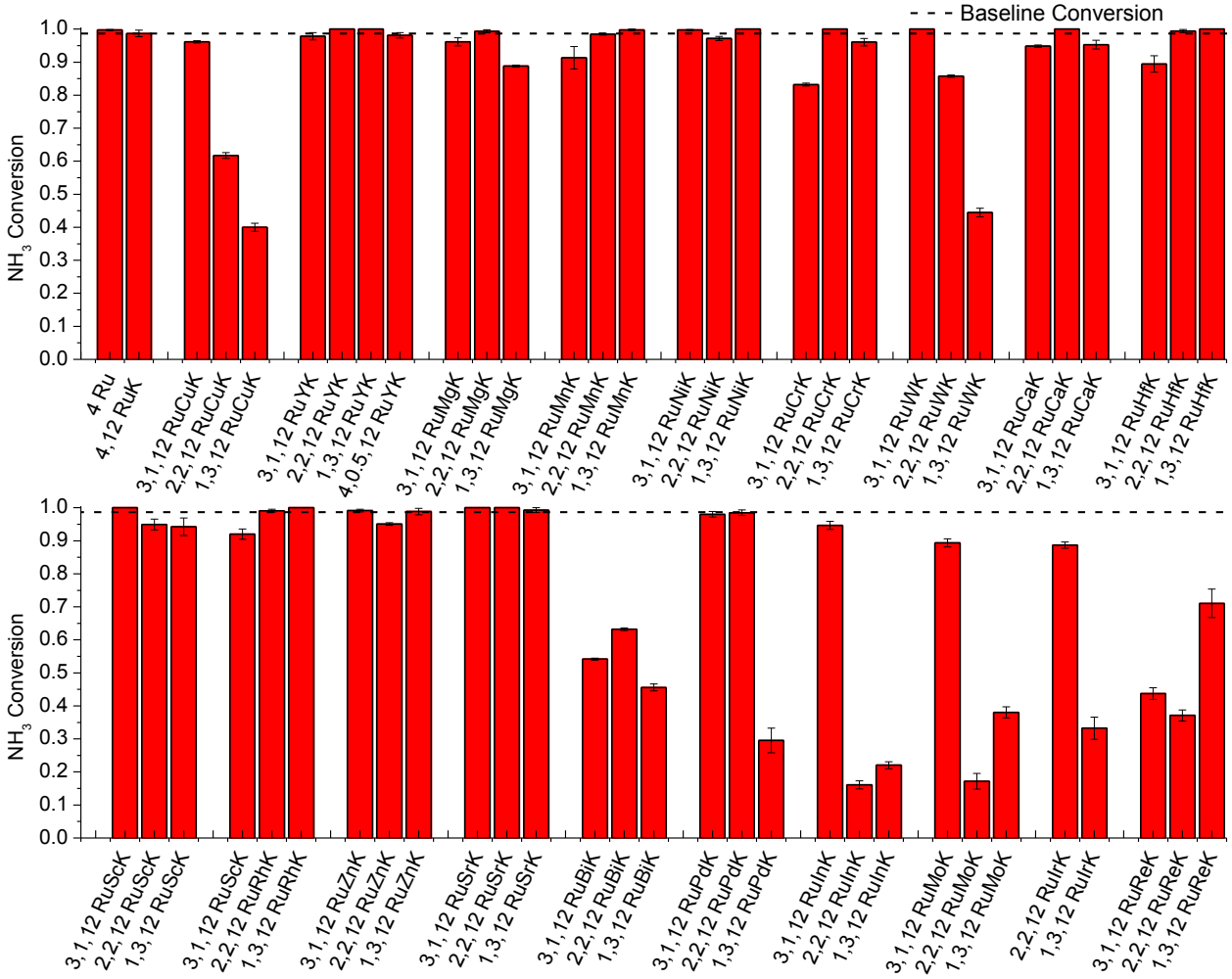
Snively, C.M. and J. Lauterbach *Applied Spectroscopy* **59**(2005)

Parallel FTIR Imaging



Reaction Results

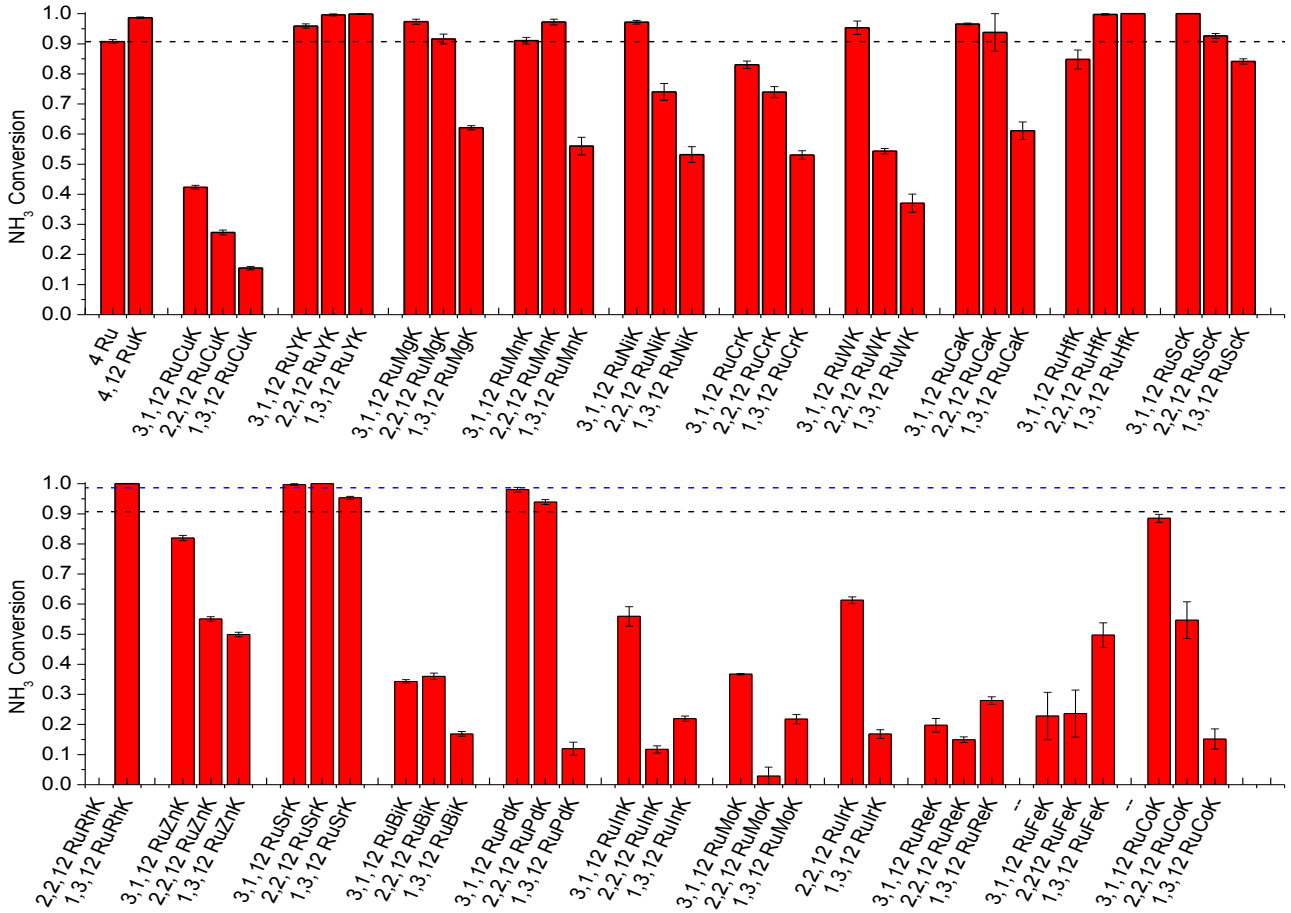
T = 400°C



Reaction Conditions: 1% NH_3 in balance Ar, Pressure = 1.01 bar, 200 mg catalyst, 30,000 $mL/g{\downarrow}cat$ ·hr

