Supplementary Materials

Promoted Ru/PrO_x Catalysts for Mild Ammonia Synthesis

Samuel M. Drummond[1], Jennifer Naglic[1], Thossaporn Onsree[1], S. K. Balijepalli[2], Alexis Allegro[1], Stephanie N. Orraca Albino[1], Katherine M. O'Connell[1], and Jochen Lauterbach[1,*]

[1]Department of Chemical Engineering, University of South Carolina, Columbia SC 29208

[2]College of Engineering and Computing, University of South Carolina, Columbia SC 29208

[*]Corresponding Author: lauteraj@cec.sc.edu

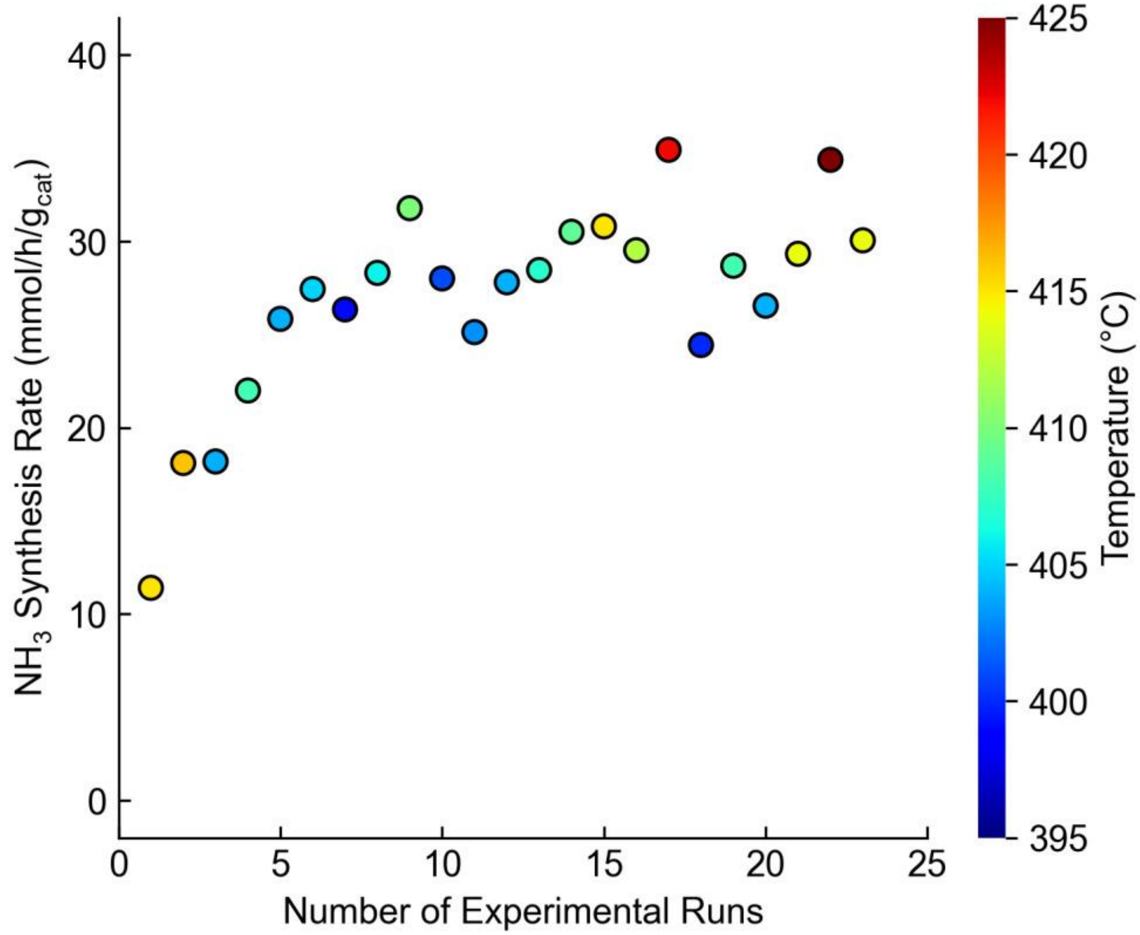


Figure S1: 1 wt.% Ru/PrO_x catalyst tested over several pressurization, depressurization, and reduction cycles. Catalyst was tested at a space velocity of 36,000 mL/g_{cat}/hr, 1:1 H_2:N_2 and 30 bar.

