Material Discovery and Investigation of Novel Y Containing Ru Catalysts for Low Temperature Ammonia Decomposition

Katie McCullough and Jochen Lauterbach

November 12th, 2019

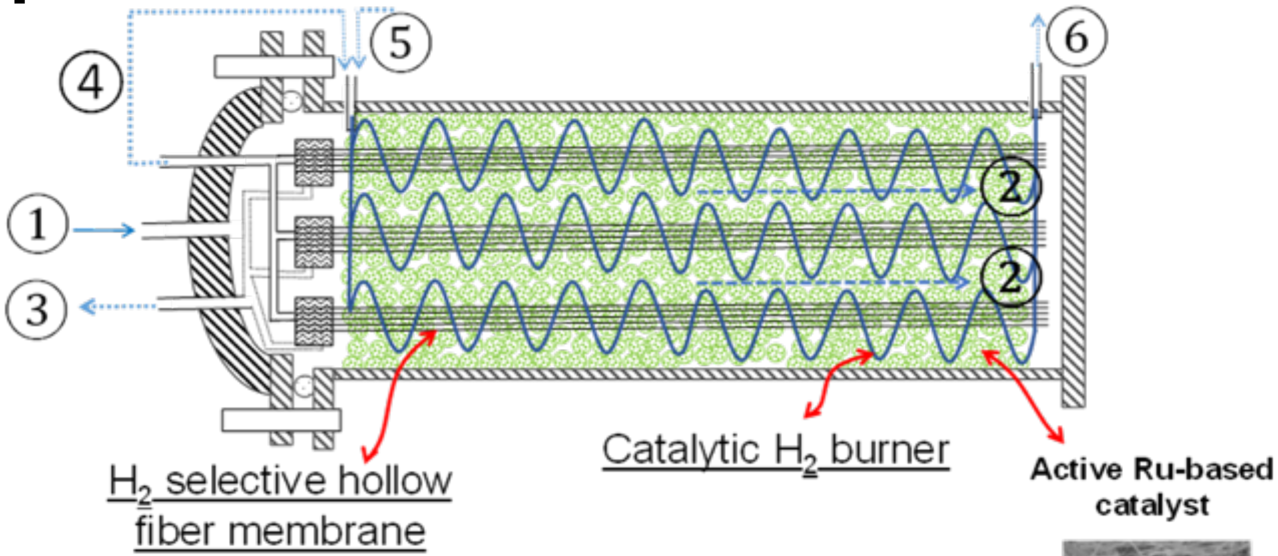
Ammonia Fuel and Energy Storage: Ammonia Cracking

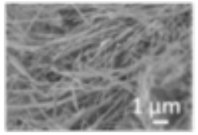
AIChE Annual Conference

Orlando, FL

Department of Chemical Engineering, University of South Carolina, Columbia, SC 29205 USA

Compact Membrane Reactor for H_2 Generation



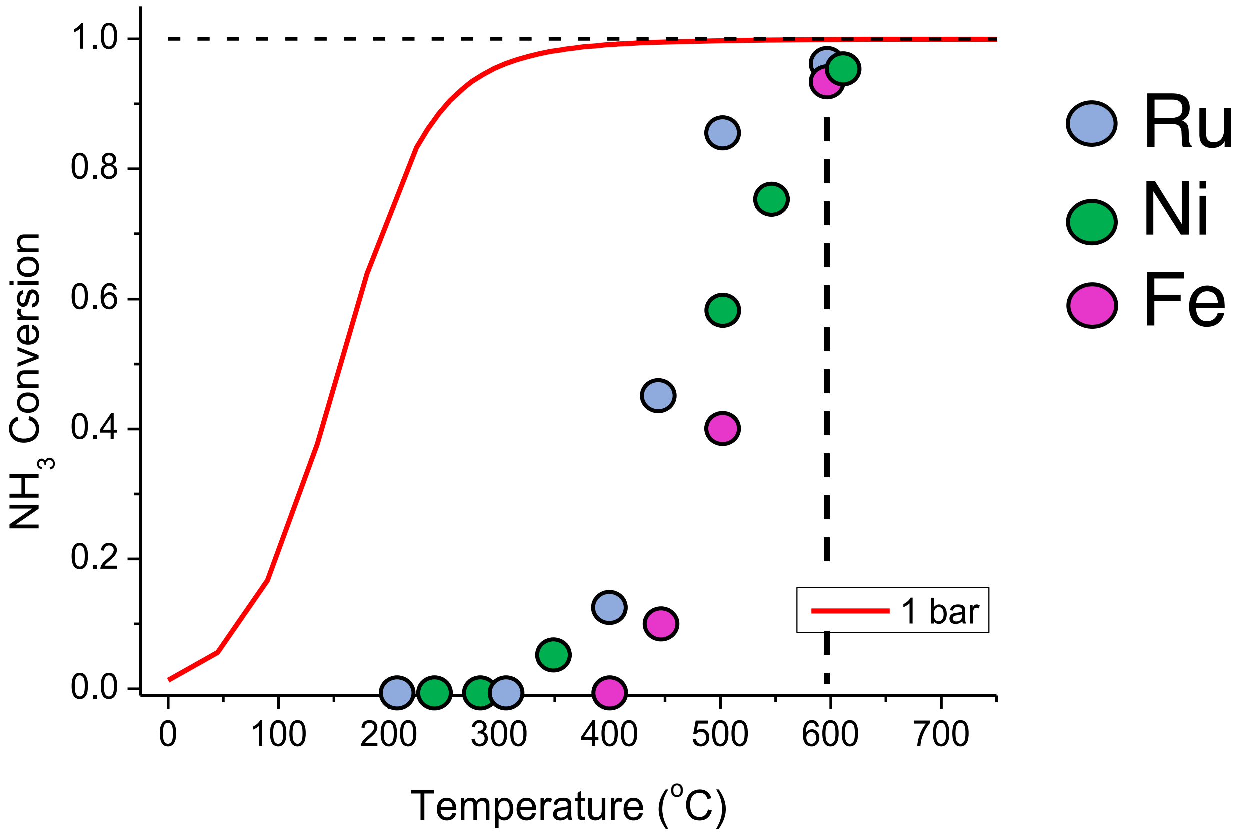


Stream	Composition
1	NH_3
2	$N_2 + H_2$ (~70%)+NH_3 (~6%)
3	H_2 (>99%) + N_2
4	$N_2 + H_2$ (~25%)
5	Air
6	$N_2 + H_2O$

“A Novel Hollow Fiber Membrane Reactor For High Purity H_2 Generation From Thermal Catalytic NH_3 Decomposition” 2018. Department of Energy, ARPA-E REFUEL.

Catalytic Ammonia Decomposition

Thermodynamic Equilibrium of NH_3



Dehydrogenation

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

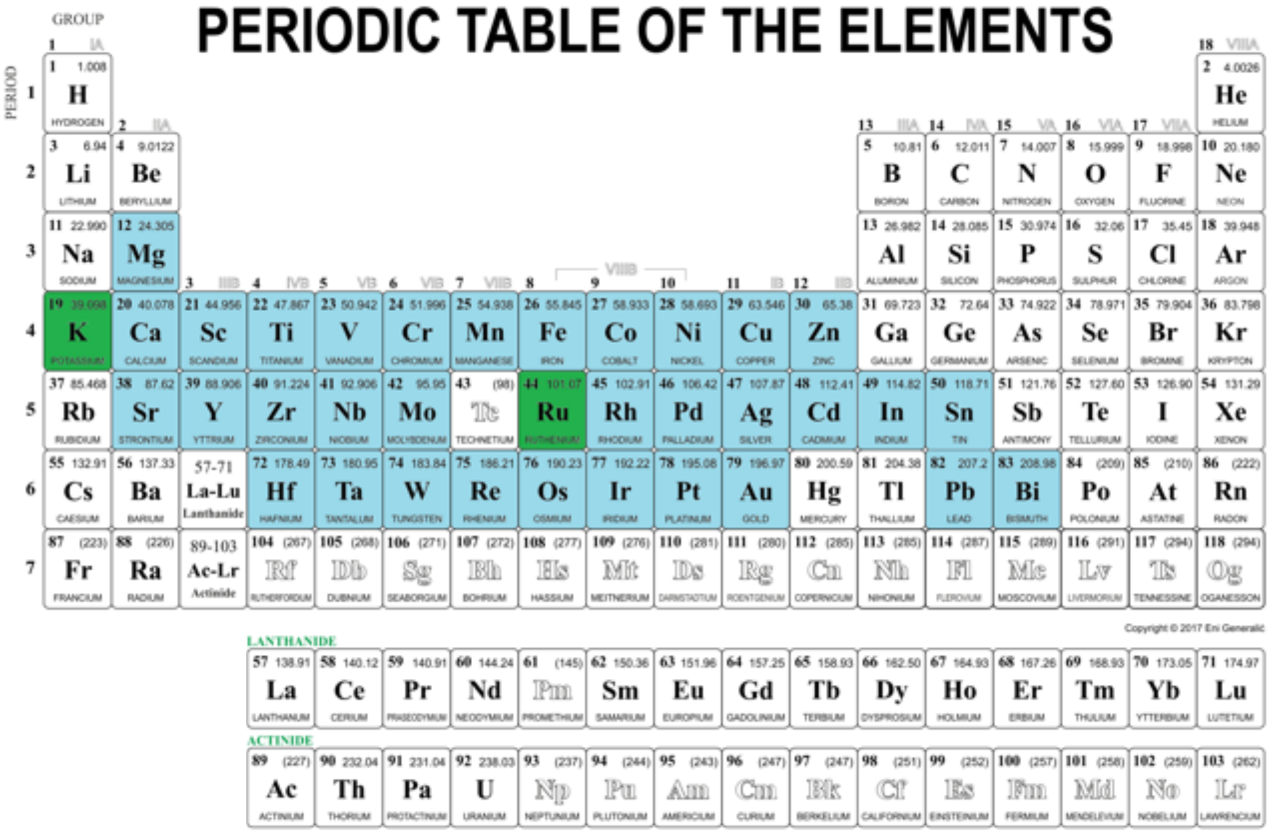
Recombination

$$N + N \rightarrow N_2$$

$$H + H \rightarrow H_2$$

Mukherjee et al., *App. Catal B: Environ.,* 226 (2018) 162-181.