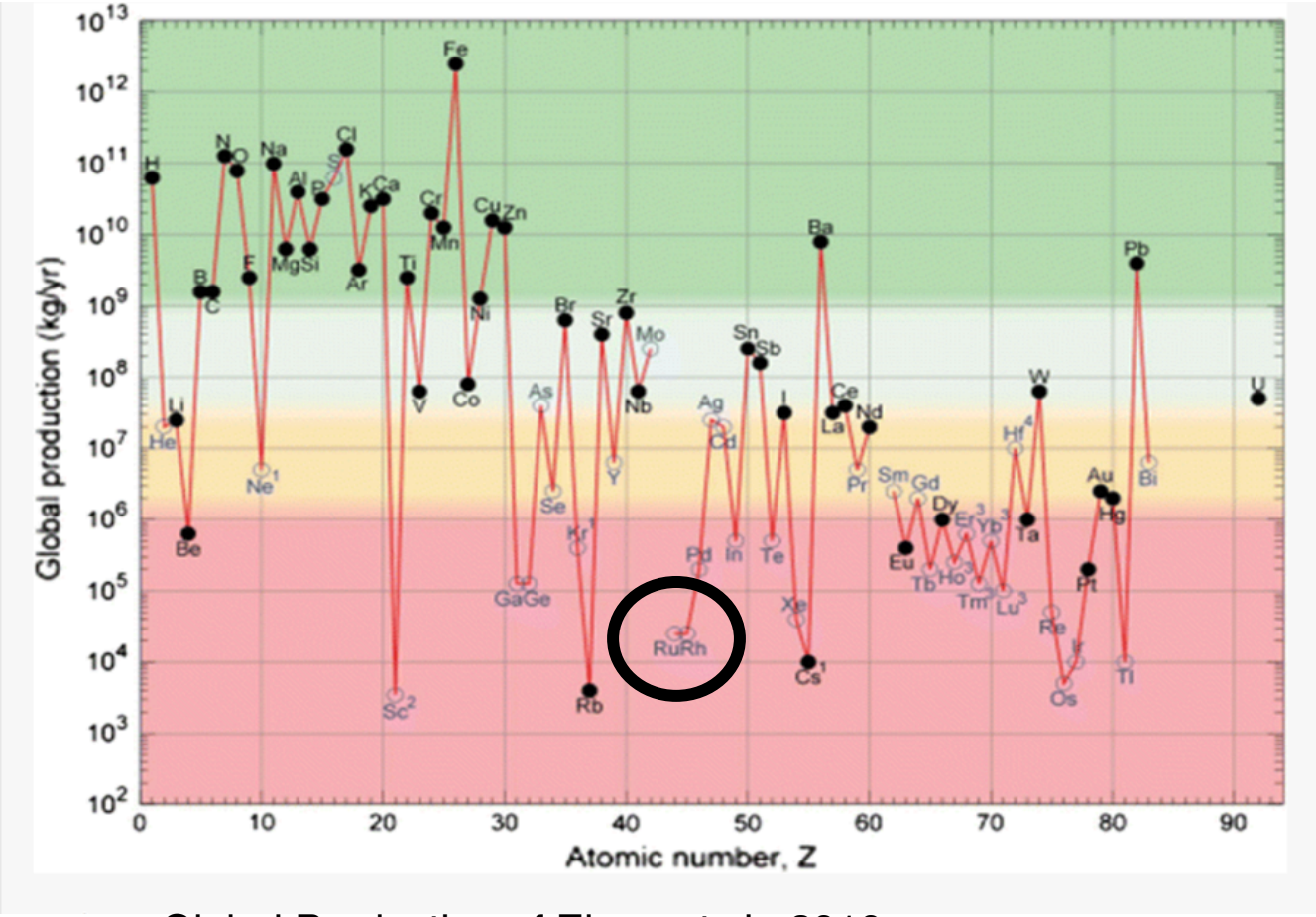
Reaction Results

T = 350°C



Reaction Conditions: 1% NH_3 in balance Ar, Pressure = 1.01 bar, 200 mg catalyst, 30,000 $mL/g_{cat} \cdot hr$

Ammonia Decomposition



Global Production of Elements in 2010

Bell, T. E. *Top. Catalysis.* (2016) 15:1438-1457.

Substitutional Metals for Low T Ammonia Decomposition

Promising Ru Substitutes

- Hf
- Mg
- Ca
- Mn
- Sc
- Rh
- Sr
- Y

Global Production 2010

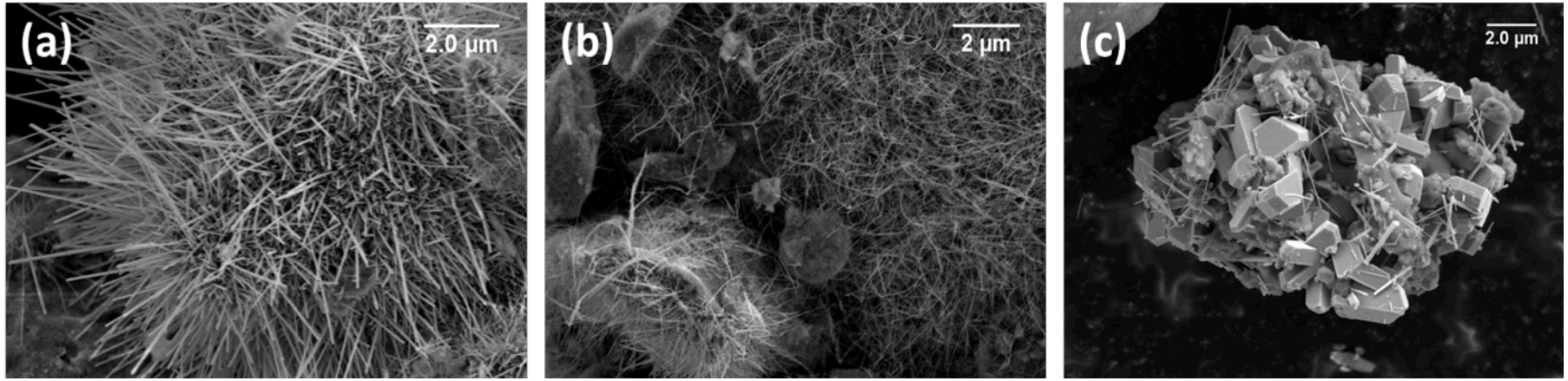
kg/yr	Ru	Hf	Mg	Ca	Sc	Sr	Rh	Y	Mn
	10^4	10^7	10^{10}	10^{11}	10^3	10^9	10^4	10^7	10^{10}

Price of Metal 2018

Au USD/g	Ru	Hf	Mg	Ca	Sc	Sr	Rh	Y	Mn
5.54	14.0	1.20	.003	.20	14.0	1.0	130.0	4.30	.065