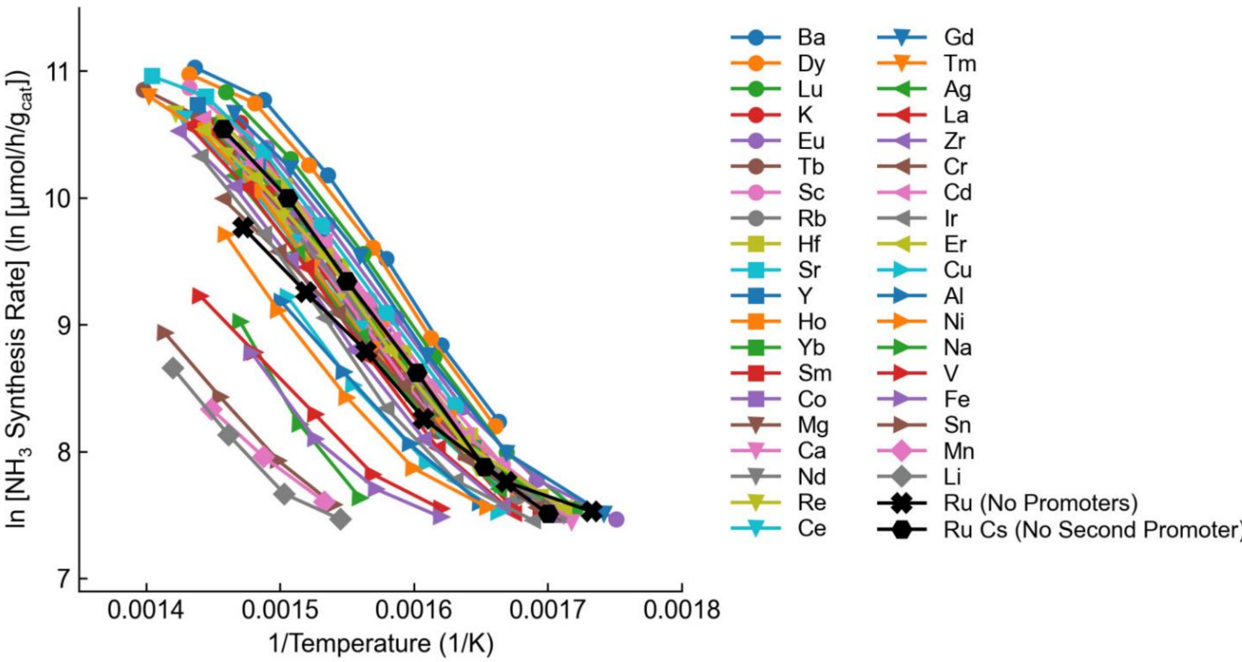
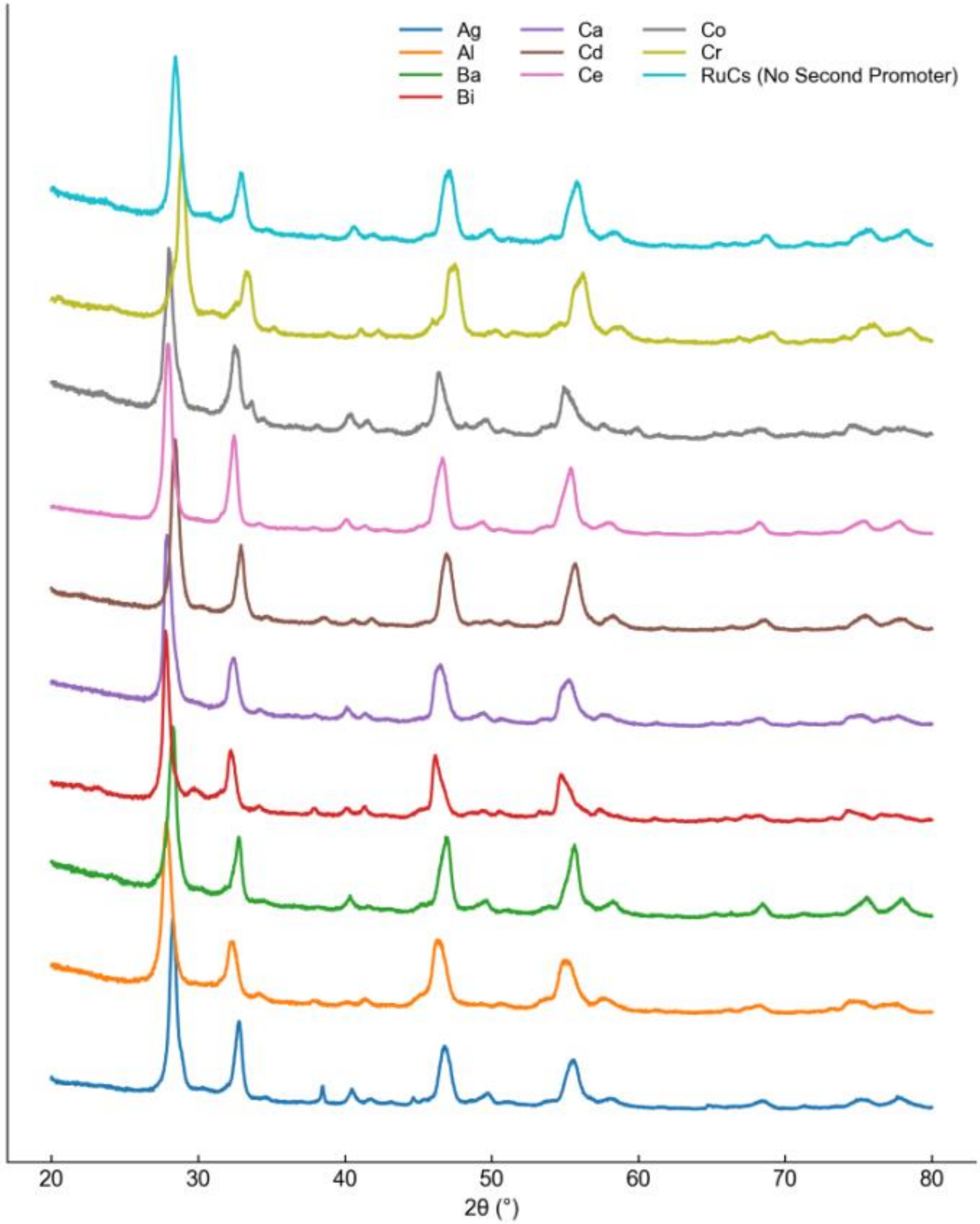


Figure S2: Arrhenius plots of doubly promoted 1 wt.% Ru, 2 wt.% Cs, 2 wt.% M/PrO_x catalysts at various temperatures. Catalysts were tested at a space velocity of 36,000 mL/g_{cat}/hr, 1:1 H_2:N_2 and 30 bar.