Design Space



⌘ All catalysts supported on ɣ-Al_2O_3 (192 ± 8 m^2/g)

Incipient Wetness Impregnation⌘

Baseline 4wt% Ru, 12wt% K on ɣ-Al_2O_3

Total 4wt% metal

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

+12 wt% K

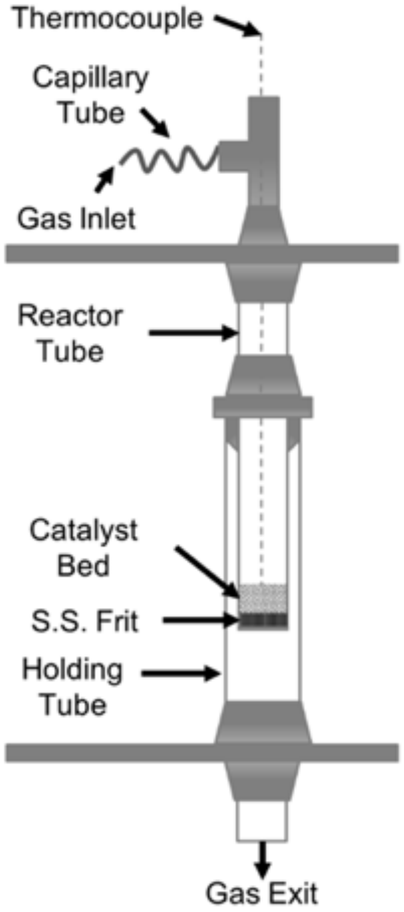
---

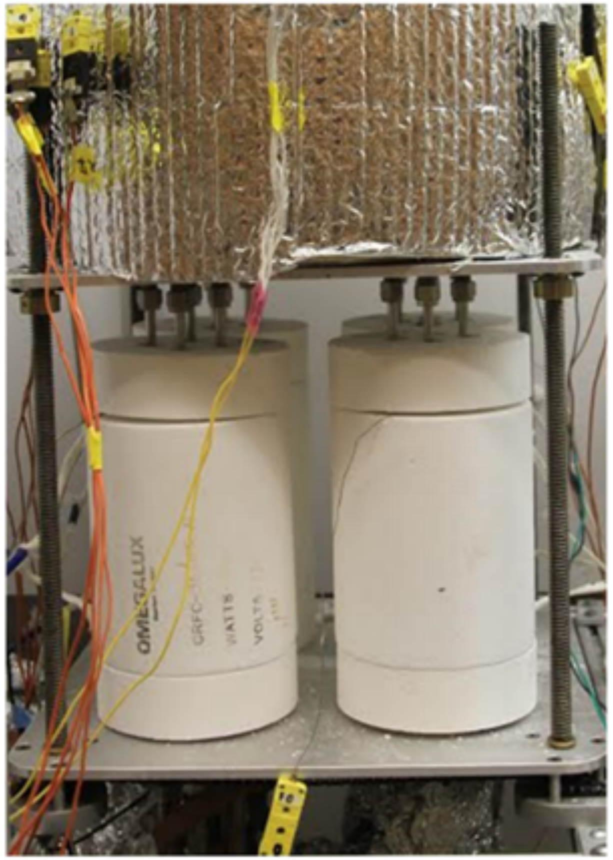
105 unique formulations + repeats

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

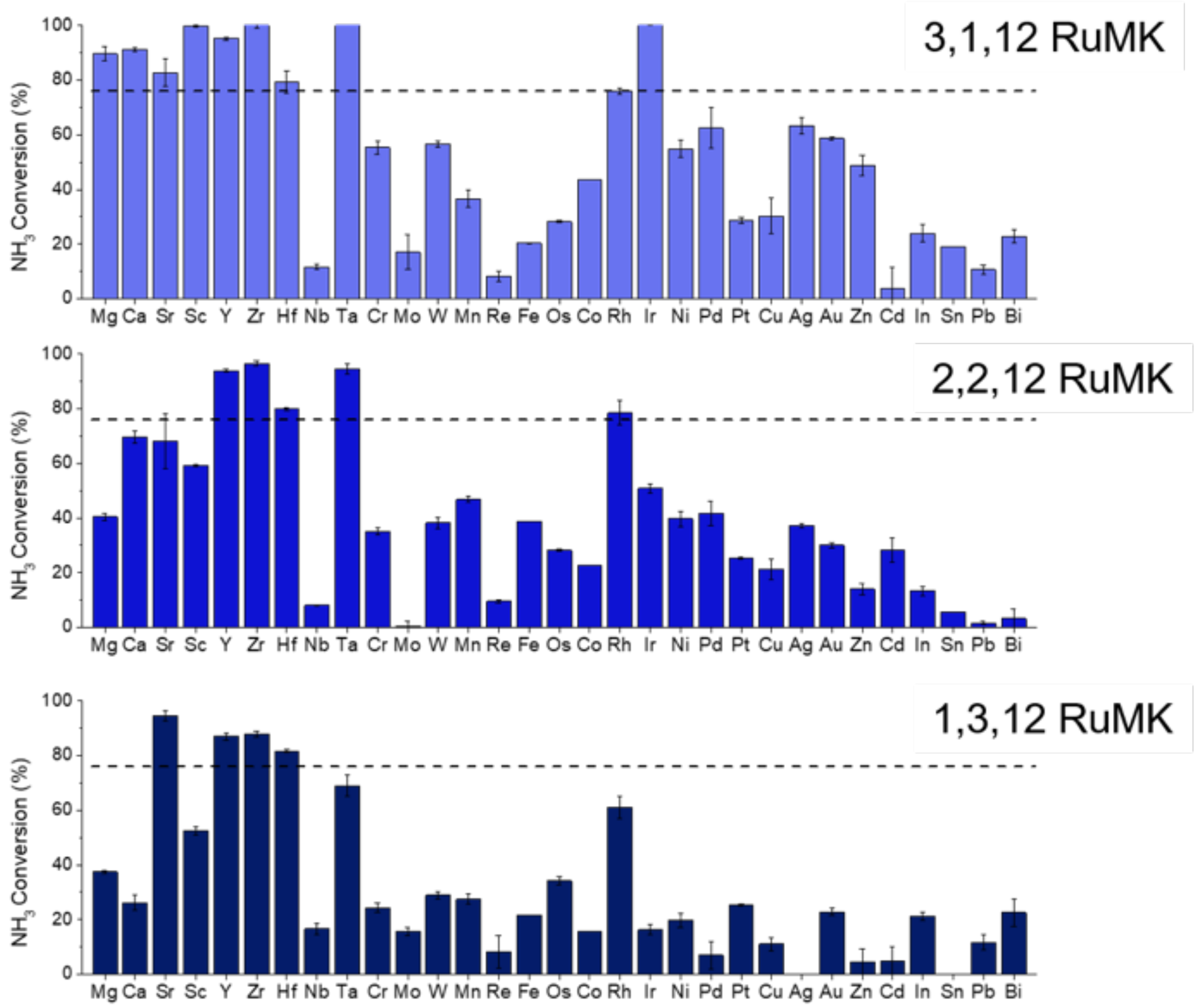
High-Throughput Reactor System

- 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
- Parallel analysis using spatially resolved, chemically sensitive infrared imaging



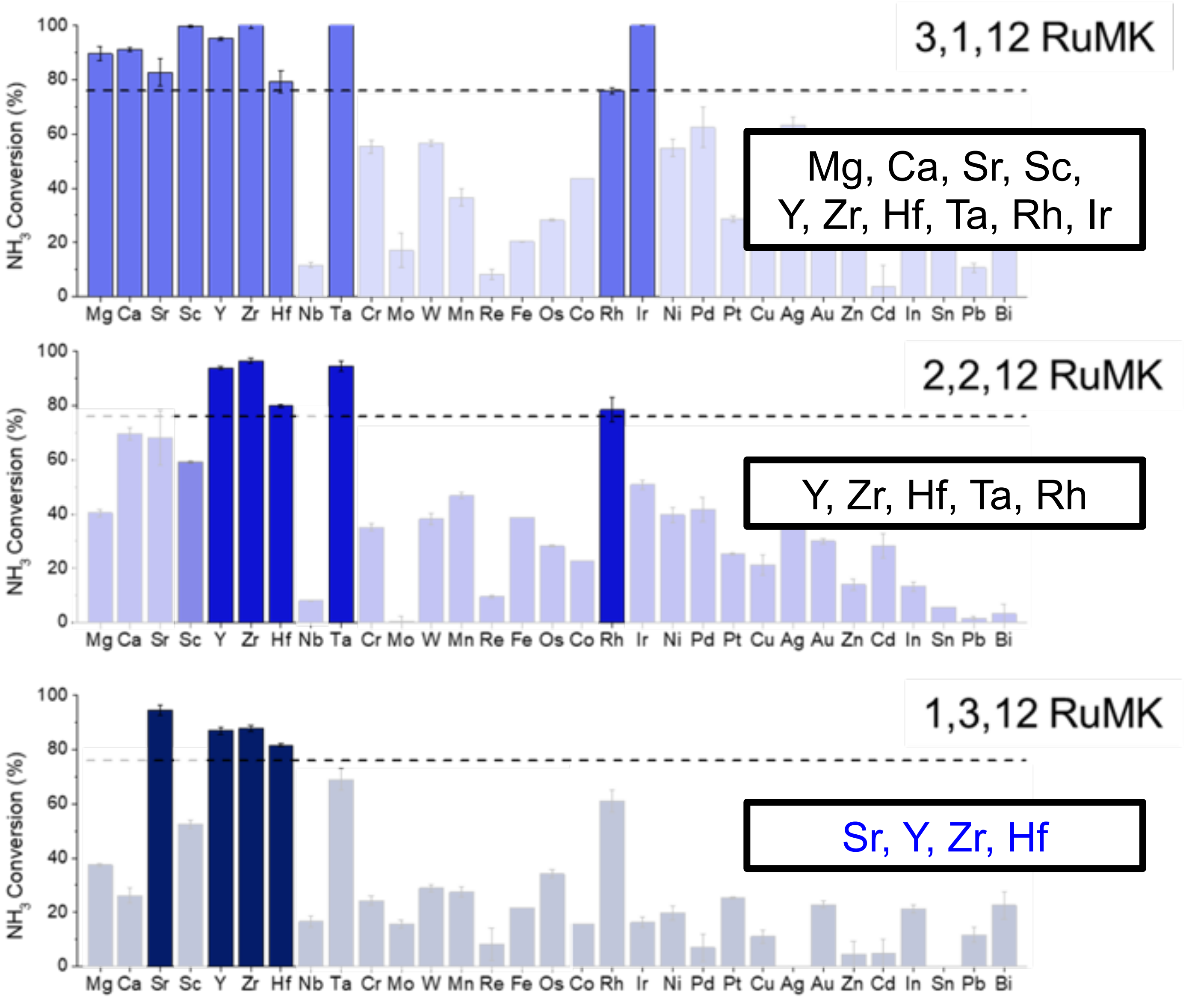


Sasmaz et al., *Engineering* 1(2), (2015) 234-242.
Hendershot et al., *Appl. Catal. A* 254, (2003) 107 – 120.