Metal prices https://www.chemicool.com/

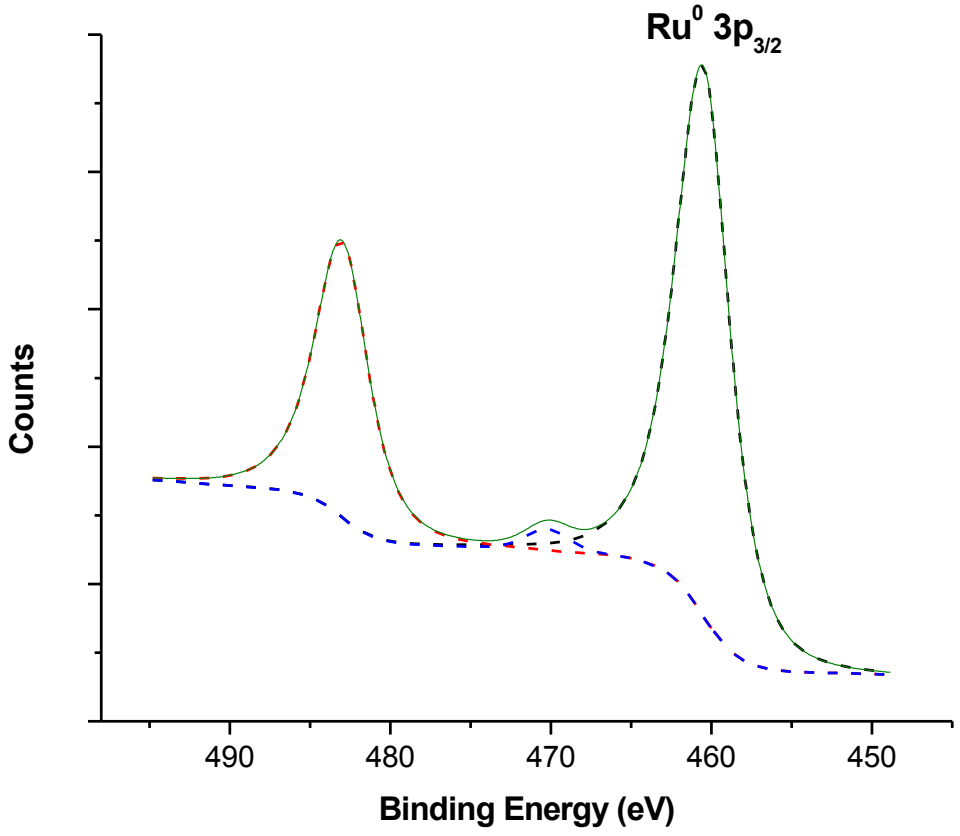
Unknown Structures



(a) 2,2,12 RuFeK **(b)** 2,2,12 RuIrK **(c)** 2,2,12 RuCoK

- Defect density is increased from decomposition of needle like precursor state, increasing catalytic activity over the nanoparticle counterparts

XPS 4,12 RuK Hollandites



4,12 RuK Hollandite XPS after reduction in H_2 for 1hr at 450°C

Ru^0 Binding Energy (eV)	3p$_{3/2}$	3p$_{1/2}$
Reference	462.0	484.0
Actual	462.1	484.1

Briggs, D., 1981. Handbook of X-ray Photoelectron Spectroscopy

Machine Learning Features

Elemental Properties

- Atomic Number
- Atomic Volume
- Atomic Weight
- Boiling Temperature
- Column - Periodic Table
- Conductivity
- Covalent Radius
- Density
- Dipole Polarizability
- Electron Affinity
- Electronegativity
- Fusion Enthalpy
- Ground State Bandgap
- Ground State Energy
- Heat Capacity
- Heat of Fusion
- 1st – 8th Ionization Energy
- Melting Temperature
- Mendeleev Number
- Polarizability
- Row – Periodic Table
- Work Function

Electron Properties

- Number s-shell valance electrons
- Number p-shell valance electrons
- Number d-shell valance electrons
- Number f-shell valance electrons
- Number unfilled s-shell valance electrons
- Number unfilled p-shell valance electrons
- Number unfilled d-shell valance electrons
- Number unfilled f-shell valance electrons
- Total number valence electrons
- Total number unfilled electrons

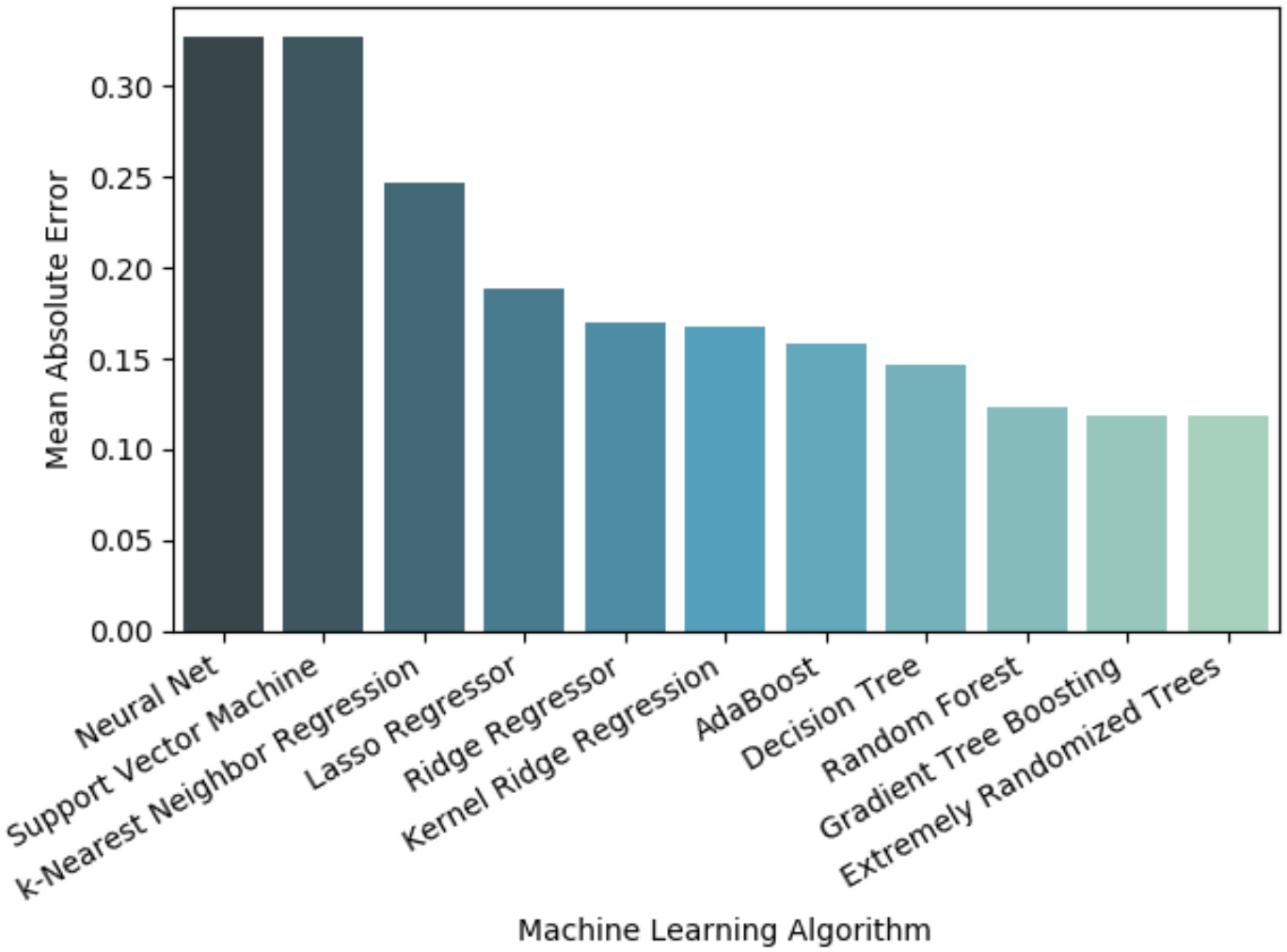
Binary Properties

- Is Alkali metal?
- Is metal?
- Is metalloid?
- Is nonmetal?
- Is d block?
- Is f block?