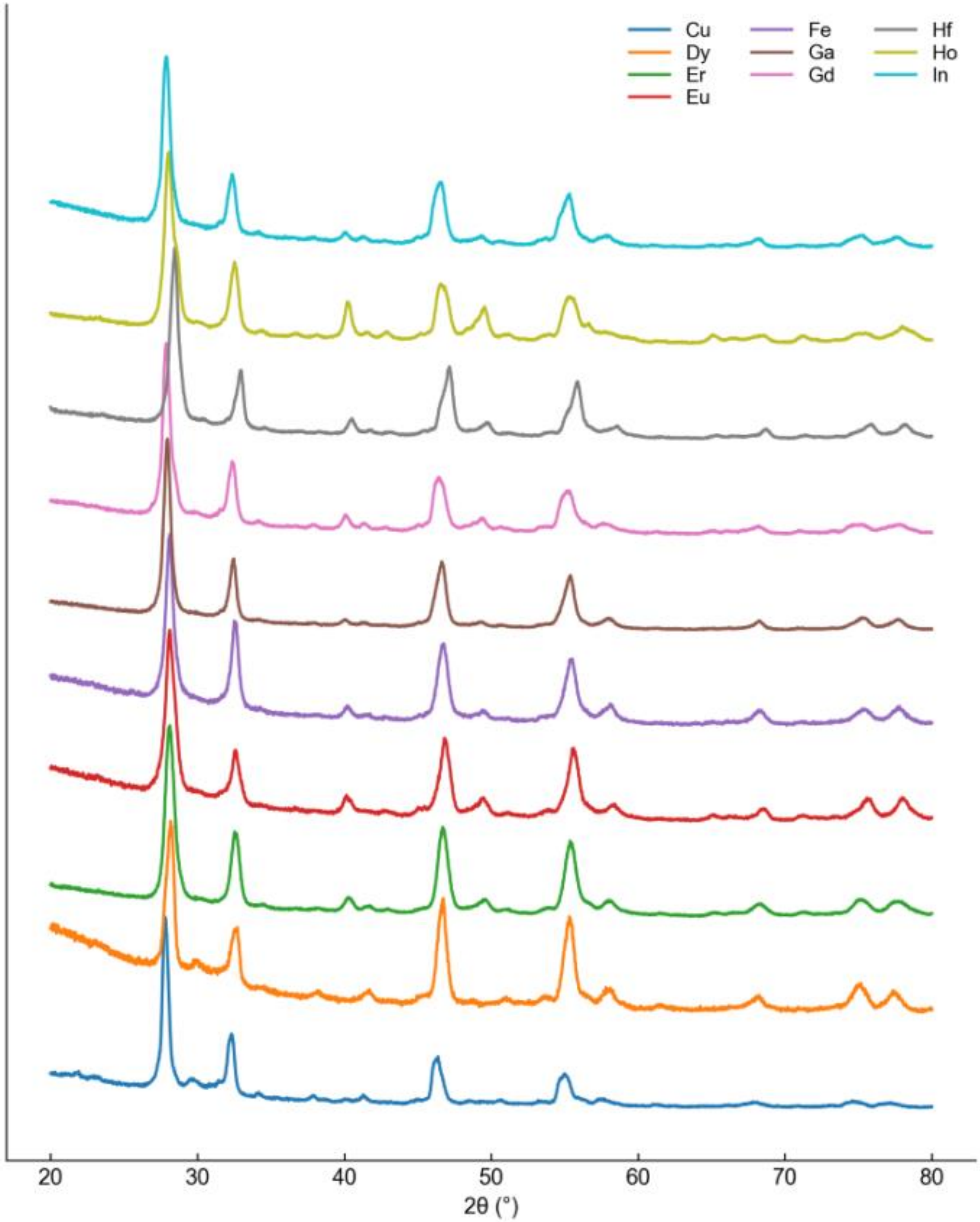
Table S1: Comparison of current state of the art ammonia synthesis catalysts.

Catalyst	Ru wt.%	Temperature (°C)	Pressure (bar)	H_2:N_2	Ammonia Synthesis Rate (mmol/g_{cat}/hr)	Synthesis Rate (mmol/g_{Ru}/hr)
Cs-Ru/MgO[1]	5	423	50	3:2	68.65	1370
KM1R[1]	N/A	450	107	3:1	68.76	N/A
Ru/$La_2Ce_2O_7$[2]	4	425	100	3:1	52.7	1320
Ru/CeO_2[3]	10	400	100	3:1	115	1150
Ru/Pr_2O_3[4]	5	400	30	3:1	64	1280
Ba-Ru/AC[5]	10	400	100	3:1	312.5	3125
Ba-Ru/CNT[6]	3.4	450	100	3:1	110	3235
K-Ru/$La_2Ce_2O_7$[7]	5	400	10	3:1	34	680
[a]Ba-Cs-Ru/PrO_x	[b]1	400	30	1:1	65.42	6540[d]
[a]Ba-Cs-Ru/PrO_x	[c]3	400	30	1:1	126.7	4220[d]

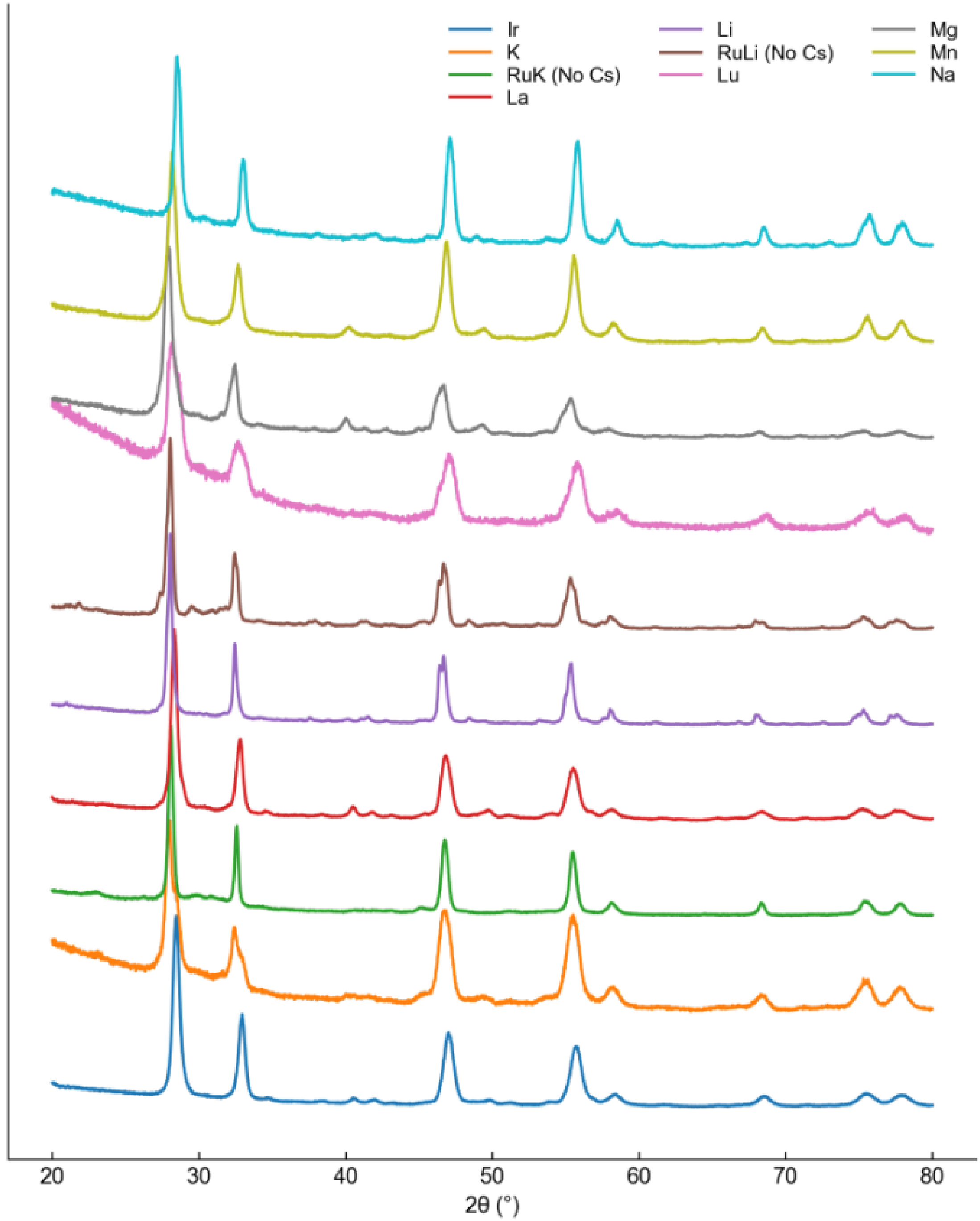
[a]This Work
[b]Actual Ru content closer to 0.6 wt.%
[c]Actual Ru content closer to 1.8 wt.%
[d]Assuming that the nomial amount of Ru is the actual amount



