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Supplementary Information

Experimental Discovery of Novel Ammonia Synthesis Catalysts *via* Active Learning

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Table S1. Initial features used for data mining.

Feature Category	Feature	Unit
Active metal/Promoter	Ru metal loading	wt%
	Ru precursor	-
	Promoter 1	-
	Promoter 1 precursor	-
	Promoter 1 loading	wt%
	Promoter 2	-
	Promoter 2 precursor	-
	Promoter 2 loading	wt%
Support	Support	-
	BET surface area	$m^2\ g^{-1}$
Support pretreatment	H_2 in the support pretreatment (step 1)	vol%
	O_2 in the support pretreatment (step 1)	vol%
	Support pretreatment temperature (step 1)	K
	Support pretreatment time (step 1)	h
	H_2 in the support pretreatment (step 2)	vol%
	O_2 in the support pretreatment (step 2)	vol%
	H_2O in the support pretreatment (step 2)	vol%
	CO_2 in the support pretreatment (step 2)	vol%
	Support pretreatment	K

	temperature (step 2)	
	Support pretreatment time (step 2)	h
	H_2 in the support pretreatment (step 3)	vol%
	Support pretreatment temperature (step 3)	K
	Support pretreatment time (step 3)	h
Catalyst pretreatment	H_2 in catalyst pretreatment medium mean	vol%
	H_2 in catalyst pretreatment medium standard deviation	vol%
	Catalyst pretreatment temperature mean	K
	Catalyst pretreatment temperature standard deviation	K
	Catalyst pretreatment time mean	h
	Catalyst pretreatment time standard deviation	h
Reaction conditions	H_2/N_2 ratio	-
	Initial ammonia concentration	vol%
	Space velocity	ml h^{-1} g_{cat}^{-1}
	Reaction pressure	MPa
	Reaction temperature	K

Table S2. Distribution of datapoints based on promoter and support combined.

Catalyst group name	Number of data points
Ru/CeO_2	89
Ru/MgO	87
Ru,Cs/MgO	75
Ru/Pr_2O_3	63
Ru,Cs/α-Al_2O_3	58
Ru,K/Graphite	49
Ru,K/C-pyrolytic	40
Ru,Ba/C-pyrolytic	34
Ru,Ba/MgO	28
$Ru/BaCeO_3$	26
Ru,Li/Graphite	24
Ru,Na/Graphite	18
Ru/α-Al_2O_3	17
Ru,Ba/Graphite	16
Ru,Rh,K/C-pyrolytic	16
Ru,Cs/Graphite	16

Catalyst group name	Number of data points
Ru,Co,K/C-pyrolytic	16
Ru,Ir,K/C-pyrolytic	16
Ru,Cs/$Sr_2Nb_2O_7$	15
Ru,K/MgO	15
Ru,Cs/$BaCeO_3$	14
Ru,Ba,Cs/Graphite	14
Ru,Ba/$Sr_2Nb_2O_7$	12
Ru,Ba/γ-Al_2O_3	12
Ru/$MgFe_2O_4$	11
Ru/Sm_2O_3	10
Ru,Ba/$MgAl_2O_4$	10
Ru,Rb/MgO	8
Ru,Ce/C-pyrolytic	6
Ru,B,Cs/MgO	5
Ru/$Sr_2Nb_2O_7$	5
Ru/La_2O_3	5
Ru/$MgAl_2O_4$	5
Ru,Cs/C-pyrolytic	5
Ru,Gd/MgO	5
Ru,Ba/α-Al_2O_3	5
Ru,La/MgO	5
Ru,Ce/MgO	5
Ru,Pr/MgO	5
Ru,Nd/MgO	5
Ru,Dy/MgO	5
Ru,Ba/θ-Al_2O_3	5
Ru,K/$BaCeO_3$	4
Ru/Nd_2O_3	4
Ru/γ-Al_2O_3	4
Ru,Ba/$BaCeO_3$	4
Ru,Sm/MgO	4
Ru/Gd_2O_3	4
Ru/Tb_2O_3	4
Ru/Ho_2O_3	4
Ru,Na/MgO	4
Ru/Yb_2O_3	4
Ru/Er_2O_3	4
Ru/$BaZrO_3$	3
Ru,Sr/MgO	3
Ru,Ca/MgO	3
Ru/$BaTiO_3$	3

Table S3. Elemental properties used to generate elemental features.