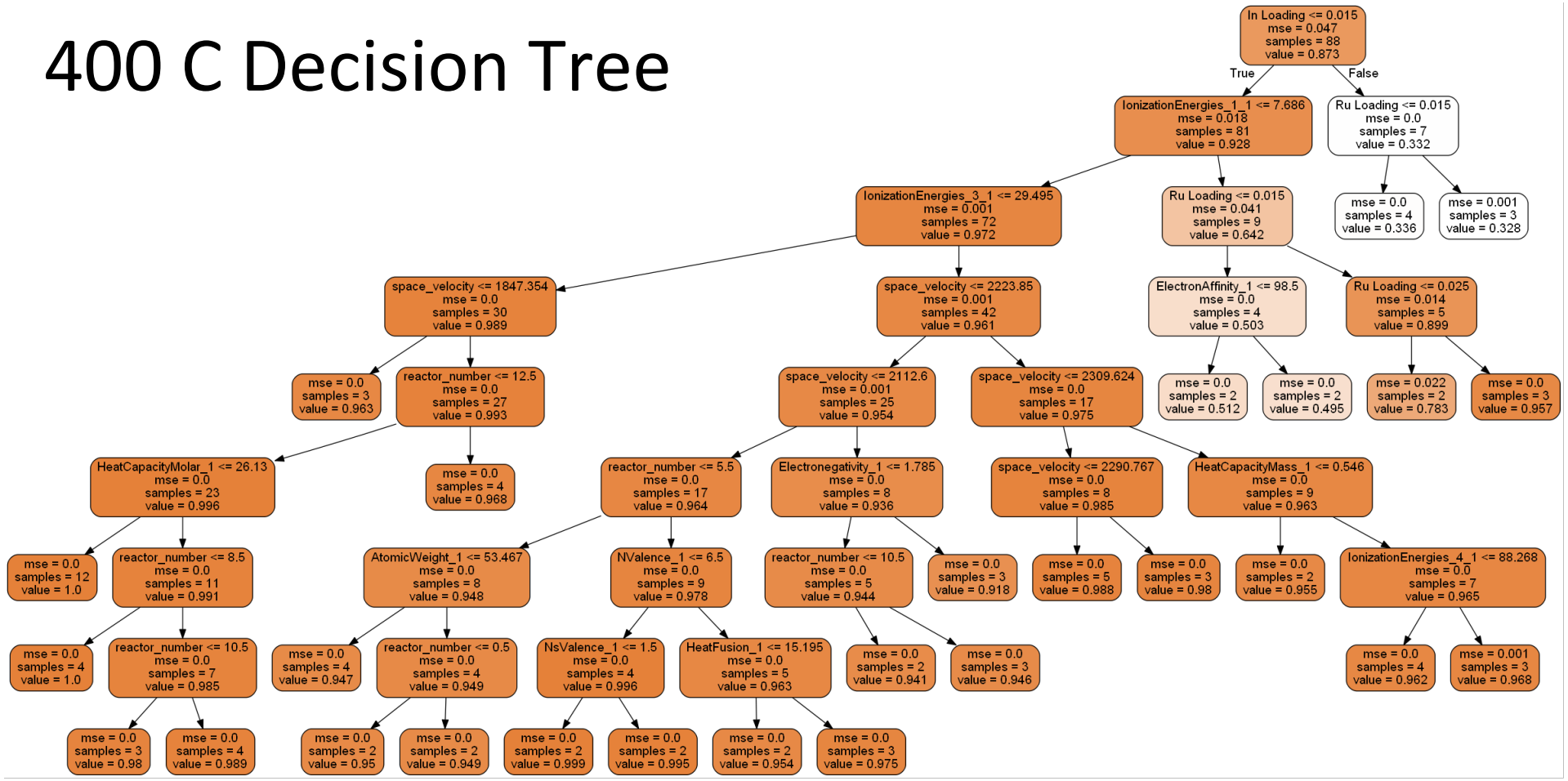
Other Properties

- Weight Loadings
- Reaction Temperature
- Space Velocity
- # of precursor Cl ligands

Algorithm Selection

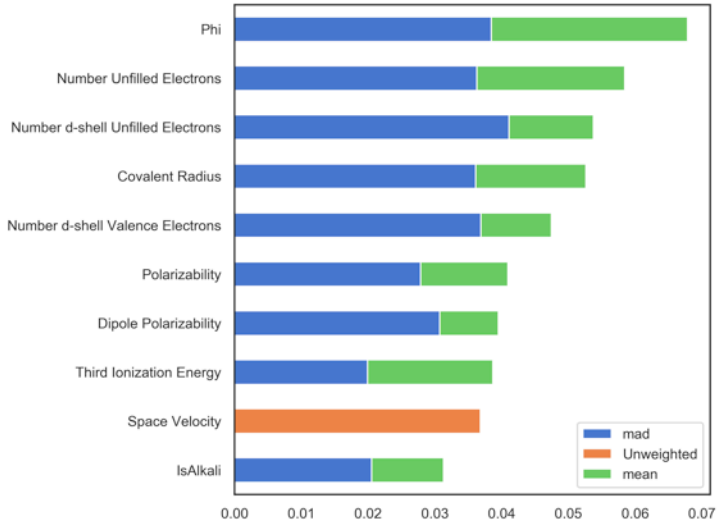


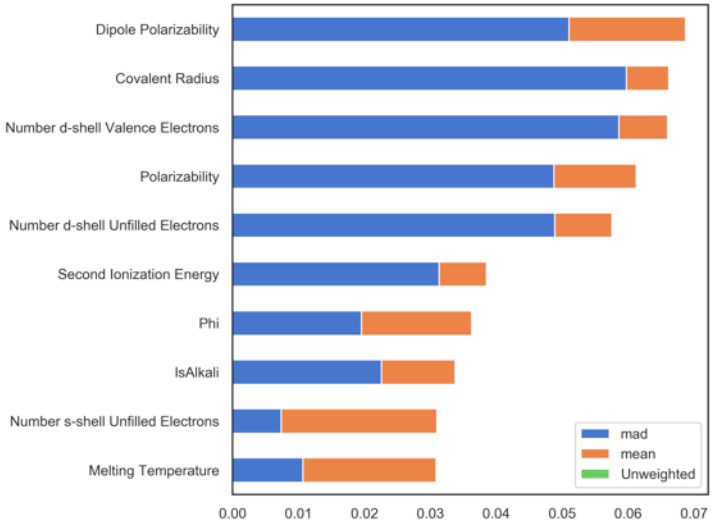
400 C Decision Tree

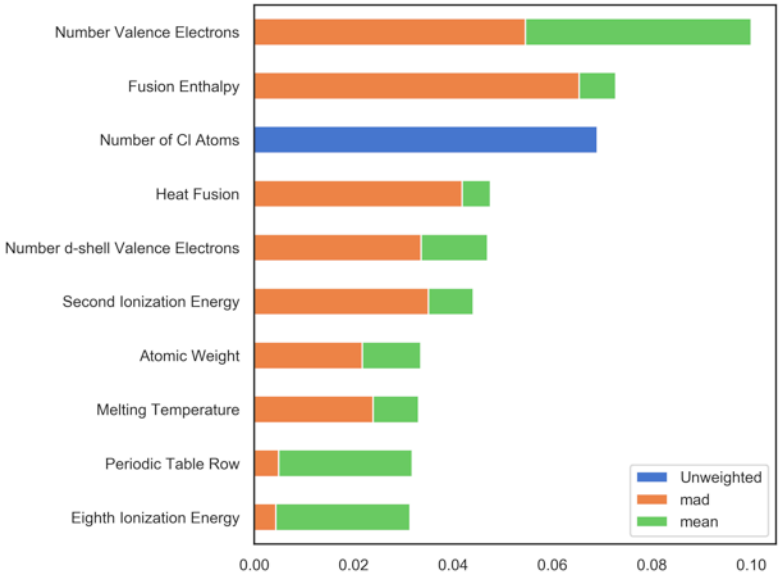


Ward, L., Agrawal, A., Choudhary, A. & Wolverton, C. A general-purpose machine learning framework for predicting properties of inorganic materials. npj Computational Materials, 2016