Ag
Al
Ba
Bi
Ca
Cd
Ce
Co
Cr
RuCs (No Second Promoter)
20
30
40
50
60
70
80
2θ (°)



Cu
Dy
Er
Eu
Fe
Ga
Gd
Hf
Ho
In
20
30
40
50
60
70
80
2θ (°)


Ir
K
RuK (No Cs)
La
Li
RuLi (No Cs)
Lu
Mg
Mn
Na
20
30
40
50
60
70
80
2θ (°)

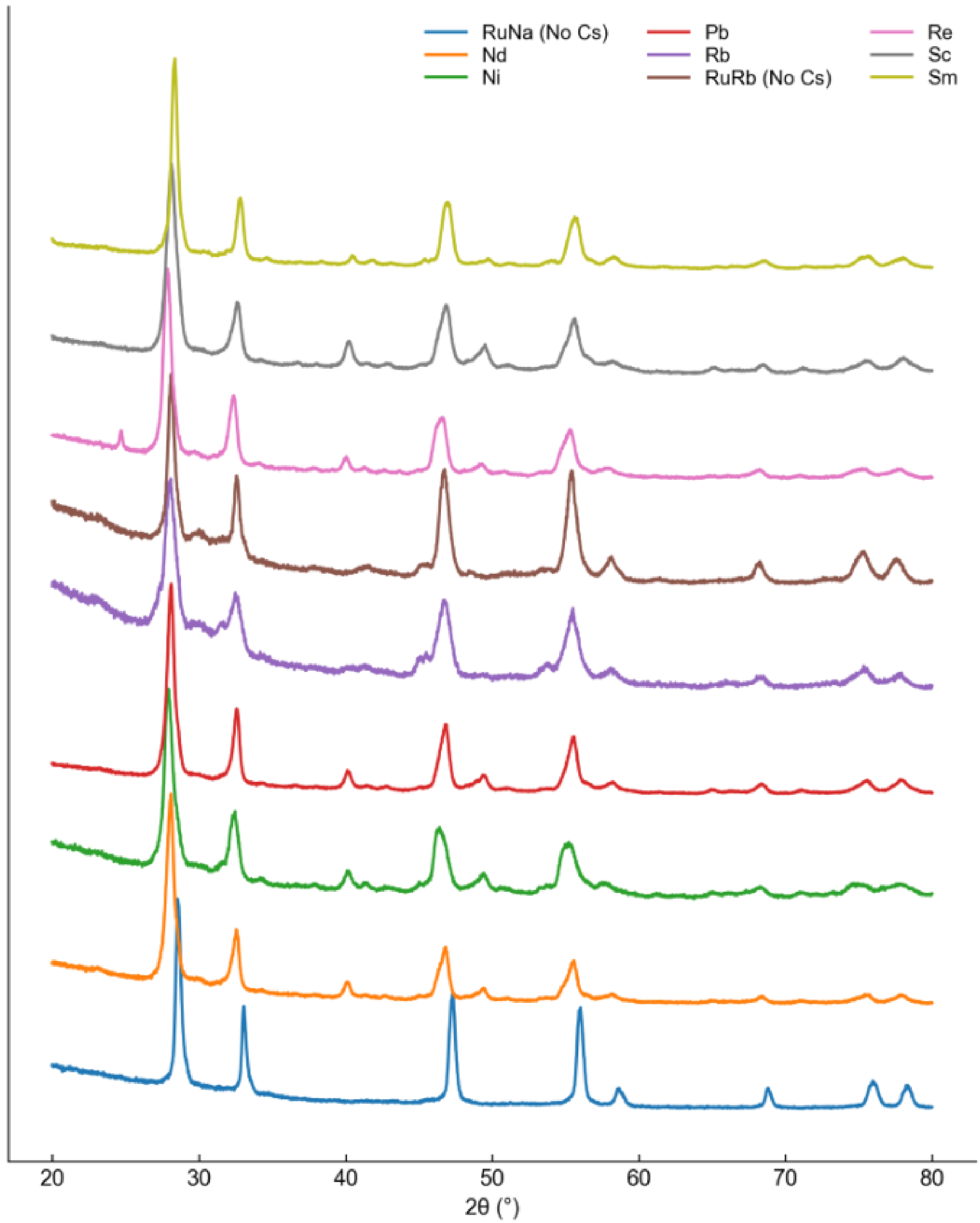


Figure S3: XRD patterns for each of the catalysts (1 wt.% Ru, 2 wt.% Cs, 2 wt.% M/PrO_x) used in this study.