Reaction Conditions: T=300°C, 1% NH_3/Ar, 30,000 mL/hr/g_{cat}, P=1.01 bar

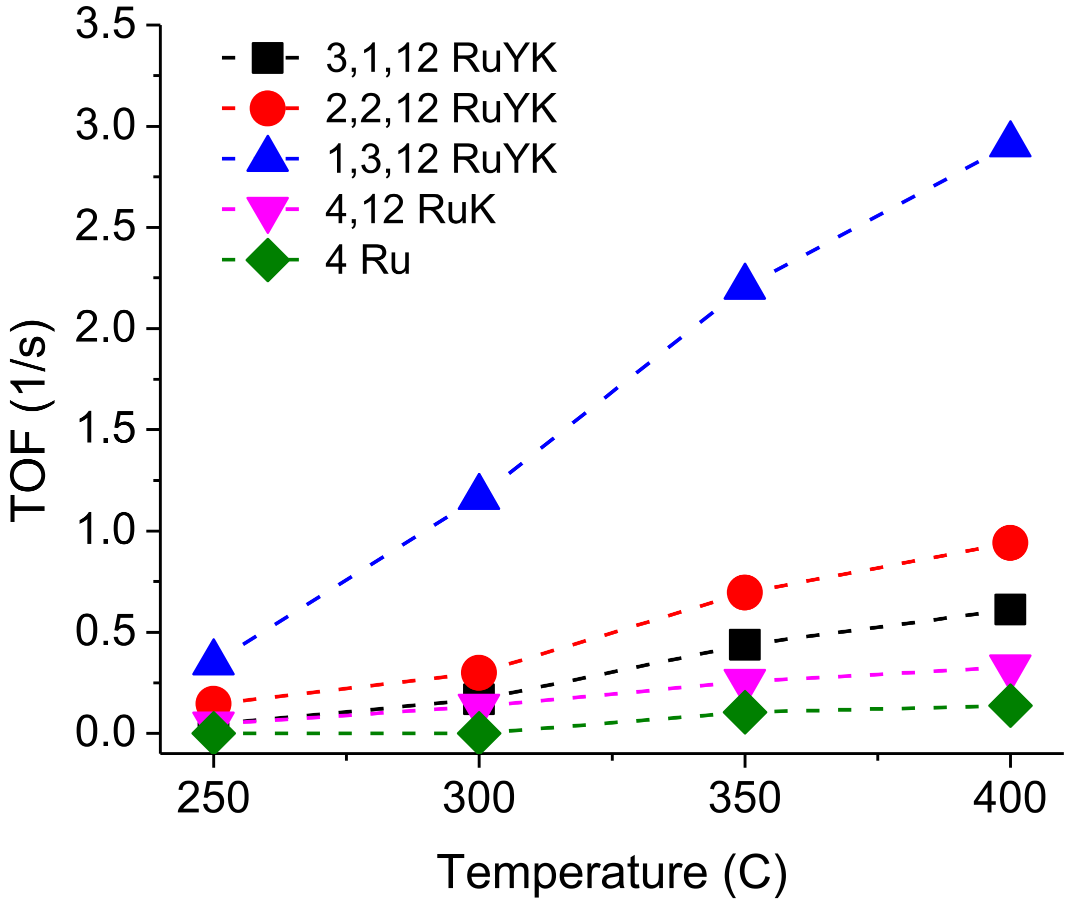
Ogawa et al., *J. Phys. Chem. C.*, 122 (2018) 10468-10475.
K. McCullough et al., *Material discovery and high throughput exploration of Ru based catalysts for low temperature ammonia decomposition.* [Submitted]
K. McCullough et al., *Enabling catalyst discovery through machine learning and high throughput experimentation.* [Submitted]



Reaction Conditions: **T=300°C,** **1% NH_3/Ar, 30,000 mL/hr/g_{cat}, P=1.01 bar**

Ogawa et al., *J. Phys. Chem. C.*, 122 (2018) 10468-10475.
K. McCullough et al., *Material discovery and high throughput exploration of Ru based catalysts for low temperature ammonia decomposition.* [Submitted]
K. McCullough et al., *Enabling catalyst discovery through machine learning and high throughput experimentation.* [Submitted]

RuYK Activity



Reaction Conditions: 100% NH_3, 5,400 mL/hr/g_{cat}, P=1.01 bar

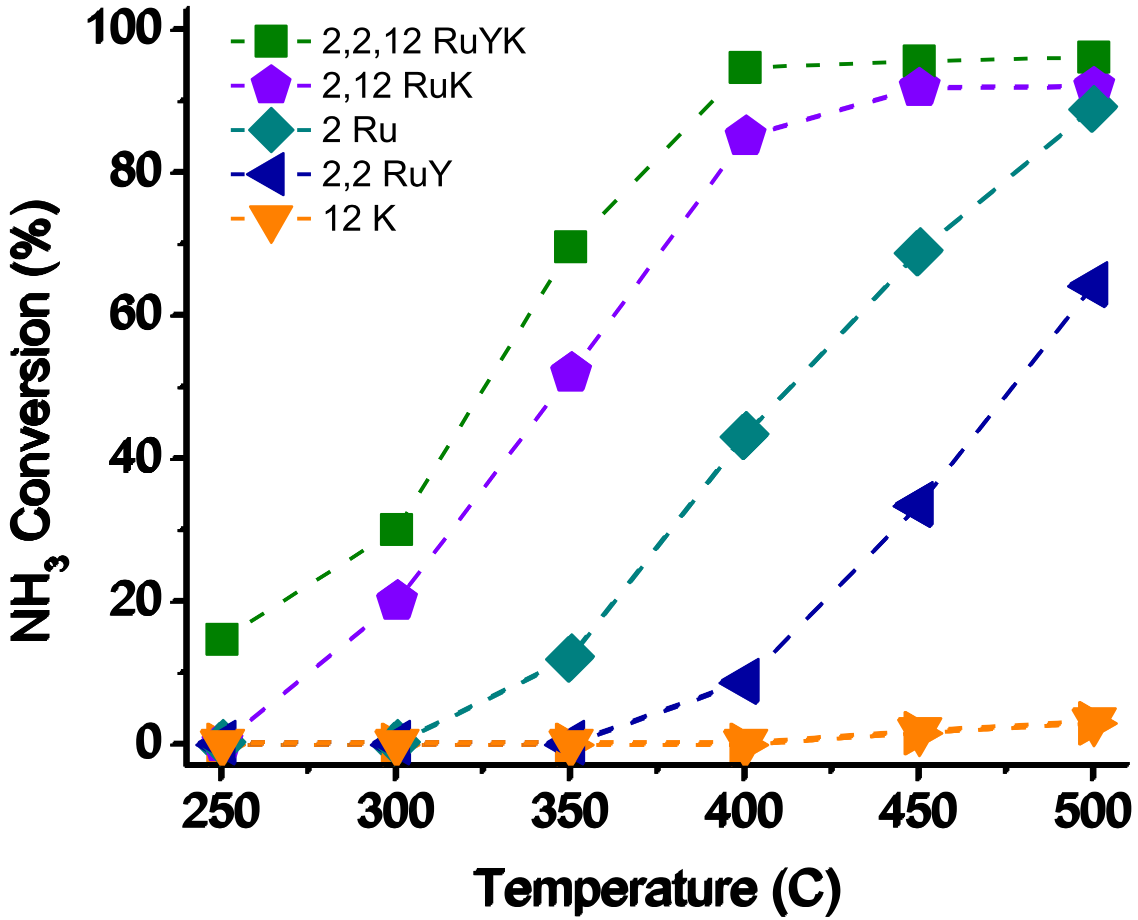
	NH_3 Conversion (%) @ 400°C	TOF[a] (1/s) @ 400°C	E_a[b] (kJ/mol)
4 Ru	52.7	0.14	179.2
4,12 RuK	91.9	0.33	134.0
3,1,12 RuYK	92.0	0.61	75.3
2,2,12 RuYK	94.6	0.94	85.6
1,3,12 RuYK	93.3	2.91	139.7

[a] H_2 Chemisorption. Ru:H_2 1:1

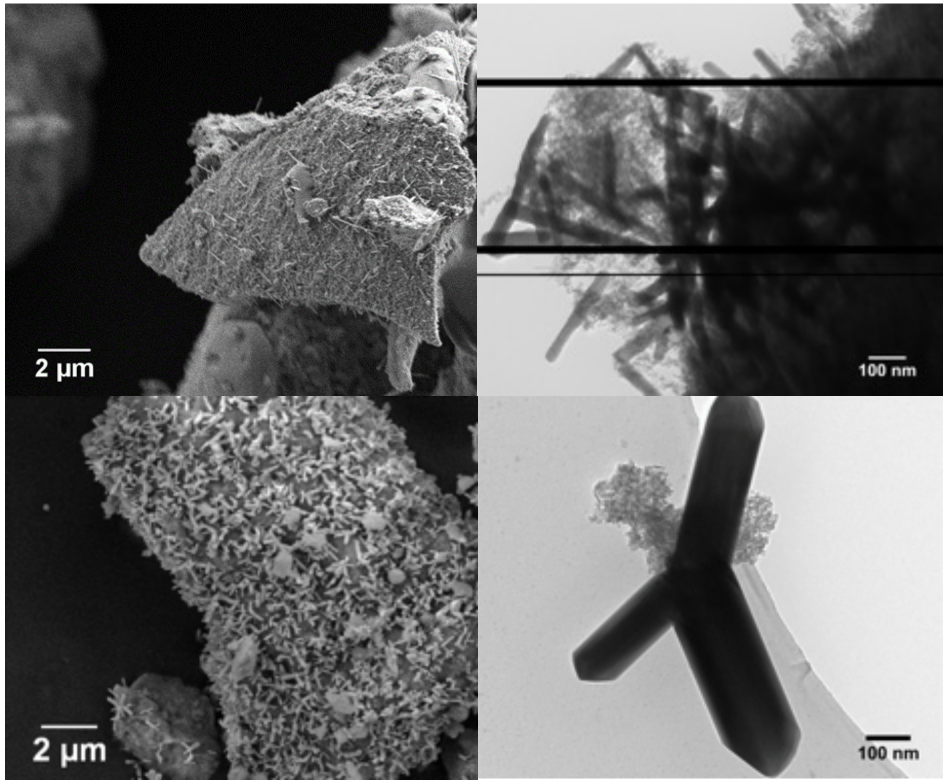
[b] Reaction Conditions: 100% NH_3, 5,400 mL $NH_3 \cdot (hr \cdot g_{cat})^{-1}$, x = 0-10%

Prasad et al., *Ind. Eng. Chem. Res.*, 48 (2009) 5255-5265.
Bradford et al., *J. Catal.*, 172 (1997) 479-484.
Okal et al., *Appl. Catal: A Gen.*, 319 (2006) 202-209.
K. McCullough, et al., *"Material discovery and high throughput exploration of Ru based catalyst for low temperature ammonia decomposition"* [Submitted].

Role of Secondary Elements



2,2,12 RuYK on Al_2O_3



2,2 RuY on Al_2O_3

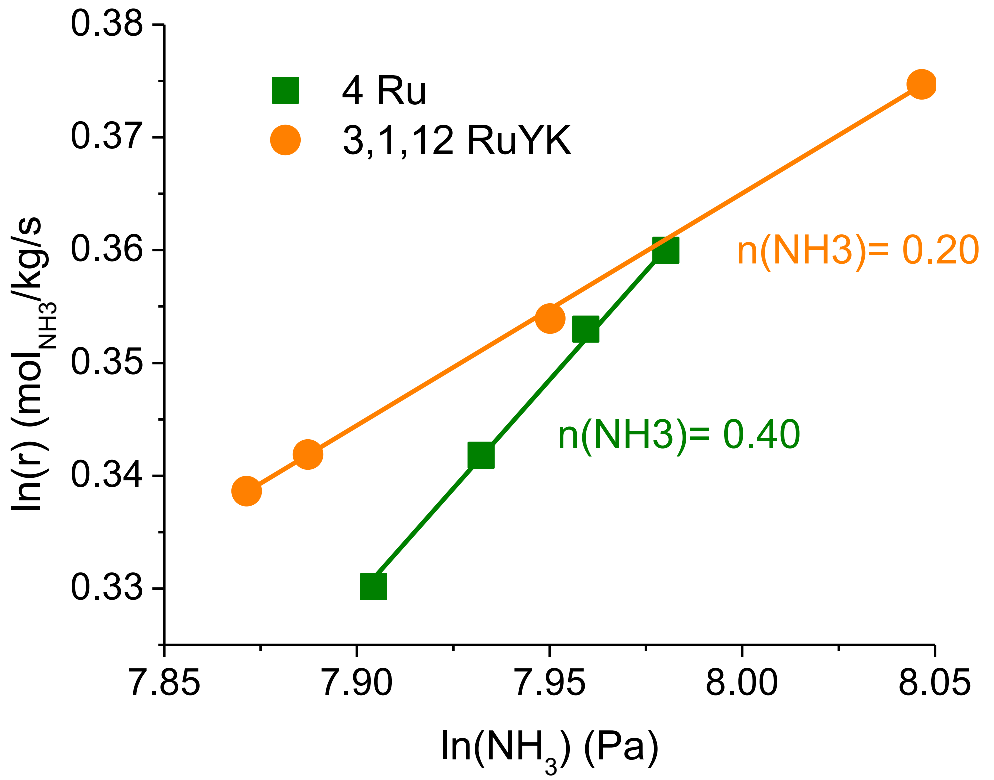
Reaction Conditions: 100% NH_3, 5,400 mL/hr/g_{cat}, P=1.01 bar