Feature Importance T slices







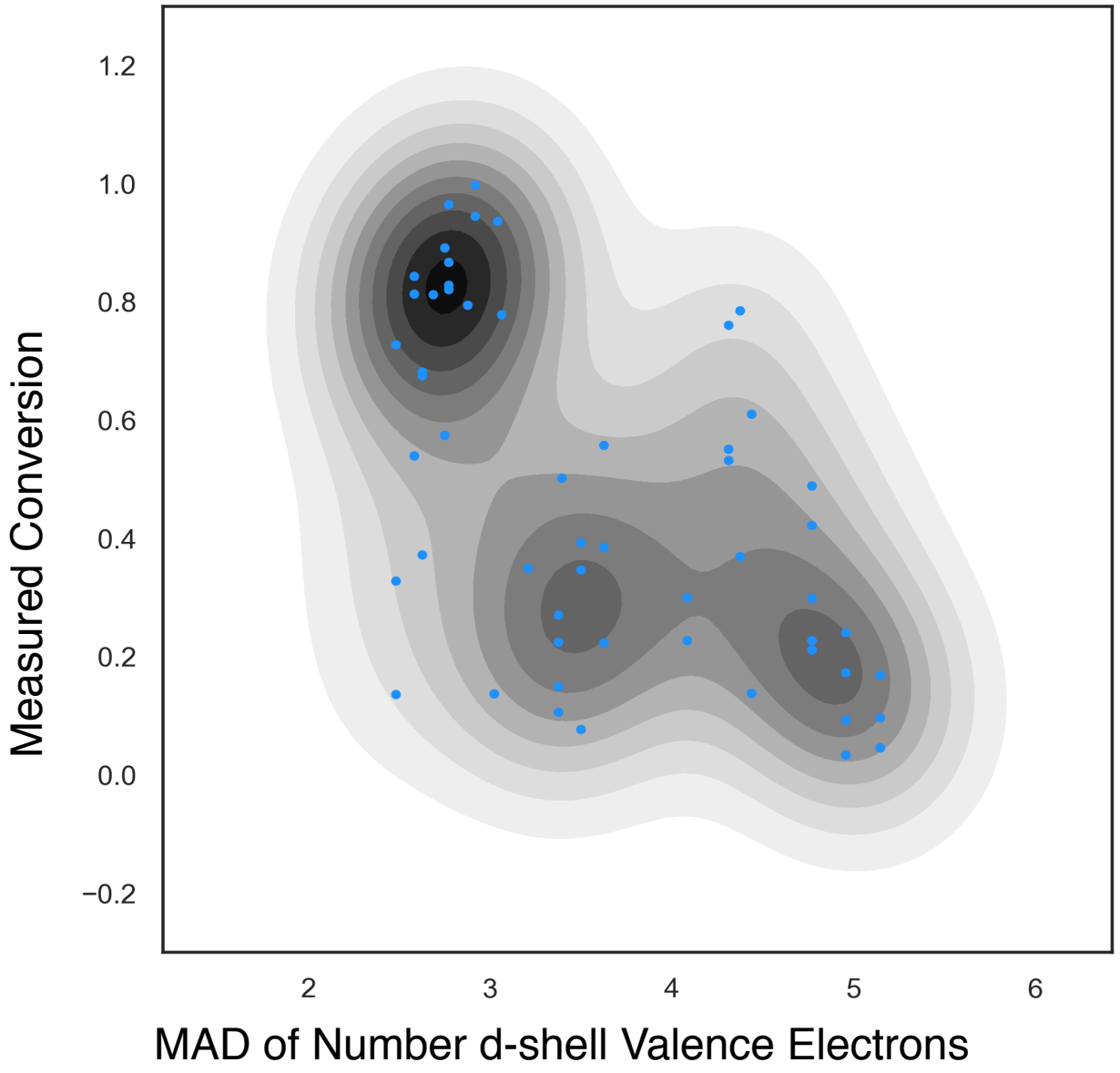
Feature Trends
T = 300°C

Mean Absolute Deviation (MAD)

$$\sum_{i=1}^{n} 1/n\,(x_i - \mu)$$

---

x_i = value of property
μ = average
n = number of samples



Li et al., J. Mater. Chem. A, 2017 5, 24131-24138.
Liu et al., J. Materiomics, 2017 3 (3) 159-177.