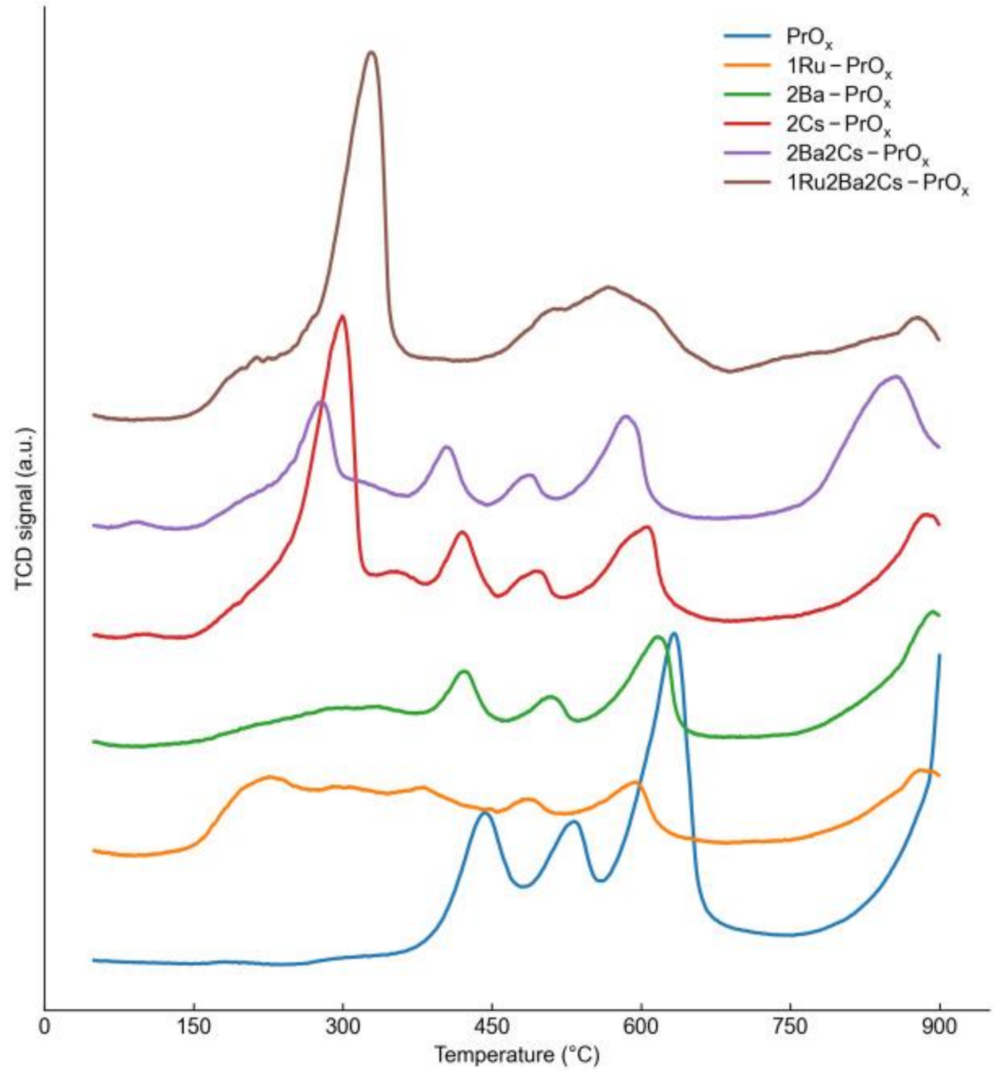


Figure S4: TPR profiles of various variations of the 1 wt.% Ru, 2 wt.% Cs, 2 wt.% Ba/PrO_x. Samples were ramped at 20°C/min under pure hydrogen.

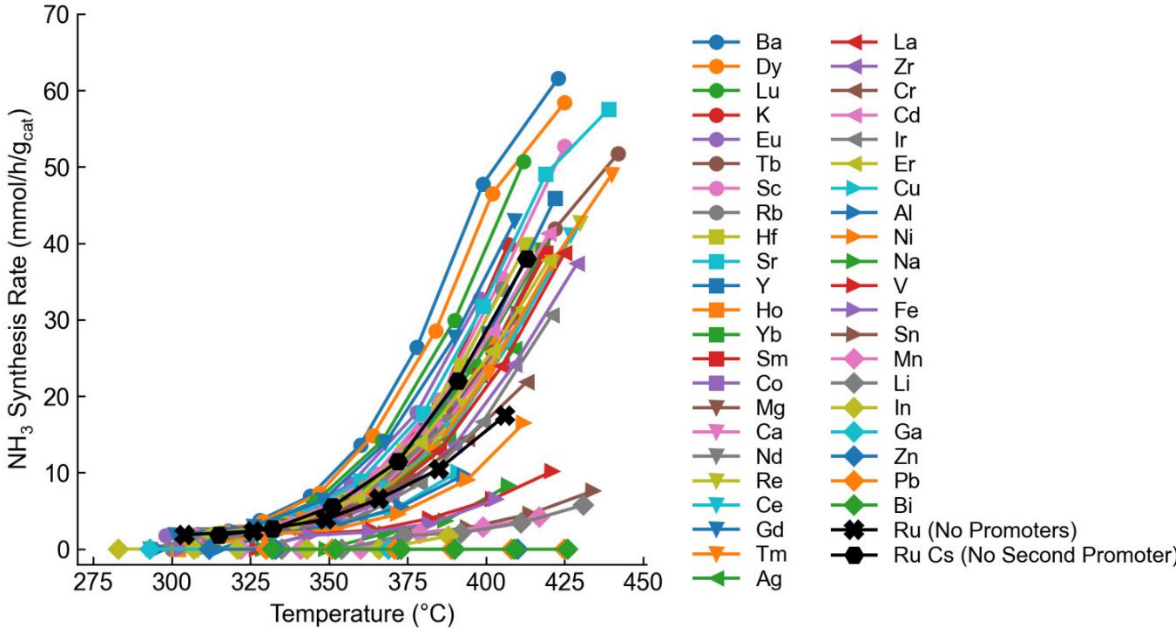


Figure S5: Comparison of doubly-promoted 1 wt.% Ru, 2 wt.% Cs, 2 wt.% M/PrO_x catalysts at various temperatures. Catalysts were tested at a space velocity of 36,000 mL/g_{cat}/hr, 1:1 H_2:N_2 and 30 bar.