Evaluation of reaction order

$$r = k' P_{NH3}^{\alpha} P_{H2}^{\gamma}$$

$$k' = k_o \cdot \exp(-E_{app}/RT)$$

	α	γ	γ_{ref}^{1}
4 Ru	**0.40**	-0.55	-0.60
3,1,12 RuYK	**0.20**	-0.35	-



NH_3 activation more easily facilitated over 4 Ru

Okura et al., *Appl. Catal., A: Gen.* 505 (2015) 77-85.
Bradford et al., *J. Catal.,* 172 (1997) 479-484.
1. Egawa et al., *J. Chem. Soc., Faraday Trans.* 1, (1984) 80,1595-1604. Reaction Conditions: Ru(1110) surface, T = 247^{o}C, P = 10^{-5} Pa

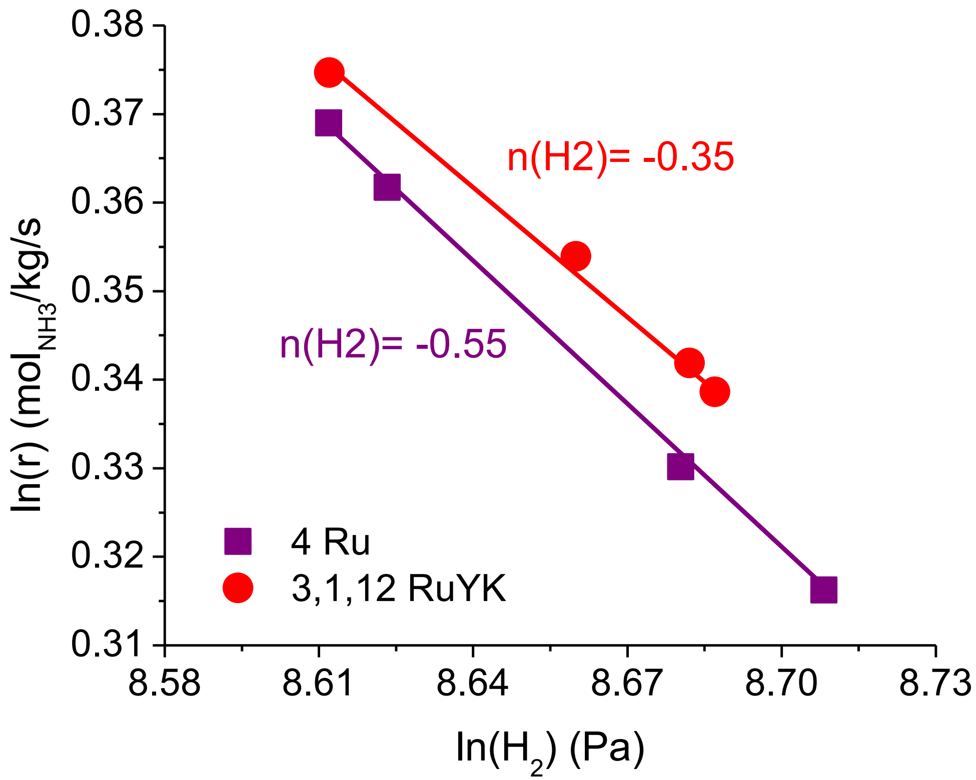
Reaction Conditions: 10-30% NH_3, 10-30% H_2 in balance Ar, T = 450^{o}C, P = 1.01 bar, 5,400 mL $\cdot$(hr$\cdot$g$_{cat}$)$^{-1}$

Evaluation of reaction order

$$r = k' P_{NH3}^{\alpha} P_{H2}^{\gamma}$$

$$k' = k_o \cdot \exp(-E_{app}/RT)$$

	α	γ	γ_{ref}^{1}
4 Ru	0.40	**-0.55**	-0.60
3,1,12 RuYK	0.20	**-0.35**	-



H_2 inhibition suppressed over 3,1,12 RuYK

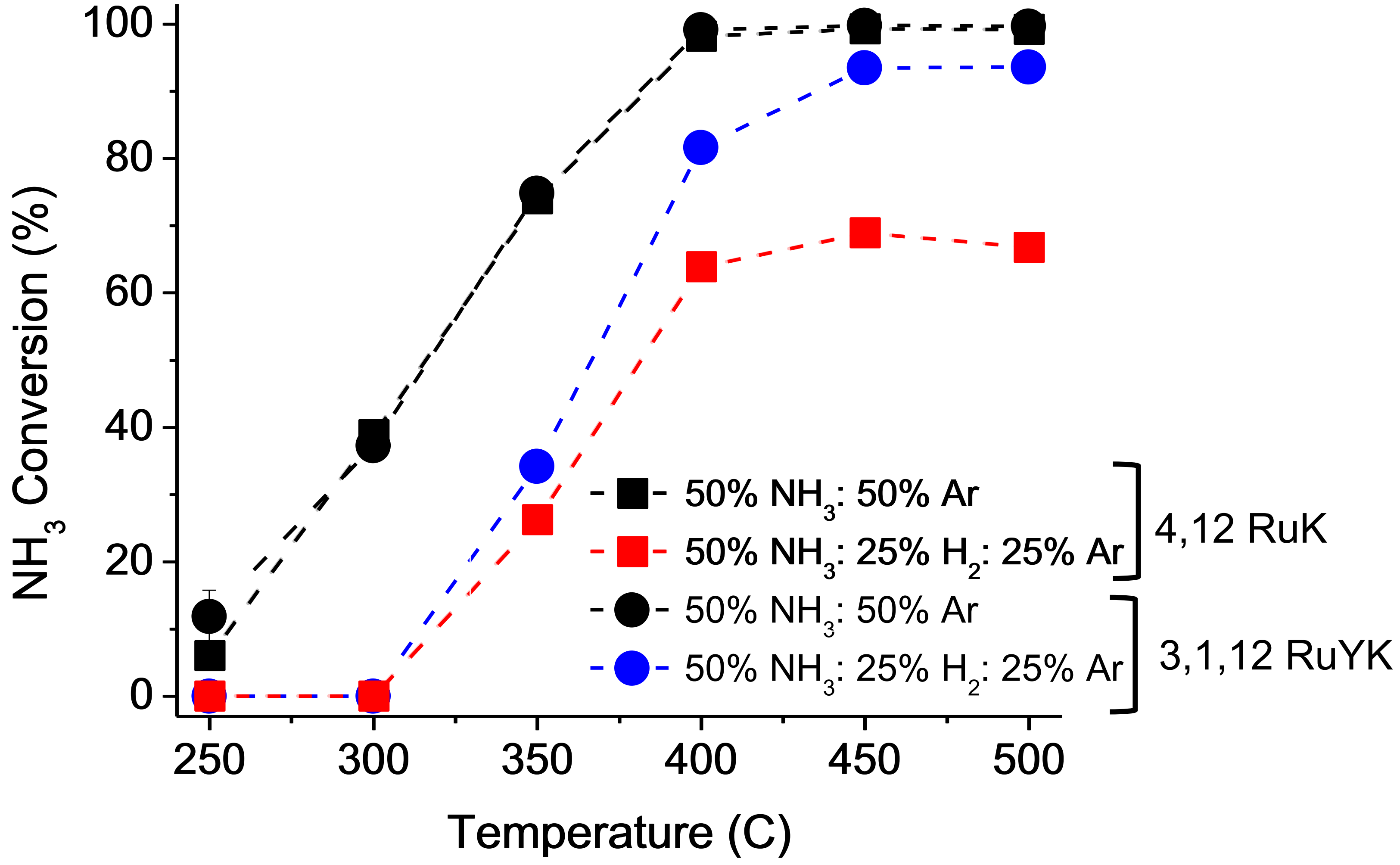
Okura et al., *Appl. Catal., A: Gen.* 505 (2015) 77-85.
Bradford et al., *J. Catal.,* 172 (1997) 479-484.
1. Egawa et al., *J. Chem. Soc., Faraday Trans.* 1, (1984) 80,1595-1604. Reaction Conditions: Ru(1110) surface, T = 247°C, P = 10^{-5} Pa

Reaction Conditions: 10-30% NH_3, 10-30% H_2 in balance Ar, T = 450°C, P = 1.01 bar, 5,400 mL ·(hr·g_{cat})$^{-1}$

H_2 Co-feeding: Effect of Y Addition

H_2 inhibits NH_3 decomposition activity by blocking active sites

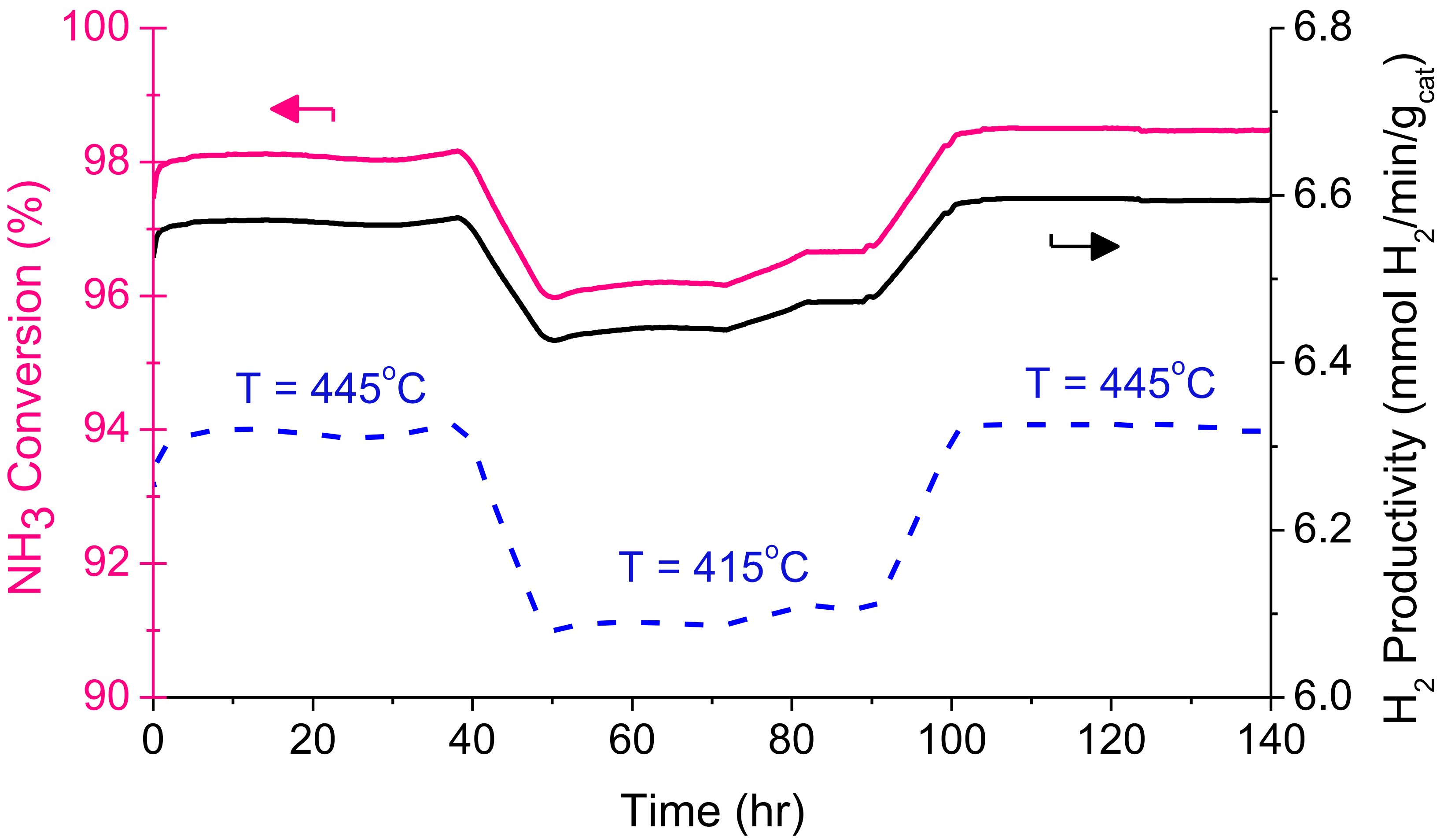
Addition of Y suppresses H_2 inhibition on Ru



Salciccioli et al., *Chem. Eng. Sci.* 66 (2011) 4319-4355.