Feature Interaction
T = 300°C

2212 RuYK

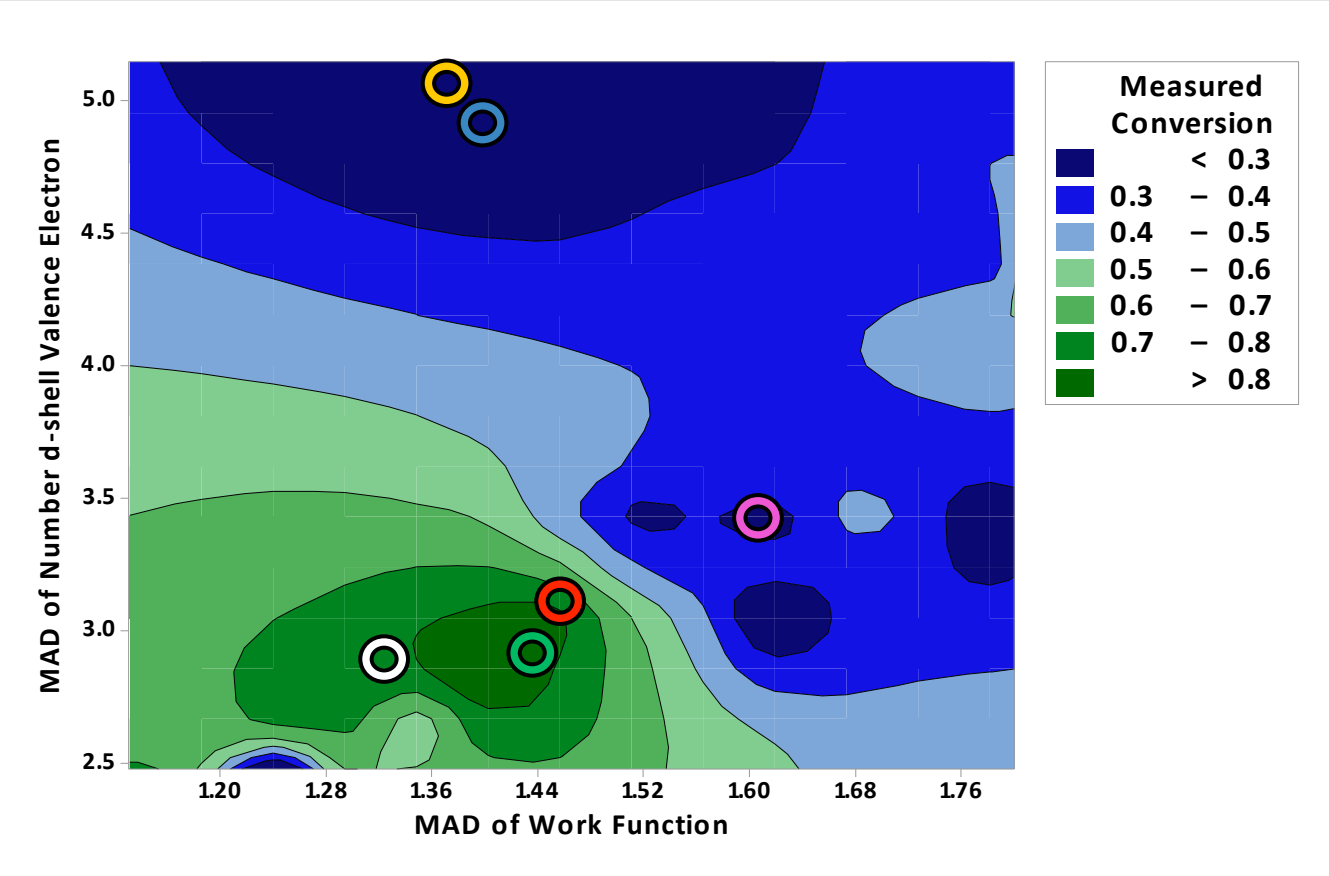
3112 RuMgK

3112 RuHfK

2212 RuInK

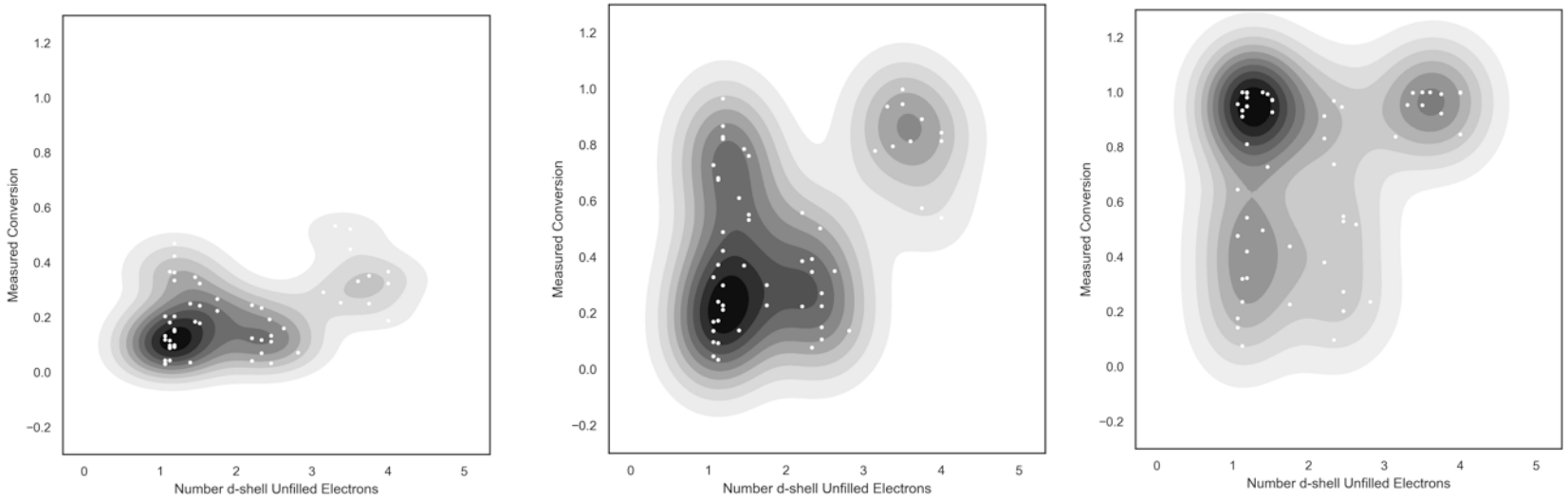
1312 RuZnK

3112 RuMoK

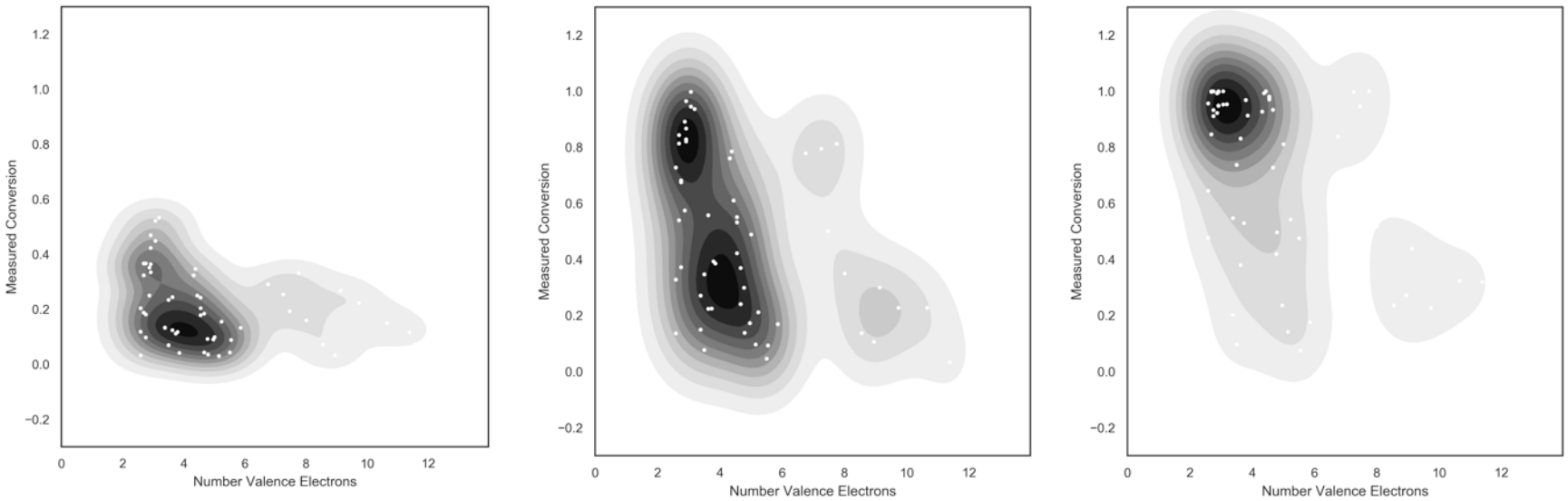


Vayenas et al., Nature 1990. 343, 625-627.
Haller, J. Catal. 216 (2003) 12-22.
Binninger et al., Phys. Rev. B. 96, 165405 (2017).