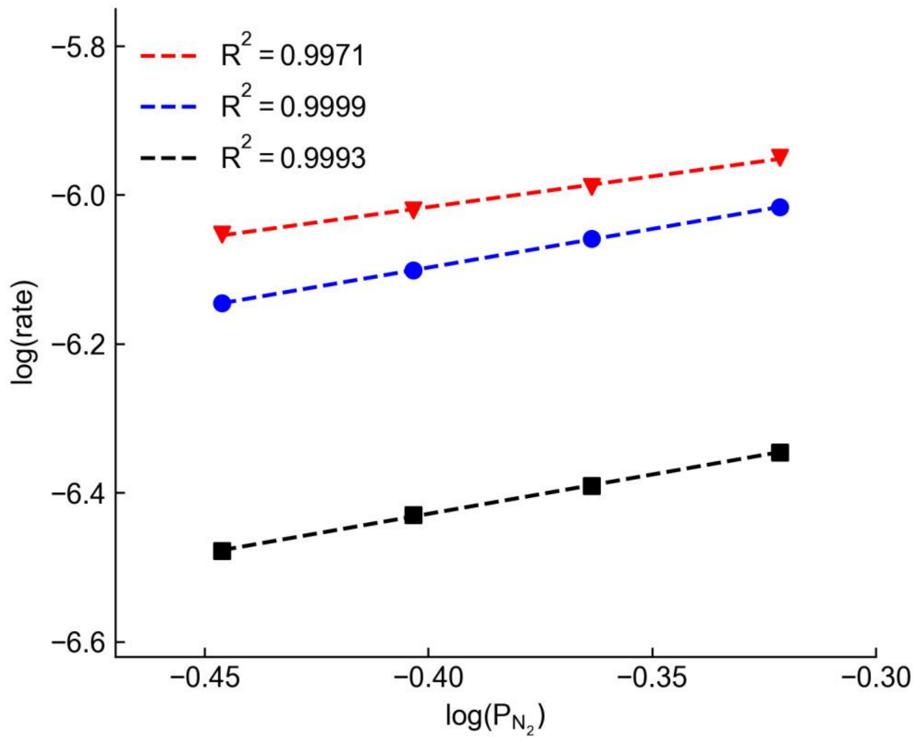


Figure S6: Activity vs partial pressure of nitrogen tested at 400°C, 30 bar, 72000 mL/g_{cat}/hr. The catalysts tested were 1 wt.% Ru/PrO_x (black), 1 wt.% Ru, 2 wt.% Cs/PrO_x (blue), 1 wt.% Ru, 3.86 wt.% Ba, 4.12 wt.% Cs/PrO_x (red).

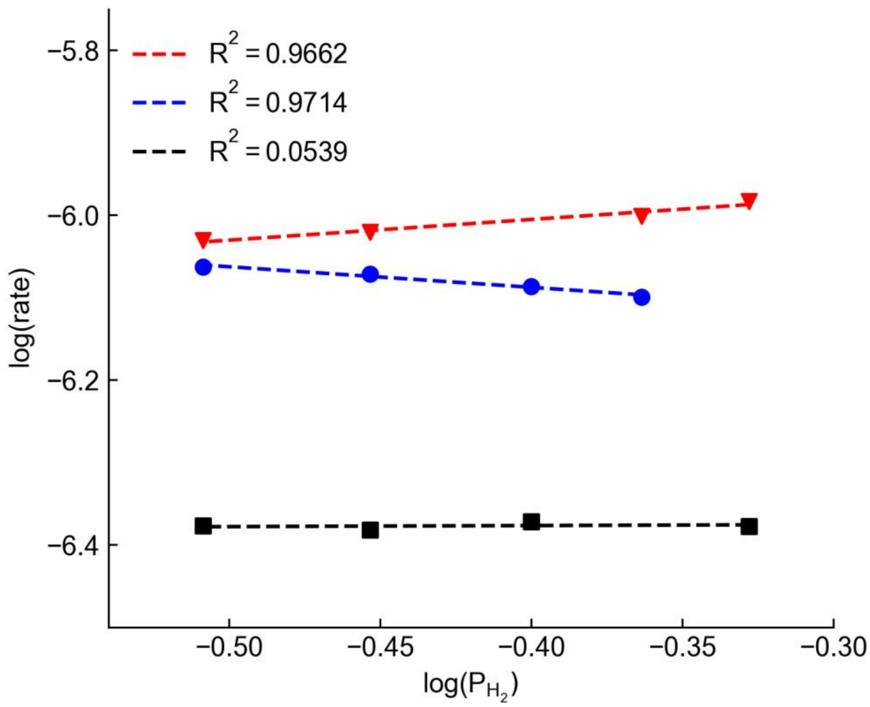


Figure S7: Activity vs partial pressure of hydrogen tested at 400°C, 30 bar, 72000 mL/g_{cat}/hr. The catalysts tested were 1 wt.% Ru/PrO_x (black), 1 wt.% Ru, 2 wt.% Cs/PrO_x (blue), 1 wt.% Ru, 3.86 wt.% Ba, 4.12 wt.% Cs/PrO_x (red).