Reaction Conditions: 5,400 mL·(hr·g_{cat})$^{-1}$, P = 1.01 bar

3,1,12 RuYK Stability under High Pressure NH_3

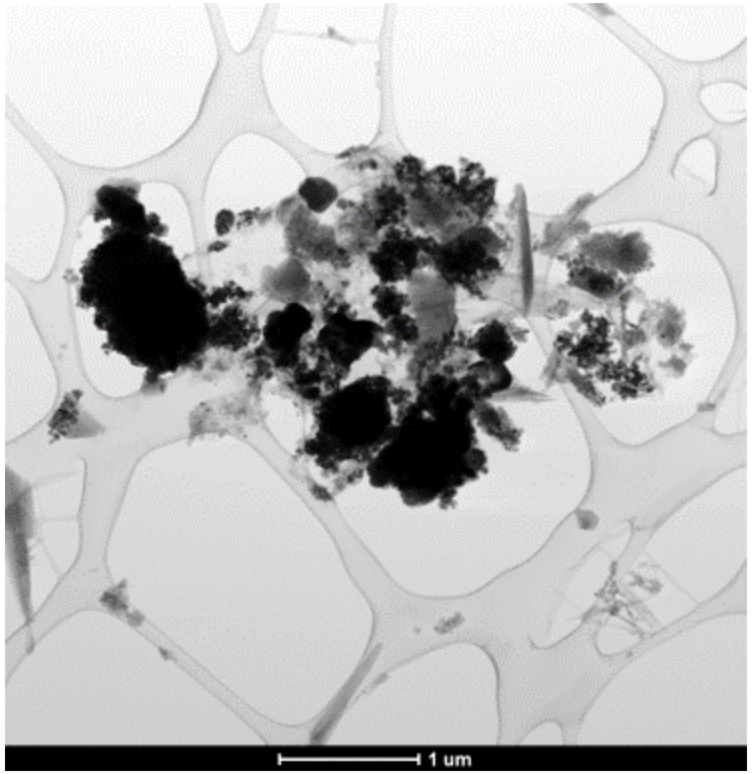


Reaction Conditions: P = 5 bar, 100% NH_3, 6,000 mL/hr/g_{cat}

Data collected at Gas Technologies Institute, Chicago IL

3,1,12 RuYK after reaction

Ru, Y and K maintain close proximity after reaction



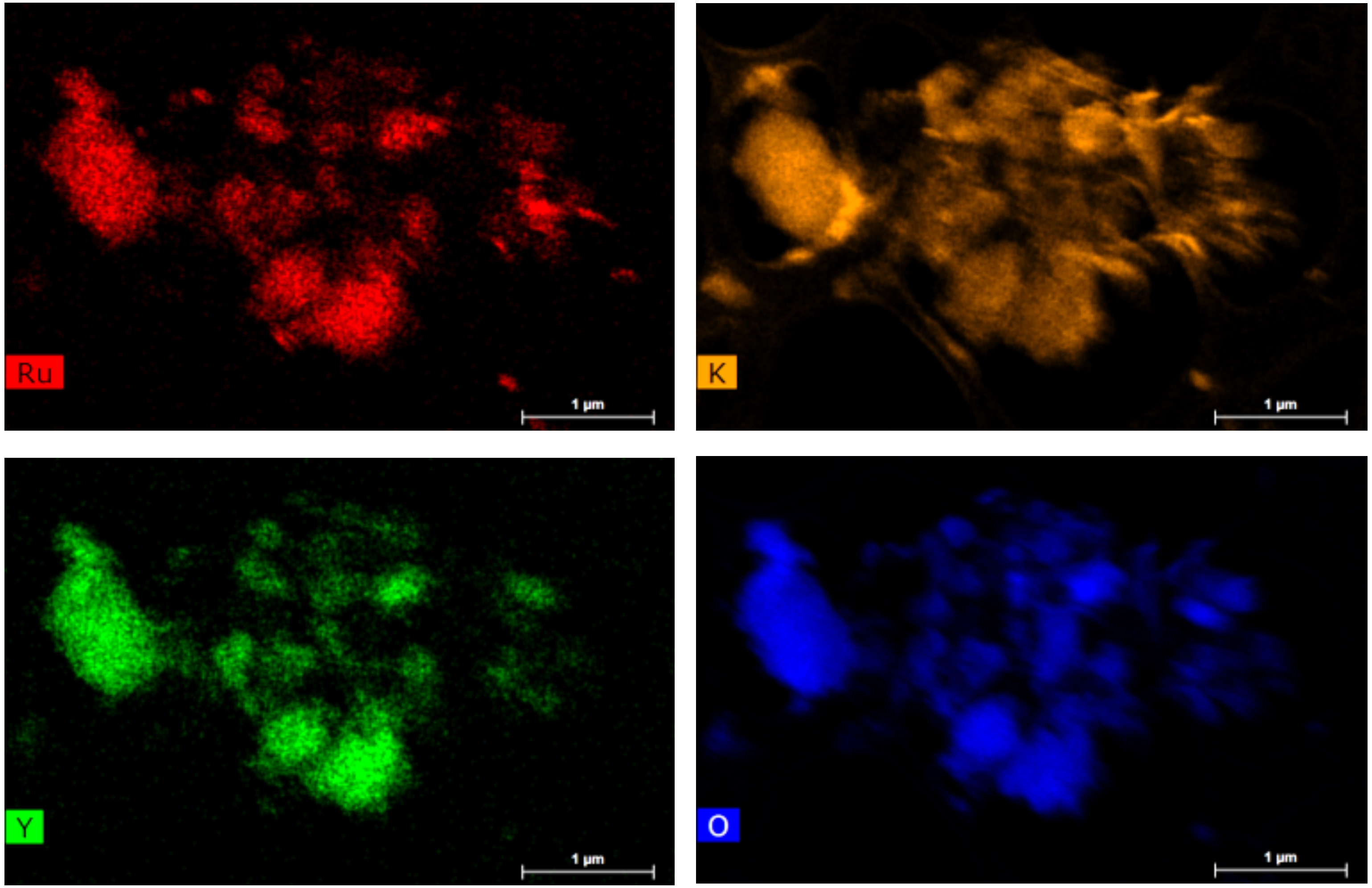
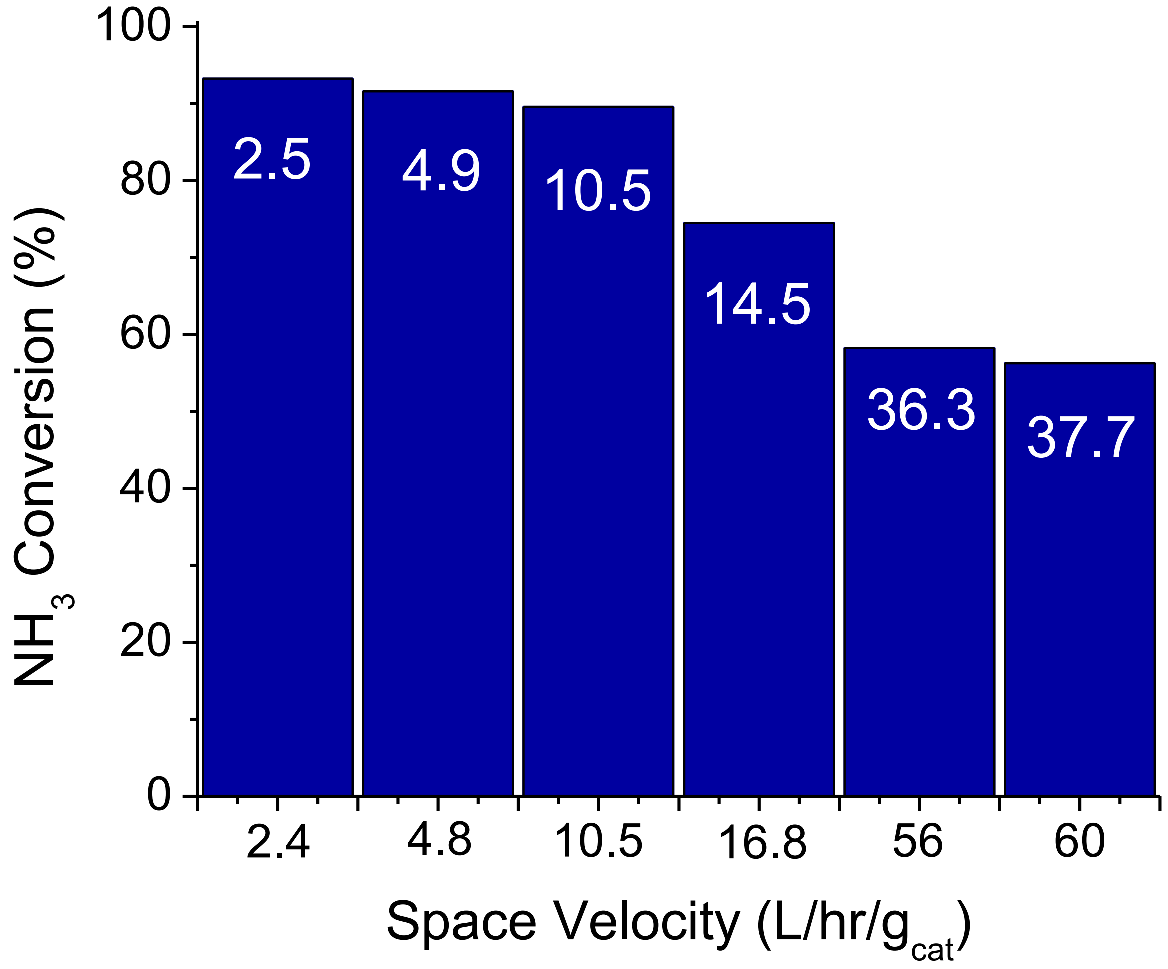


Image taken by Michael Lance at Oakridge National Lab

Effect of Space Velocity on Activity 3,1,12 RuYK



Reaction Conditions:
T = 450°C, 100% NH_3

Hydrogen Production ($mmol\ H_2/min/g_{cat}$) listed within columns

Cost Savings and Market Interest

1.0 MWe Scale up	
	Cost of Catalyst ($)[1]
4 Ru / ɣ-Al_2O_3	109,000
3,1,12 RuYK / ɣ-Al_2O_3	87,000
1,3,12 RuYK / ɣ-Al_2O_3	37,000

[1]Costs calculated by precursor materials and hydrogen production rates @ 400^{o}C, 5,400 mL/min/g_{cat}

H2U Australia -
5 MW fuel cell demonstration plant (construction 2019)

1. Renewable H_2 produced from water splitting
2. H_2 + N_2 to produce ammonia (Haber Bosch)
3. Export of ammonia to be cracked for H_2 fuel

Trevor Brown, "Renewable energy plant announced in South Australia". Ammonia Industry. 2018.