Properties from Magpie dataset [1] in Python package matminer (version 0.8.0) [2]	
Atomic Radius	Number of f-shell Valence Electrons
Atomic Volume	Number of p-shell Valence Electrons
Atomic Weight	Number of s-shell Valence Electrons
Boiling Temperature	Number of Valence Electrons
Column Number	Polarizability
Covalent Radius	Row Number
Density	Space group Number
Electron Affinity	Thermal Conductivity
Electronegativity	Cohesive Energy
Ground State Energy	1^{st} Ionization Energy
Heat Capacity (Molar)	2^{nd} Ionization Energy
Heat of Fusion	3^{rd} Ionization Energy
Heat of Vaporization	4^{th} Ionization Energy
Melting Temperature	5^{th} Ionization Energy
Mendeleev Number	6^{th} Ionization Energy
Molar Volume	7^{th} Ionization Energy
Number of d-shell Valence Electrons	8^{th} Ionization Energy

Properties from Python package matminer (version 0.8.0) [2]
Band Center (band center estimated based on atomic orbitals)
Valence Orbital Energy

Properties from other sources
Work Function [3]
Log Electrical Conductivity [4]
Bulk Modulus [5–9]
Shear Modulus [5–9]

Table S4. Extra features considered for the support.

Features from Python package matminer (version 0.8.0) [2]
HOMO energy (HOMO energy estimated based on atomic orbitals)
LUMO energy (LUMO energy estimated based on atomic orbitals)
gap AO (band gap estimated based on atomic orbitals)

Properties from materials project [10]
Formation enthalpy
Band gap (DFT calculated)
Density

Table S5. Material ID numbers for material project database [10].

Support	ID number	Selection
MgO	mp-1265	Based on cubic structure
CeO_2	mp-20194	Based on cubic structure

Support	ID number	Selection
$BaCeO_3$	mp-3187	Based on reported structure [11]
Pr_2O_3	mp-16705	Based on reported structure [12], [13]
$Sr_2Nb_2O_7$	mp-3870	Based on reported structure [14]
$MgAl_2O_4$	mp-3536	Based on cubic structure
La_2O_3	mp-2292	Based on reported structure [13]
Sm_2O_3	mp-218	Based on reported structure [13]
Ho_2O_3	mp-812	Based on reported structure [13]
Er_2O_3	mp-679	Based on reported structure [13]
Tb_2O_3	mp-1056	Based on reported structure [13]
Gd_2O_3	mp-504886	Based on reported structure [13]
Nd_2O_3	mp-1045	Based on reported structure [13]
Yb_2O_3	mp-2814	Based on reported structure [13]
$BaZrO_3$	mp-3834	Based on reported structure [15]
C(pyrolytic)	mp-47	Based on formation enthalpy and band gap of pyrolytic carbon
Graphite	mp-48	Based on hexagonal structure, formation enthalpy and band gap (0 eV) of graphite
γ-Al_2O_3	mp-776475	Approximation based on crystal structure
θ-Al_2O_3	mp-7048	Based on space group of θ-Al_2O_3
α-Al_2O_3	mp-1143	Based on space group of α-Al_2O_3
$MgFe_2O_4$	mp-608016	Based on reported structure [16]
$BaTiO_3$	mp-19990	Based on reported structure [17]

Table S6. Optimal hyperparameters for ETR, RFR, and XGB models

Algorithm	Hyperparameters	Range	Optimal Values
ETR	criterion	-	squared error
	n_estimators	25-1000	750
	max_depth	None-200	25
	min_samples_leaf	2-5	2
	min_samples_split	2-5	2
RFR	criterion	-	squared error
	n_estimators	25-500	125
	max_depth	None-200	25
	min_samples_leaf	2-5	2
	min_samples_split	2-5	5
XGB	objective	-	reg:squarederror
	learning_rate	0.01-0.60	0.50
	max_depth	5-200	10
	tweedie_variance_power	1.2-1.8	1.7

Table S7. Features selected using Boruta method.