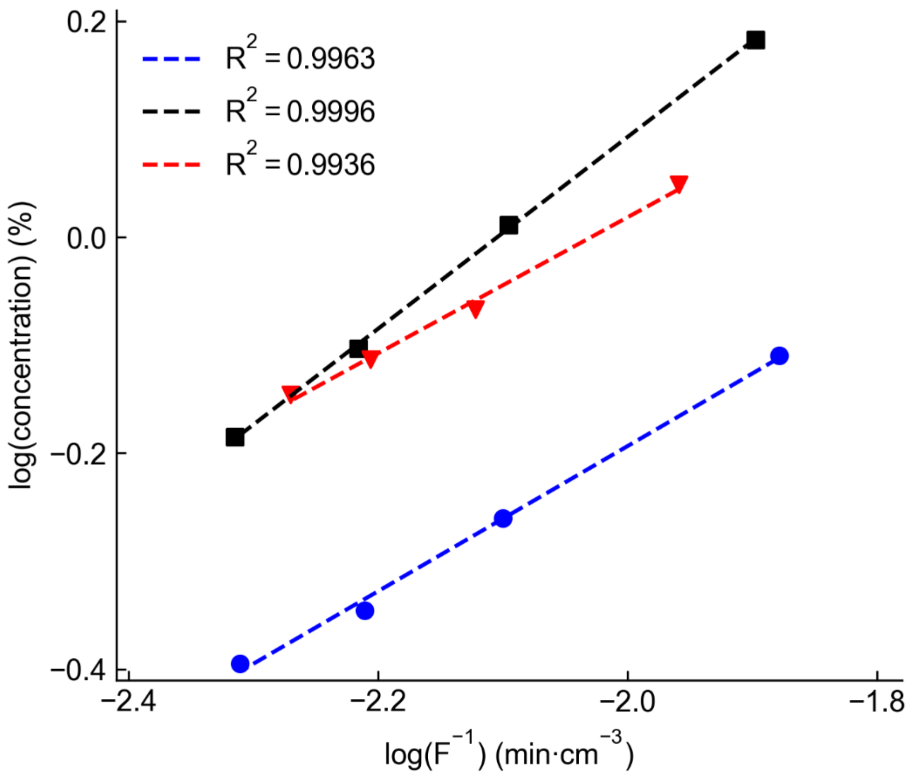


Figure S8: Outlet concentration of ammonia vs total flow rate of reactants (min cm^{-3}) tested at 400°C, 30 bar, 45000-125000 mL/g_{cat}/hr. The catalysts tested were 1 wt.% Ru/PrO_x (black), 1 wt.% Ru, 2 wt.% Cs/PrO_x (blue), 1 wt.% Ru, 3.86 wt.% Ba, 4.12 wt.% Cs/PrO_x (red).

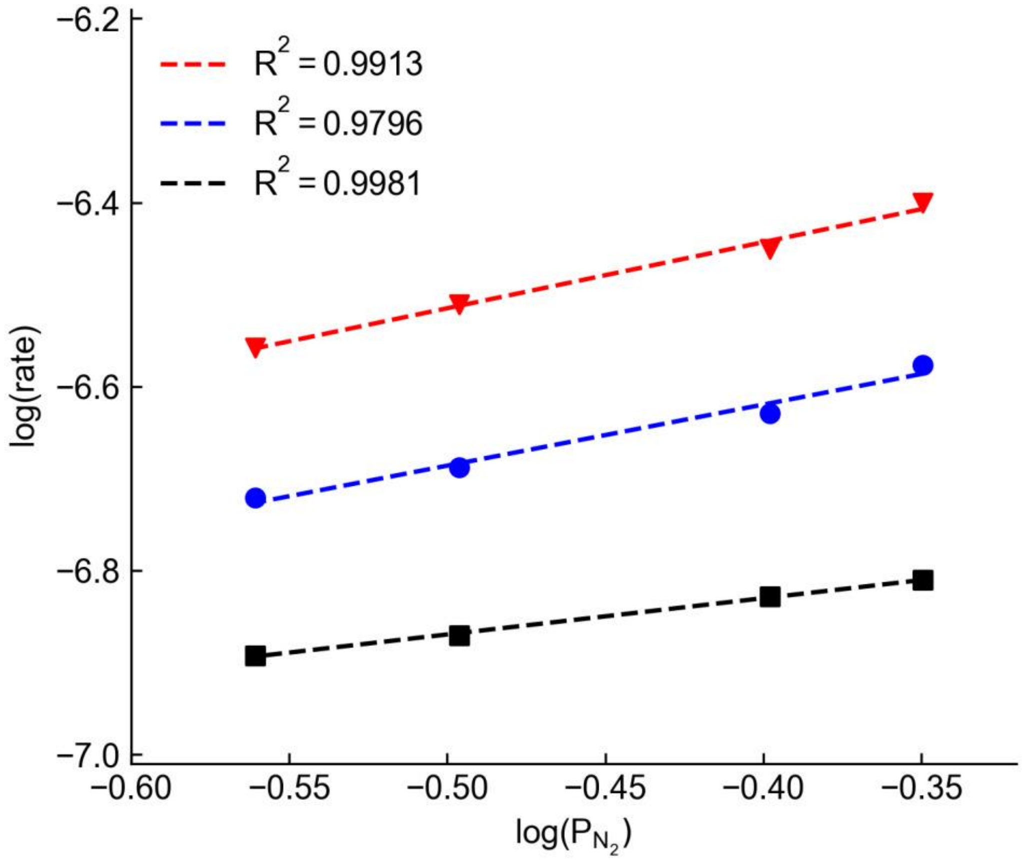


Figure S9: Activity vs partial pressure of nitrogen tested at 360°C, 30 bar, 72000 mL/g_{cat}/hr. The catalysts tested were 1 wt.% Ru/PrO_x (black), 1 wt.% Ru, 2 wt.% Cs/PrO_x (blue), 1 wt.% Ru, 3.86 wt.% Ba, 4.12 wt.% Cs/PrO_x (red).