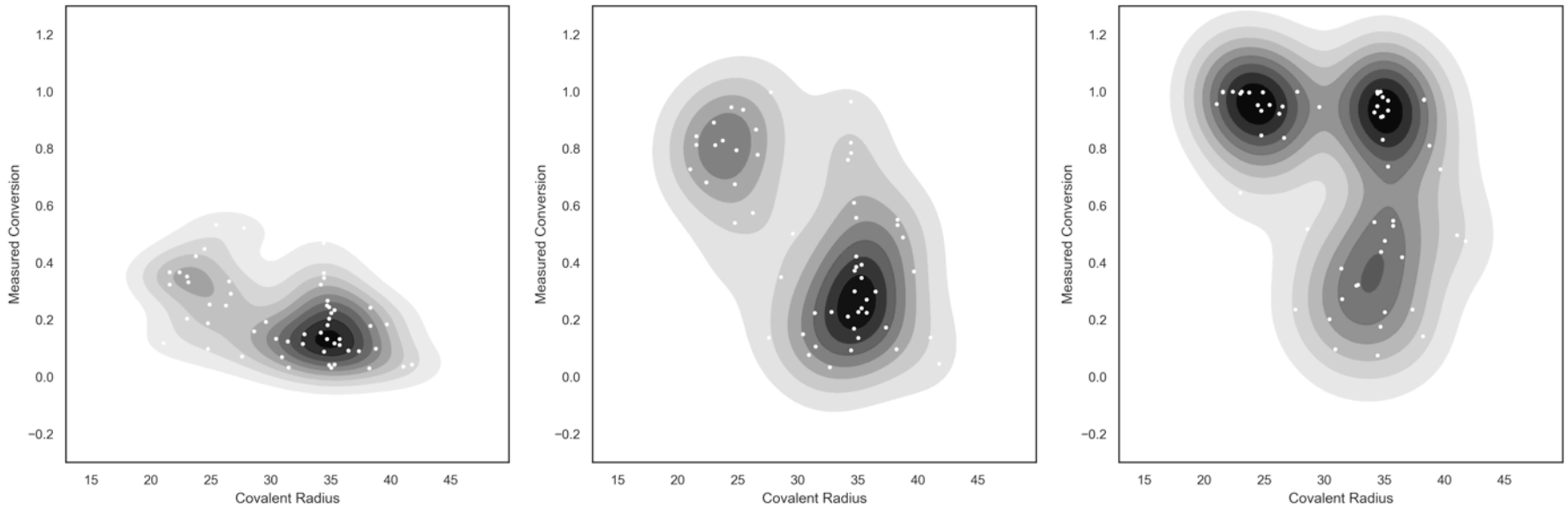
250 300 350_mad
dshell unfilled



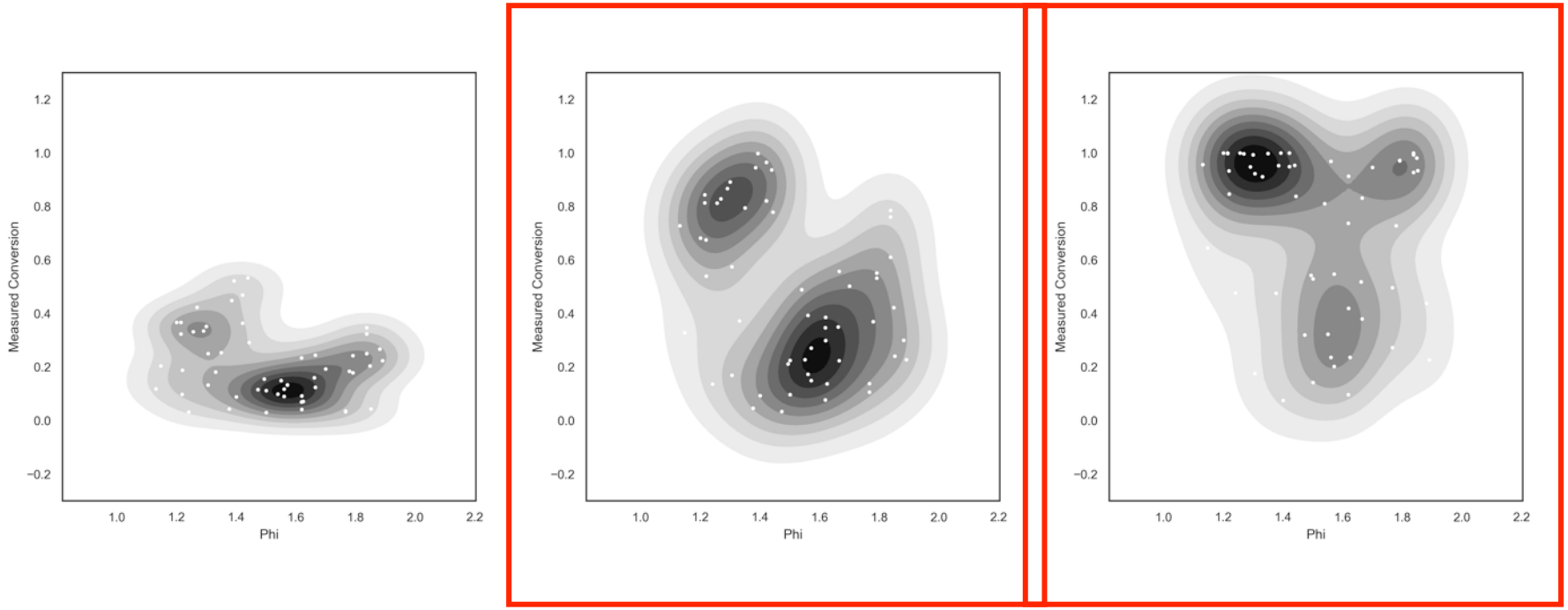
250 300 350_mad
valence



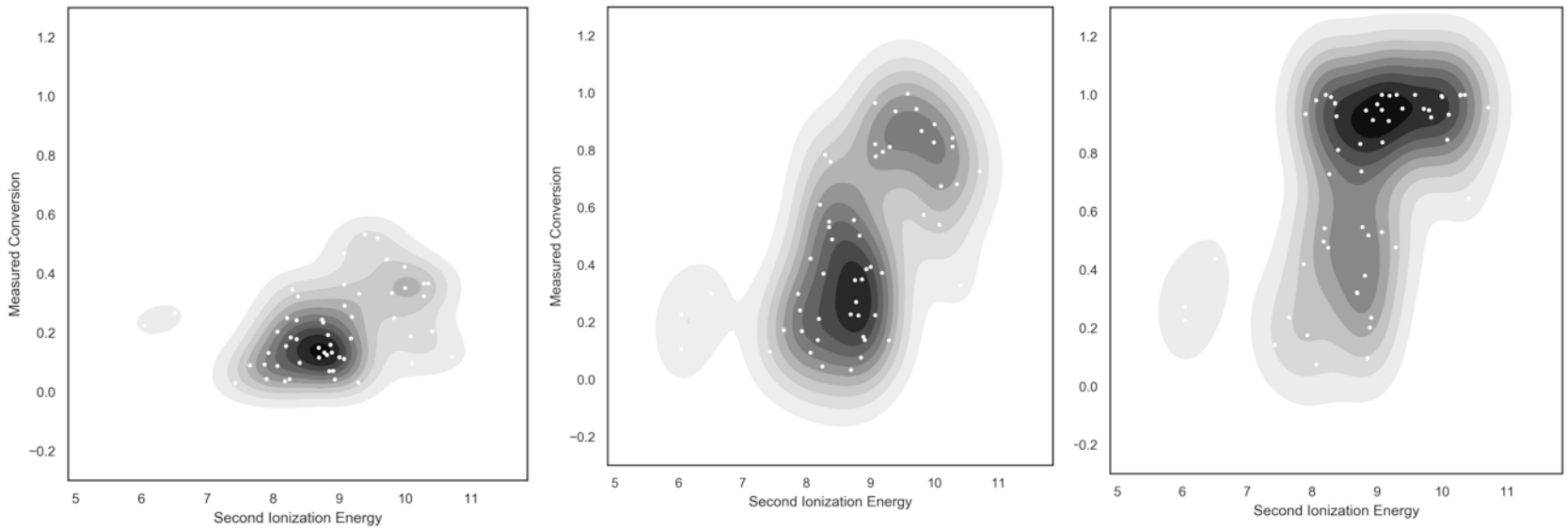
250 300 350 _mad
Covalent radius



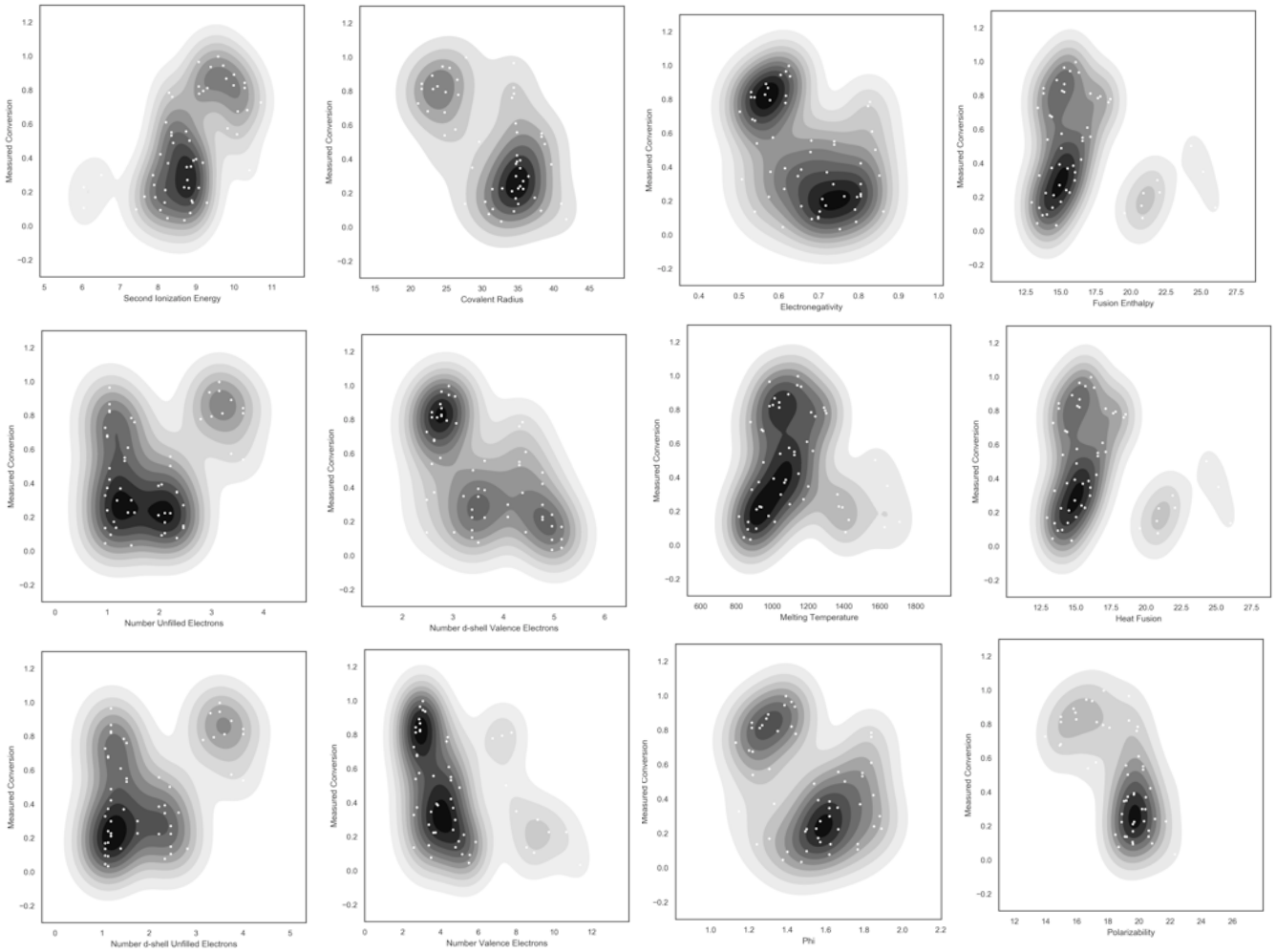
250 300 350_mad
Work Function



250 300 350_mad
2nd ionization E

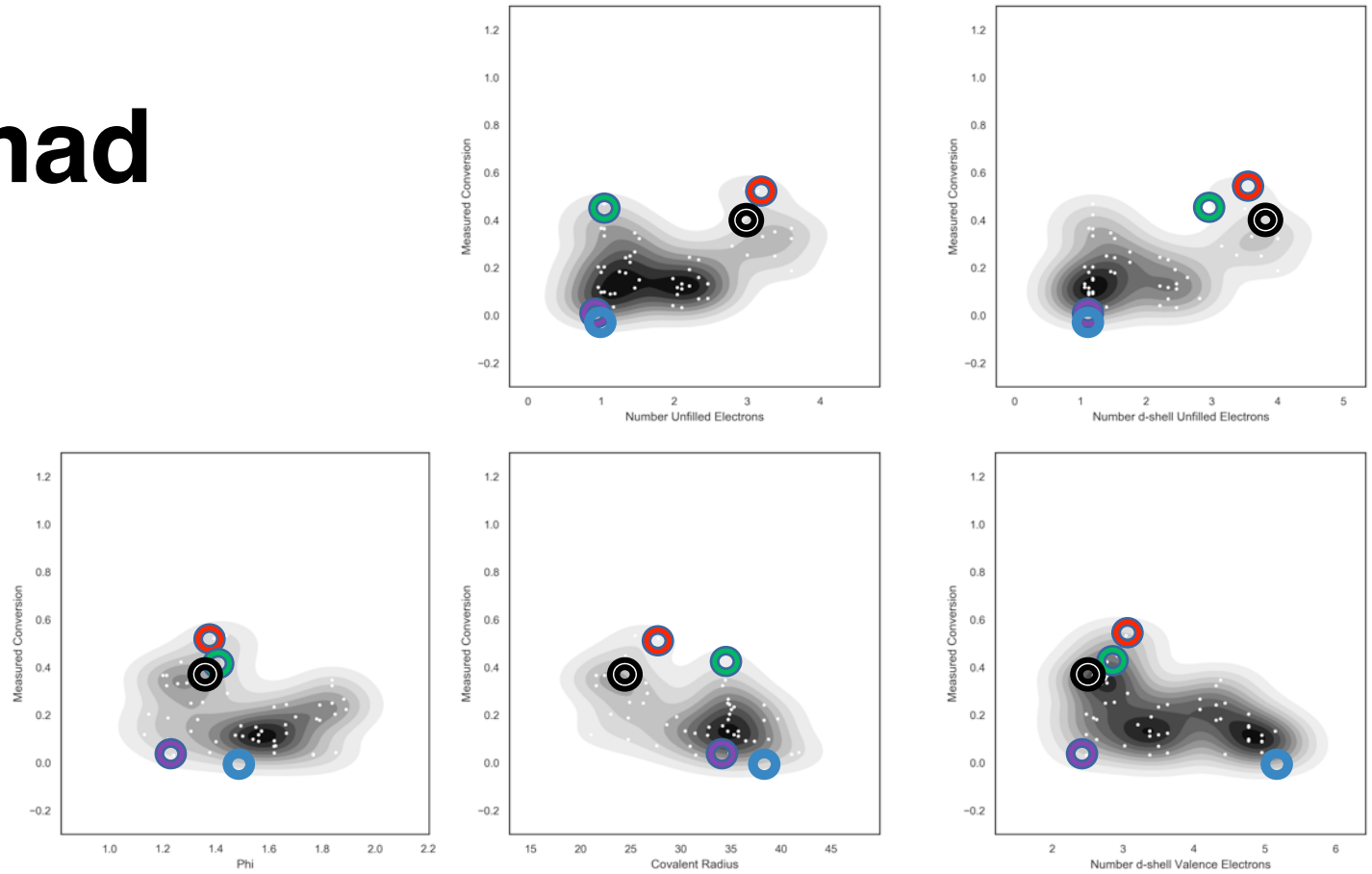


300 mad

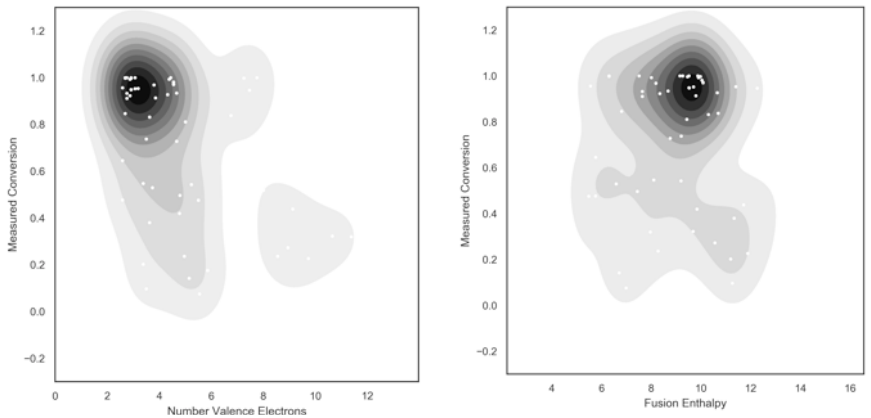

Measured Conversion
Second Ionization Energy
Covalent Radius
Electronegativity
Fusion Enthalpy
Number Unfilled Electrons
Number d-shell Valence Electrons
Melting Temperature