Conclusions

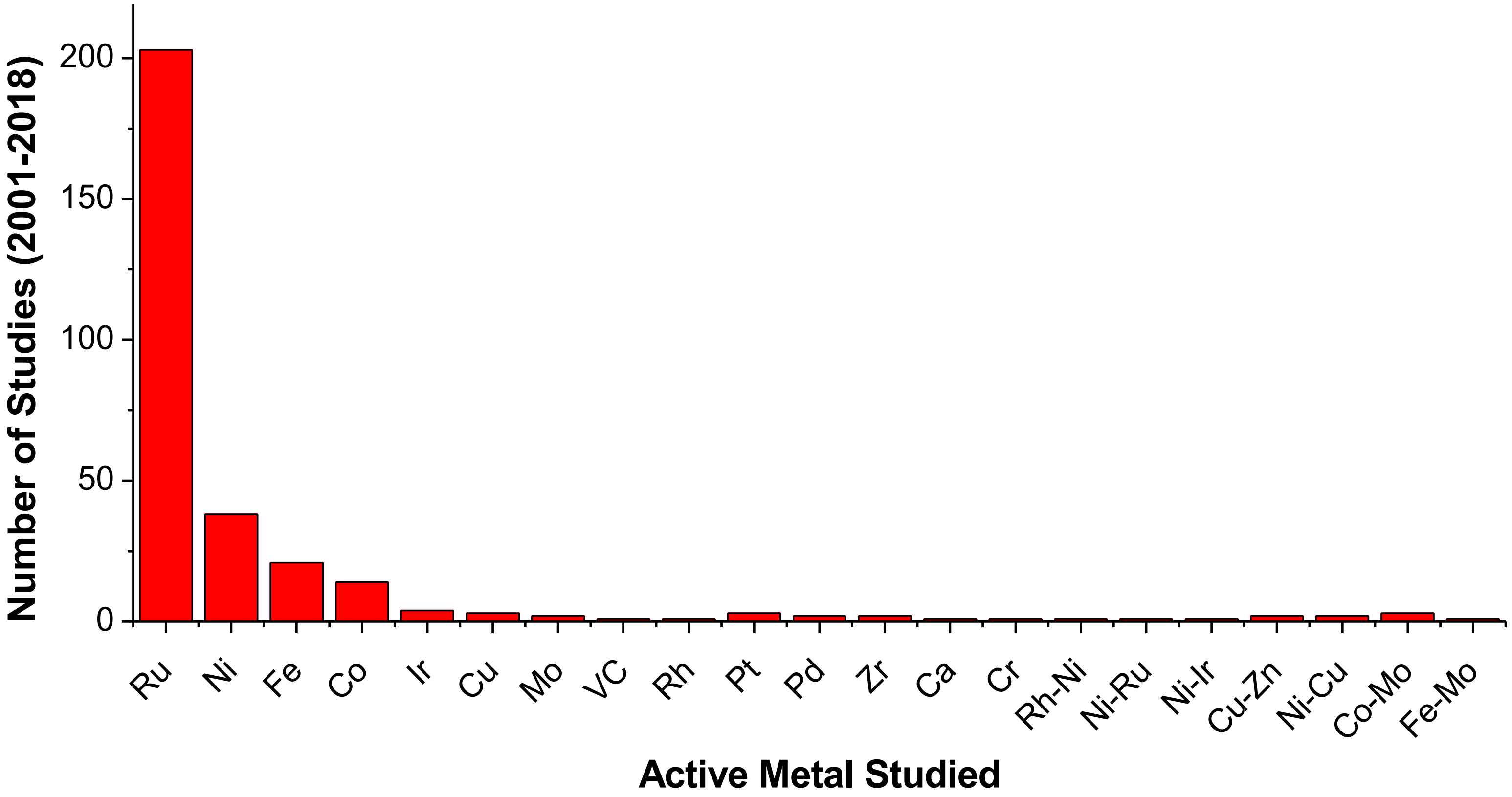
- Discovered multiple novel catalyst formulations through high throughput screening
- Achieved 93% NH_3 conversion @ 400^{o}C in pure NH_3 with 1% Ru
- Y suppresses H_2 poisoning over Ru and lowers apparent activation energy
- Substitution of Ru with Y results in a cost-effective, stable catalyst for on site H_2 generation from NH_3

Acknowledgements

- Lauterbach Group Members
- Elliott Chiang
- Strategic Approach to the Generation of Electricity Center (SAGE)
- NSF IGERT DGE-1250052
- ARPA-E DE-AR0000931

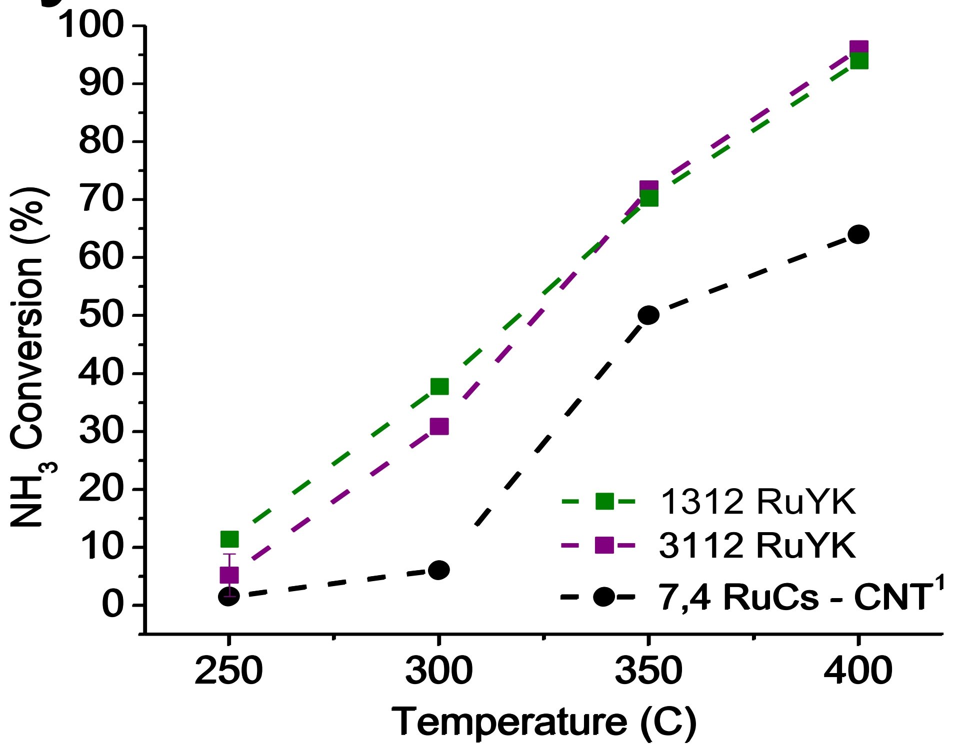
Supplemental Slides

Materials for Ammonia Decomposition



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: Environ*. 226 (2018) 162-181.
Way too many to list

RuYK Activity



Reaction Conditions: 100% NH_3, atmospheric pressure and 5,200 mL $NH_3 \cdot (min \cdot g_{cat})^{-1}$

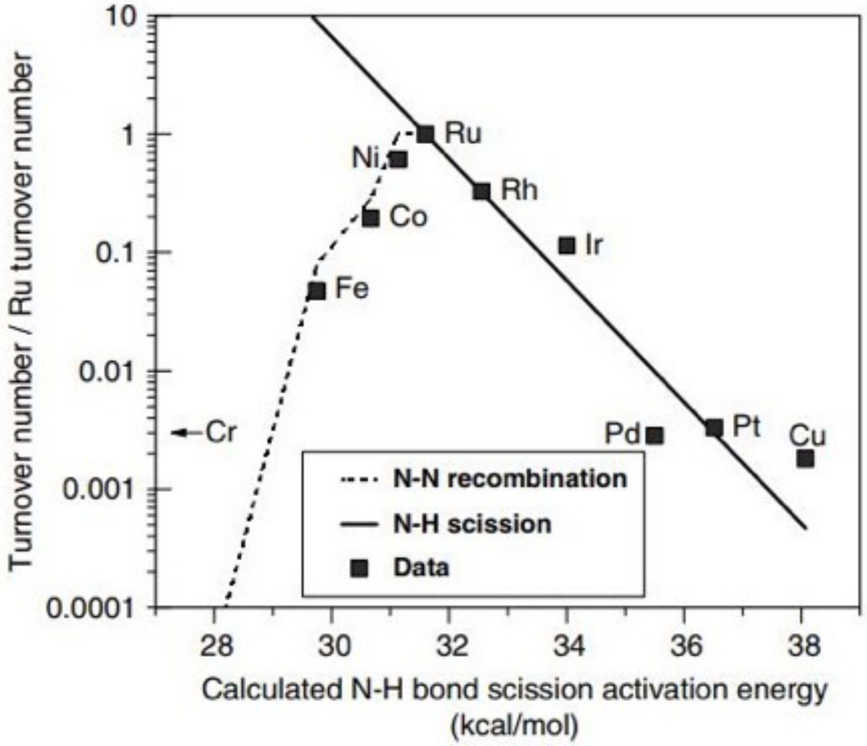
	Ru / Y / K content (%) (ICP-OES)	**Conversion** @ 400°C (%)	**Activation Energy** (kJ/mol)
7,4 RuCs – CNT[1]	-	64	78.6
3,1,12 RuYK – Al_2O_3	2.5 / 0.95 / 12.25	95	57.7
1,3,12 RuYK – Al_2O_3	0.8 / 3.09 / 10.1	94	41.6

1. Hill et al., *Appl. Catal. B: Environ.* 172–173, (2015), 129-135.
K. McCullough, et al., *Enabling catalyst discovery through machine learning and high throughput experimentation.* [Submitted]

Ammonia Decomposition

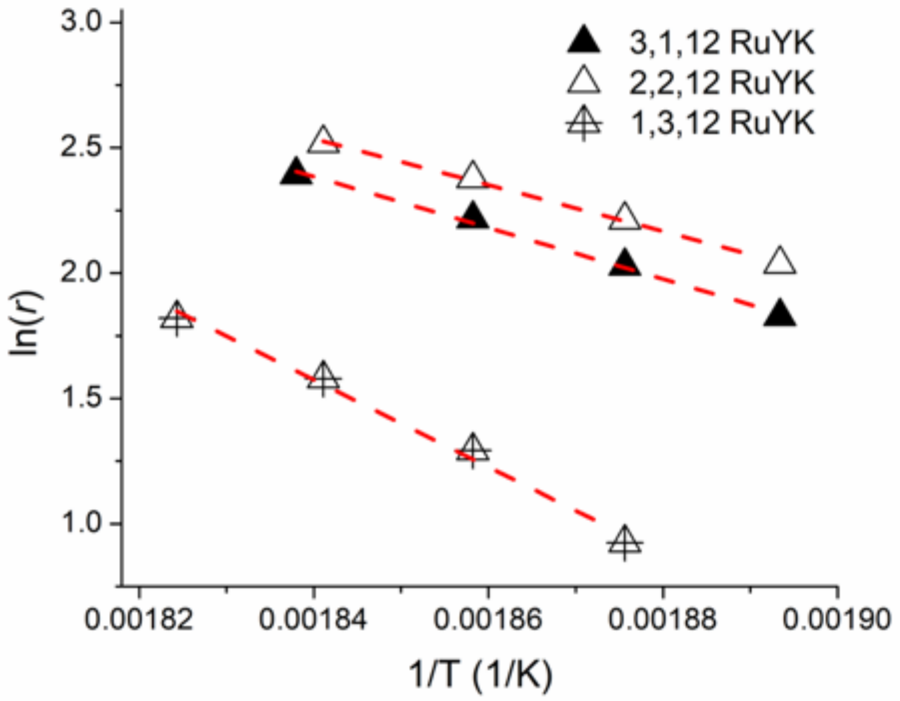
Many theoretical models exist that correlate different energies to NH_3 decomposition activity