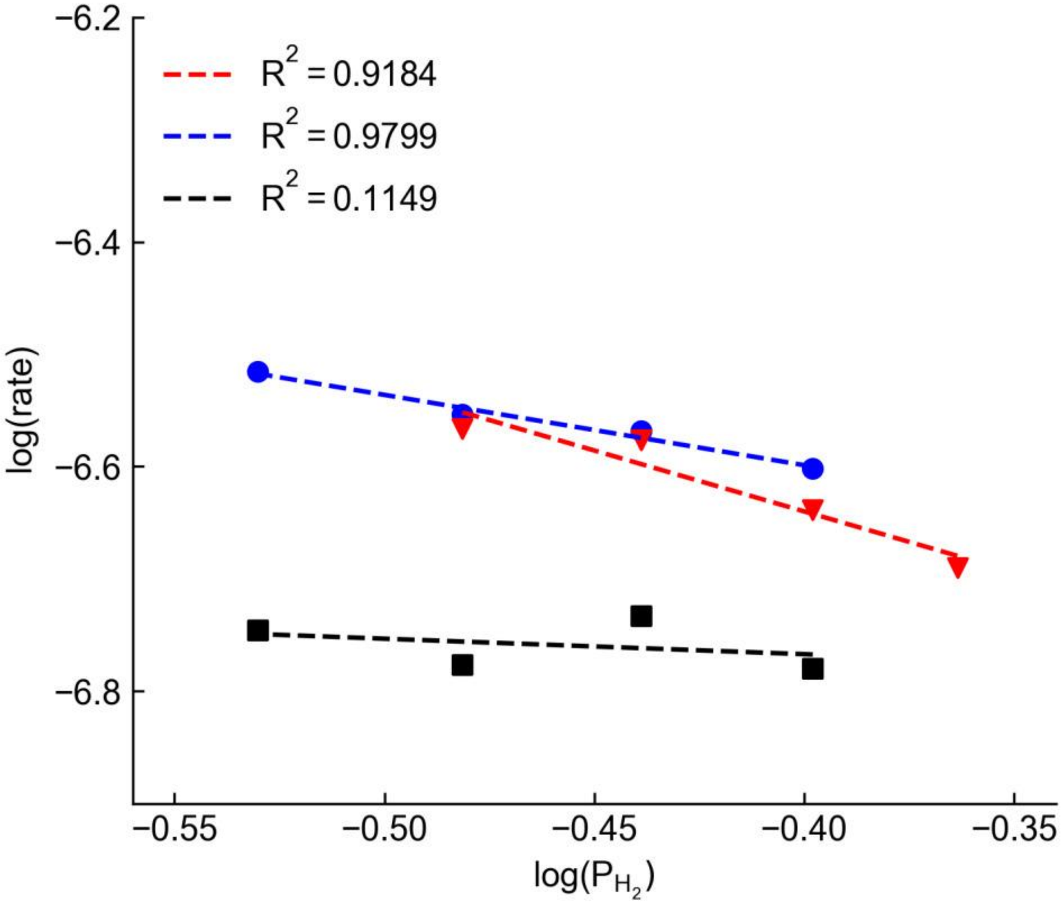


Figure S10: Activity vs partial pressure of hydrogen tested at 360°C, 30 bar, 72000 mL/g_{cat}/hr. The catalysts tested were 1 wt.% Ru/PrO_x (black), 1 wt.% Ru, 2 wt.% Cs/PrO_x (blue), 1 wt.% Ru, 3.86 wt.% Ba, 4.12 wt.% Cs/PrO_x (red).

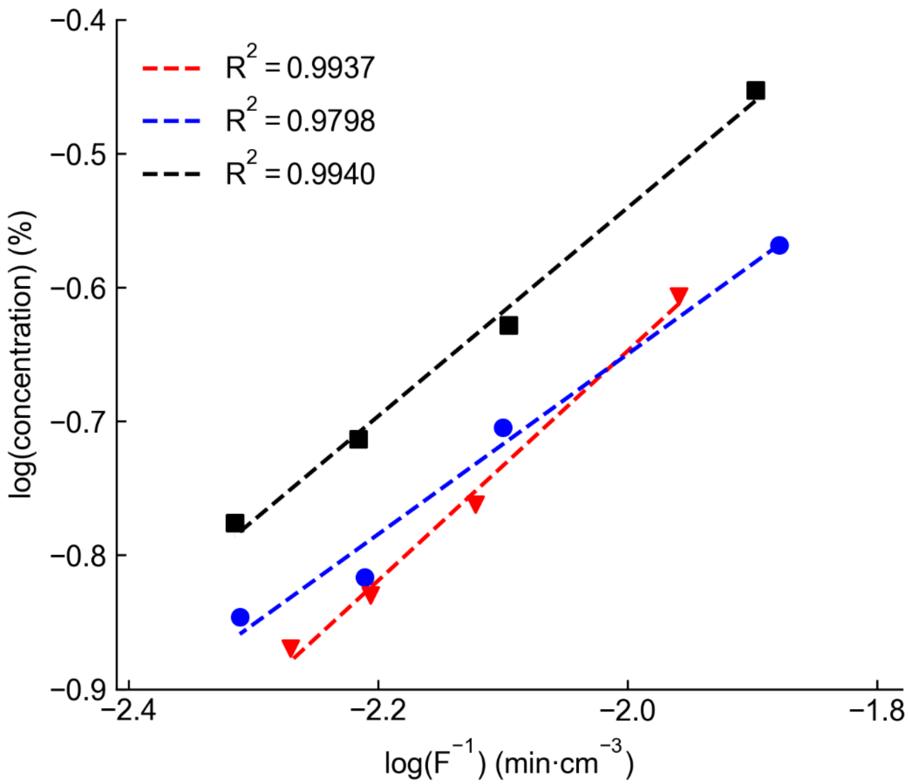


Figure S11: Outlet concentration of ammonia vs total flow rate of reactants (min cm^{-3}) at 360°C, 30 bar, 45000-125000 mL/g_{cat}/hr. The catalysts tested were 1 wt.% Ru/PrO_x (black), 1 wt.% Ru, 2 wt.% Cs/PrO_x (blue), 1 wt.% Ru, 3.86 wt.% Ba, 4.12 wt.% Cs/PrO_x (red).

Table S2: Supplier and precursor type for each of the promoters used in this research.

Element	Precursor Type	Chemical Supplier
Ag	Nitrate	Sigma Aldrich
Al	Nitrate	Alfa Aesar
Ba	Nitrate	Alfa Aesar
Bi	Nitrate	Fisher Scientific
Ca	Nitrate	Alfa Aesar
Cd	Nitrate	Fisher Scientific
Ce	Nitrate	Sigma Aldrich
Co	Nitrate	Acros Organics
Cr	Nitrate	Sigma Aldrich
Cs	Acetate	Fisher Scientific
Cu	Nitrate	Acros Organics
Dy	Nitrate	Fisher Scientific
Er	Nitrate	Fisher Scientific
Eu	Nitrate	Alfa Aesar
Fe	Nitrate	Sigma Aldrich
Ga	Nitrate	Alfa Aesar
Gd	Nitrate	Alfa Aesar
Hf	Acetylacetonate	Fisher Scientific
Ho	Nitrate	Alfa Aesar
In	Nitrate	Alfa Aesar
Ir	Acetate	Fisher Scientific
K	Acetate	Alfa Aesar
La	Nitrate	Alfa Aesar
Li	Acetate	Acros Organics
Lu	Nitrate	Alfa Aesar
Mg	Nitrate	Sigma Aldrich
Mn	Nitrate	Sigma Aldrich
Na	Acetate	Fisher Scientific
Nd	Nitrate	Sigma Aldrich
Ni	Nitrate	Alfa Aesar
Pb	Nitrate	Fisher Scientific
Rb	Acetate	Strem Chemical
Re	Ammonium Perrhenate	Sigma Aldrich
Sc	Acetate	Alfa Aesar
Sm	Nitrate	Alfa Aesar
Sn	Acetate	Sigma Aldrich
Sr	Nitrate	Fisher Scientific
Tb	Nitrate	Fisher Scientific
Tm	Nitrate	Sigma Aldrich
V	Acetylacetonate	Fisher Scientific
Y	Nitrate	Alfa Aesar
Yb	Nitrate	Alfa Aesar
Zn	Nitrate	Alfa Aesar
Zr	Dinitrate Oxide	Fisher Scientific

References

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