Heat Fusion
Number d-shell Unfilled Electrons
Number Valence Electrons
Phi
Polarizability

250 top_mad

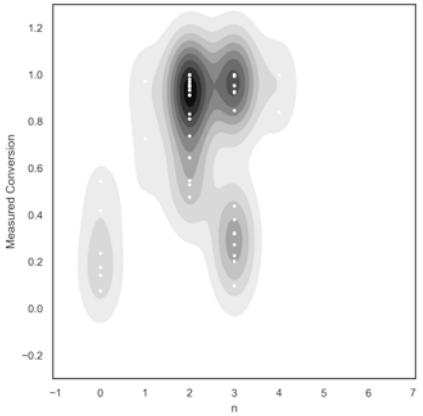
- 3112 RuYK
- 3112 RuScK
- 3112 RuMgK
- 1312 RuMgK
- 1312 RuCuK

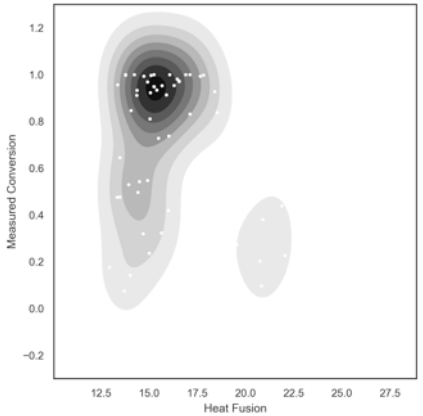


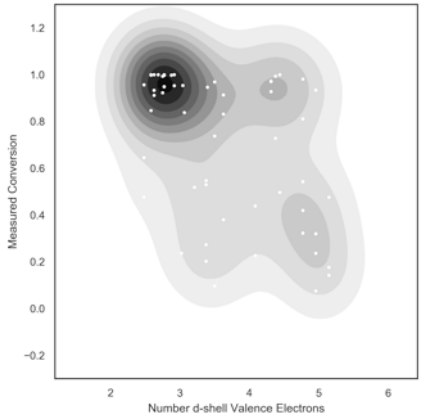
350
top_mad

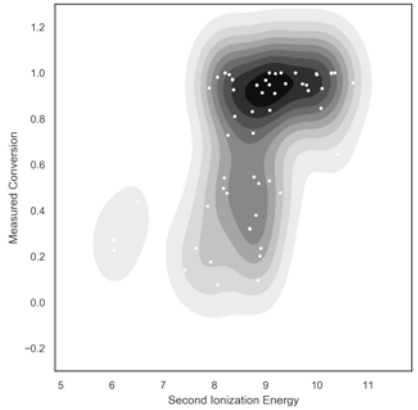

Measured Conversion
Number Valence Electrons

Measured Conversion
Fusion Enthalpy


Measured Conversion
n


Measured Conversion
Heat Fusion


Measured Conversion
Number d-shell Valence Electrons


Measured Conversion
Second Ionization Energy