No correlation found between 7 models and 13 metals



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

RuYK Activity



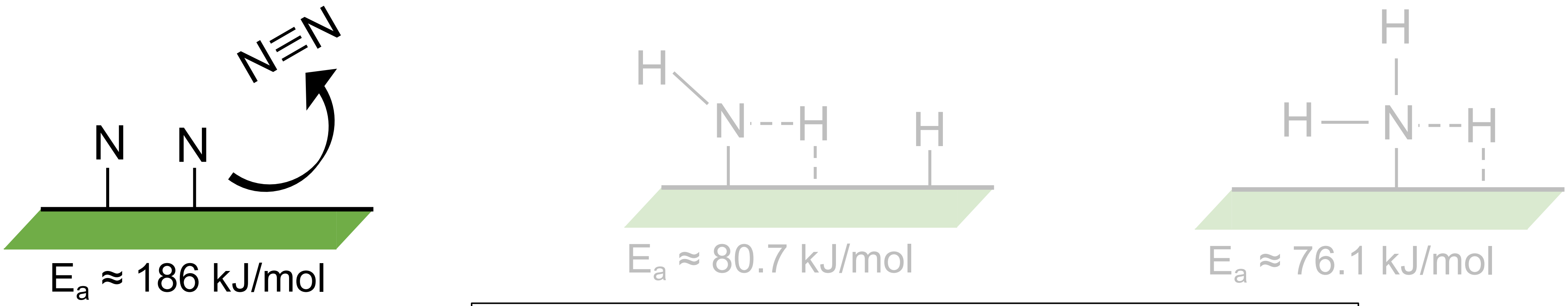
	Ru / Y / K content (%) (ICP-OES)	NH_3 Conversion @ 350C (%)	H_2 Consumption (mmol H_2/g_{cat})	H_2 Adsorption (mmol H_2/g_{cat})
3,1,12 RuYK	2.5 / 0.95 / 12.25	71.8	2.87	2.60×10^{-3}
2,2,12 RuYK	1.68 / 1.93 / 12.4	69.5	3.36	1.67×10^{-3}
1,3,12 RuYK	0.8 / 3.09 / 10.1	70.2	2.66	5.39×10^{-4}

Activation Energy

Catalyst	H_2 uptake[a] (μmol H_2/g)	E_a[b] (kJ/mol)
4 Ru	**6.5**	**179.2**
4,12 RuK	4.7	134.0
3,1,12 RuYK	2.60	75.3
2,2,12 RuYK	1.67	85.6
1,3,12 RuYK	0.54	139.7

(a) H_2 Chemisorption, Ru:H_2 1:1 (b) Reaction Conditions: 100% NH_3, 5,400 mL NH_3·(hr ·g_{cat})$^{-1}$, x = 0-10%

RDS changes as a function of Ru and Y loading



Different rate determining steps (RDS) on Ru^0 surface

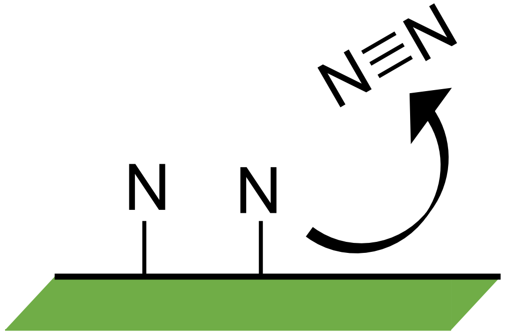
Prasad et al., *Ind. Eng. Chem. Res.*, 48 (2009) 5255-5265.
Bradford et al., *J. Catal.*, 172 (1997) 479-484.
Okal et al., *Appl. Catal: A Gen.*, 319 (2006) 202-209.
K. McCullough, et al., *"Material discovery and high throughput exploration of Ru based catalyst for low temperature ammonia decomposition"* [Submitted].

Activation Energy

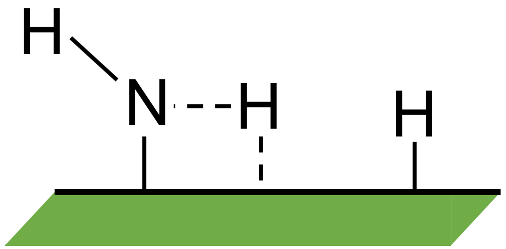
Catalyst	H_2 uptake[a] (μmol H_2/g)	E_a[b] (kJ/mol)
4 Ru	6.5	179.2
4,12 RuK	4.7	134.0
3,1,12 RuYK	2.60	75.3
2,2,12 RuYK	1.67	85.6
1,3,12 RuYK	0.54	139.7

(a) H_2 Chemisorption, Ru:H_2 1:1 (b) Reaction Conditions: 100% NH_3, 5,400 mL NH_3·(hr ·g_{cat})$^{-1}$, x = 0-10%

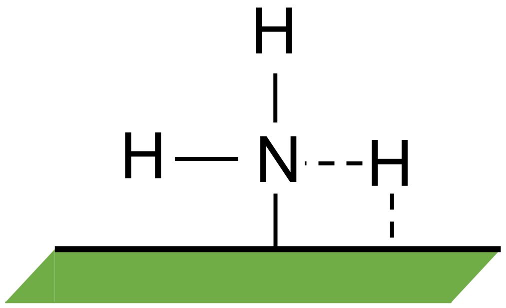
RDS changes as a function of Ru and Y loading



$E_a \approx 186$ kJ/mol



$E_a \approx 80.7$ kJ/mol

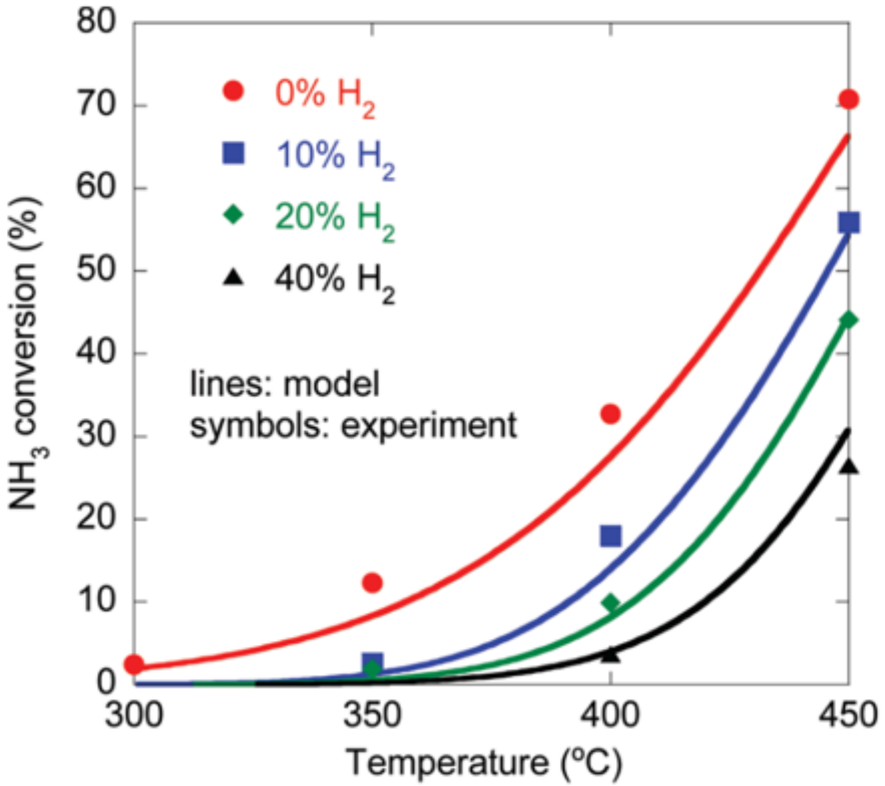


$E_a \approx 76.1$ kJ/mol

Different rate determining steps (RDS) on Ru^0 surface

Prasad et al., *Ind. Eng. Chem. Res.*, 48 (2009) 5255-5265.
Bradford et al., *J. Catal.*, 172 (1997) 479-484.
Okal et al., *Appl. Catal: A Gen.*, 319 (2006) 202-209.
K. McCullough, et al., *"Material discovery and high throughput exploration of Ru based catalyst for low temperature ammonia decomposition"* [Submitted].

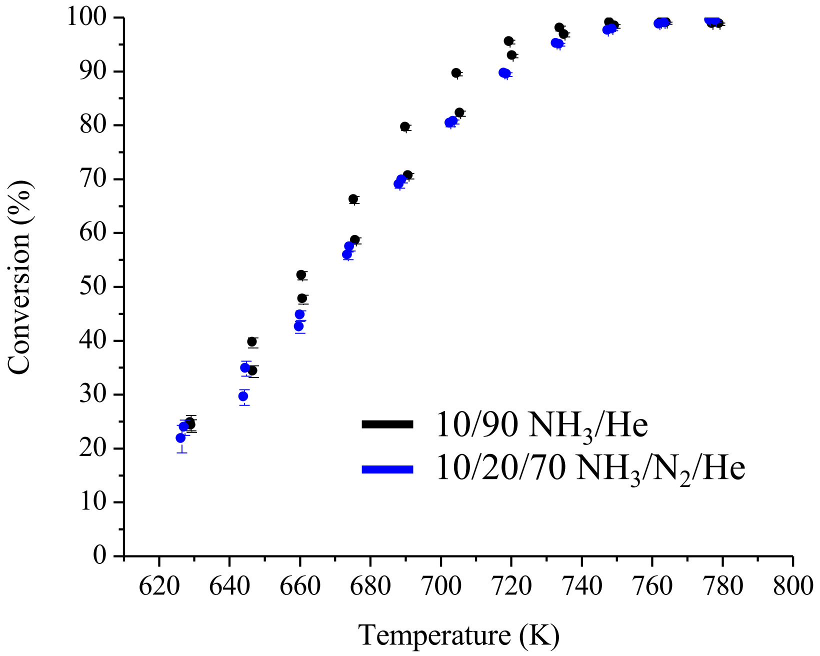
Effect of H2 on ammonia decomposition



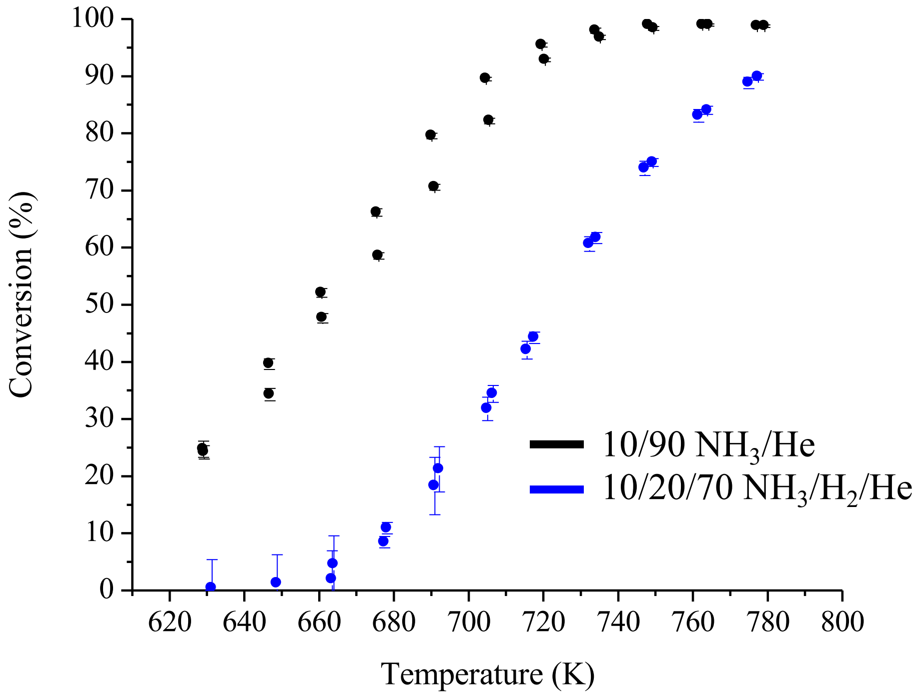
Reaction Conditions: 96 mg Ru/ɣ-Al_2O_3, 30% NH_3 in balance He, 200 sccm

Prasad et al., *Ind. Eng. Chem. Res.* **2009**,*48*,5255-5265.
Dshmukh et al., *Ind. Eng. Chem. Res.* **2004**, *43*, 12, 2986-2999.
Okura et al., *ChemCatChem* **2016**, 8, 2988-2995.

N_2 and H_2 inhibition on NH_3 decomposition



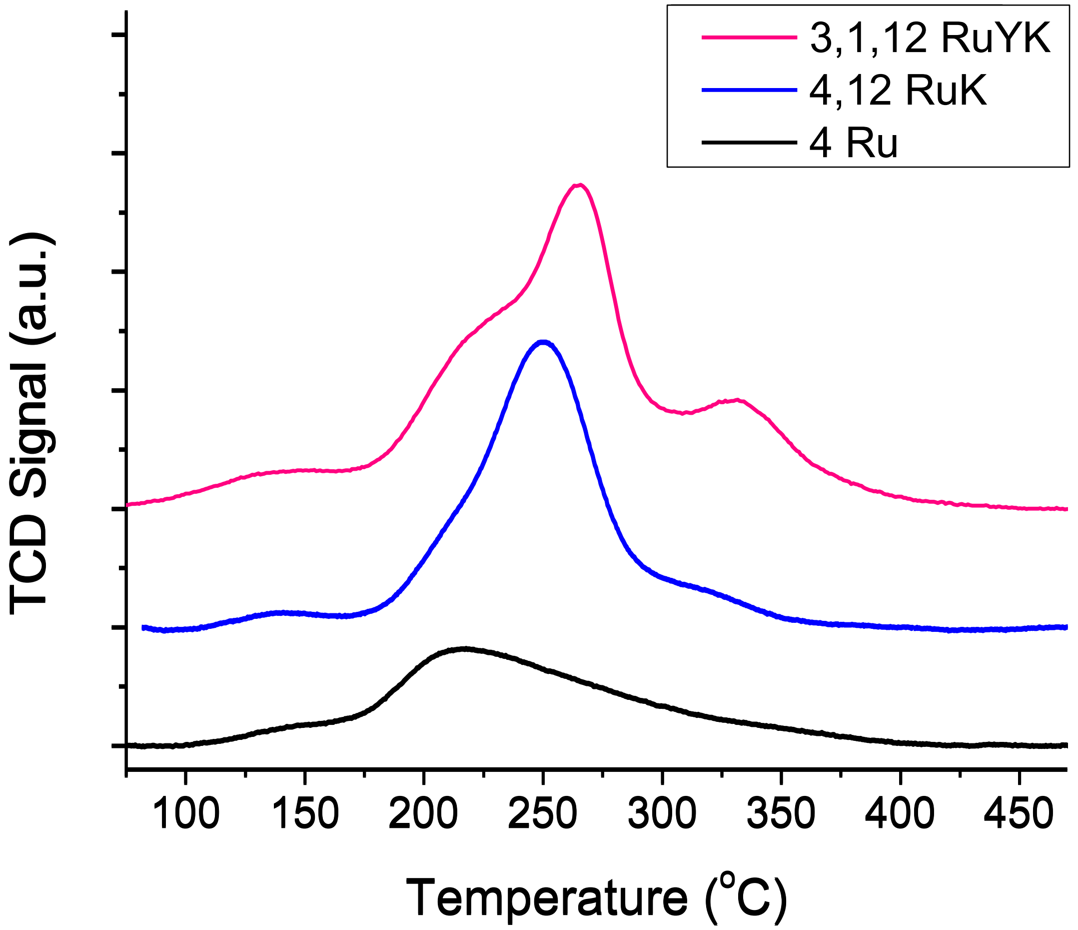
Effect of N_2 co-feeding over 3wt% Ru/ γ-Al_2O_3



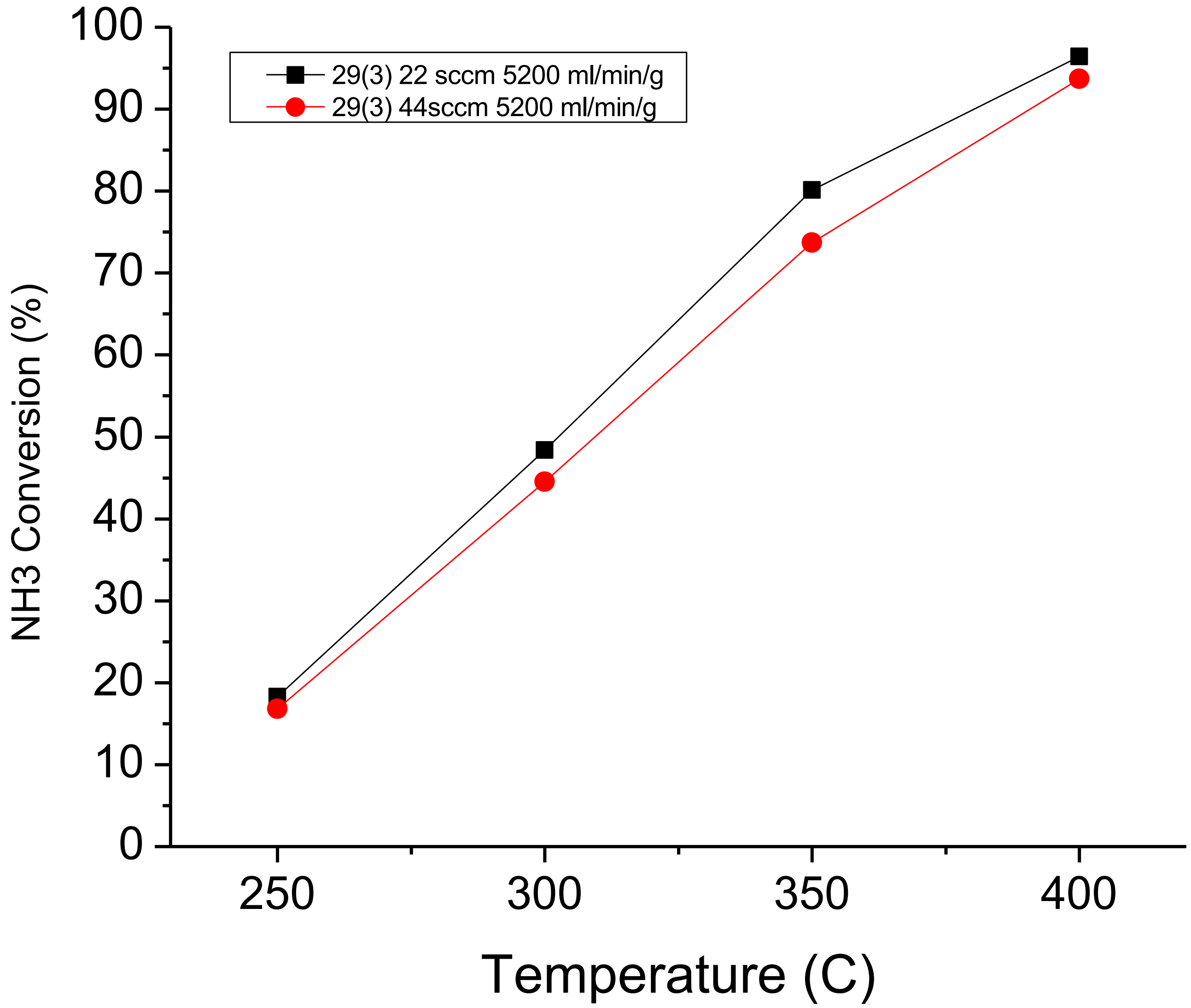
Effect of H_2 co-feeding over 3wt% Ru/ γ-Al_2O_3

Reaction Conditions: P=1.01 bar, 30,000 mL/h/gcat

H_2 Temperature Programmed Desorption



External Mass Transfer



Internal mass transfer
Weisz Prater Criterion update

$$\frac{r_a' \rho_c R_p^2}{D_e C_{as}} \ll 1$$

Satisfies criterion @ 2.81e-5

- $r_a' = reaction\ rate = .06\ \mathrm{mol/kg/s}\ @\ 450\mathrm{C}, 100\ \%\ \mathrm{NH_3}$
- $\rho_c = loose\ bulk\ density = \ 650\ g/L$
- $R_p\ \ = particle\ size = 45\ um$
- $D_e = effetive\ deffusivity = 4.27x10^{-5}\ m^2/s$
- $C_{as} = concentration\ at\ the\ surface = 17.7\frac{mol}{m^3} @\ 450C$

Prasad et al., *Ind. Eng. Chem. Res.* **2009**,*48*,5255-5265.
Reid, R. C. The properties of gases and liquids; McGraw-Hill: New York, 1987.

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/

Electricity cost	0.05	$/kWh	0.05 $/kWh Do not change.
Fuel price, $/kg	0.66048	$/kg	manual
Fuel price, $/kWh	0.128	$/kWh	manual or output from Fuel production cost spreadsheet
Hydrogen content	0.176470588	weight fraction	
Process output		kWh/day	
Conversion system	other		select from dropdown. If Other, note temperature and references.
Fuel Cell costs, $/kW	0	$/kW	Populated from "References and suggested values" sheet Fuel cell cost section
Fuel cell power density, mW/cm2	0	mW/cm2	Populated from "References and suggested values" sheet Fuel cell powre density section
Power density, mW/cm2		mW/cm2	
Conversion efficiency	**87%**	%	Please refer to "Energy efficiency calculation" tab in this excel file
Capital Cost at 150 MW scale	**1256.11**	$/kW	Please refer to "Capital cost for H2 production" tab in this excel file
O&M cost	125.6	$/kW	Assumed 10% of Capital Cost
Cost of H2 generation	0.133664328	$/kg	
Capacity factor	65%	%	
Projected lifetime of equipment	15	years	15 years is the default number.
Levelized capital cost of H2 generation	0.0203	$/kWh	
Levelized capital cost of H2 generation	0.682572124	$/kg	
Total H2 cost	0.816236452	$/kg	

RuCl3 21,000$/kg
YCl3 2,000$/kg
Alumina 15$/kg
K acetate 32$/kg

https://www.spectrumchemical.com/OA_HTML/chemical-products_Potassium-Acetate-Crystalline-Powder-USP_PO155.jsp?minisite=10020&respid=22372&phrase=Potassium%20Acetate
https://www.chemicalbook.com/Price/Ruthenium_III-chloride.htm
https://www.sigmaaldrich.com/catalog/product/aldrich/464317?lang=en&region=US