Kinetics and Thermodynamics
Initial H_2 partial pressure, Initial N_2 partial pressure, Initial NH_3 partial pressure, Equilibrium constant, Thermodynamic limit, Temperature, Space velocity, H_2/N_2 ratio, Total pressure

Catalyst Pretreatment
Catalyst pretreatment temperature mean, Catalyst pretreatment temperature s.t.d., Catalyst pretreatment time mean, Catalyst pretreatment time s.t.d., H_2% in Catalyst pretreatment medium mean

Catalyst Preparation
Precursor carbon mol, Precursor CO ligands mol, Precursor chlorine mol, Precursor anionic O mol, Precursor NO_x mol, CO_2 % in support pretreatment (step 2), Support pretreatment temperature (step 1), Support pretreatment temperature (step 2), Support pretreatment time (step 1), Support pretreatment time (step 2), BET support surface area

Metal-promoter interactions: elemental features
Alkali metal to Ru molar ratio, Alkaline earth metal to Ru molar ratio, Metal atomic radius m.a.d., Metal atomic volume m.a.d., Metal band center m.a.d., Metal boiling temperature m.a.d., Metal melting temperature m.a.d., Metal melting temperature mean, Metal covalent radius m.a.d., Metal covalent radius mean, Metal density m.a.d., Metal electron affinity mean, Metal ground state energy m.a.d., Metal ground state energy mean, Metal 1st ionization energy m.a.d., Metal 1st ionization energy mean, Metal 2nd ionization energy mean, Metal 3rd ionization energy mean, Metal 6th ionization energy mean, Metal 7th ionization energy mean, Metal log electrical conductivity m.a.d., Metal log electrical conductivity mean, Metal molar volume m.a.d., Metal molar volume mean, Metal polarizability m.a.d., Metal space group number mean, Metal thermal conductivity m.a.d., Metal thermal conductivity mean, Metal cohesive energy m.a.d.

Support: elemental properties
Support band center, Support HOMO energy, Support valence orbital energy, Support atomic radius mean, Support atomic radius m.a.d., Support band center mean, Support band center m.a.d., Support bulk modulus mean, Support column mean, Support covalent radius m.a.d., Support covalent radius mean, Support electronegativity m.a.d., Support electronegativity mean, Support 1st ionization energy mean, Support 1st ionization energy m.a.d., Support 2nd ionization energy mean, Support 6th ionization energy m.a.d., Support Mendeleev number m.a.d., Support Mendeleev number mean, Support num. of valence electrons m.a.d., Support num. of p electrons mean, Support polarizability m.a.d., Support polarizability mean, Support valence orbital energy mean, Support metal atomic radius mean, Support metal bulk modulus mean, Support metal electronegativity mean, Support metal 1st ionization energy mean, Support metal 2nd ionization energy mean, Support metal 7th ionization energy mean, Support metal 8th ionization energy mean, Support metal Mendeleev number mean, Support metal space group number mean

Support electronic properties: density of states
Support cbm hybridization, Support cbm location 1_2, Support cbm sp, Support vbm hybridization, Support vbm location 1_2, Support cbm location 1_3, Support vbm score 1

Metal-support interaction (MSI) compounds: elemental properties
Ru to support molar ratio, MSI atomic number m.a.d., MSI atomic weight m.a.d., MSI band center m.a.d., MSI 1^{st} ionization energy m.a.d., MSI 2^{nd} ionization energy m.a.d., MSI 8^{th} ionization energy m.a.d., MSI Mendeleev number mean, MSI Mendeleev number m.a.d., MSI polarizability m.a.d.

Promoter-support interaction: elemental features
Alkali metal to support molar ratio, Promoter-support atomic number m.a.d., Promoter-support atomic radius m.a.d., Promoter-support atomic radius mean, Promoter-support atomic volume m.a.d., Promoter-support atomic weight m.a.d., Promoter-support band center m.a.d., Promoter-support bulk modulus m.a.d., Promoter-support bulk modulus mean, Promoter-support boiling temperature m.a.d., Promoter-support column number m.a.d., , Promoter-support covalent radius m.a.d., Promoter-support covalent radius mean, Promoter-support density m.a.d., Promoter-support density mean, Promoter-support electron affinity m.a.d., Promoter-support electronegativity m.a.d., Promoter-support electronegativity mean, Promoter-support ground state energy m.a.d., Promoter-support molar heat capacity m.a.d., Promoter-support heat of fusion m.a.d., Promoter-support heat of vaporization m.a.d., Promoter-support 1^{st} ionization energy m.a.d., Promoter-support 2^{nd} ionization energy m.a.d., Promoter-support 2^{nd} ionization energy mean, Promoter-support 3^{rd} ionization energy m.a.d., Promoter-support 5^{th} ionization energy m.a.d., Promoter-support 6^{th} ionization energy m.a.d., Promoter-support 6^{th} ionization energy mean, Promoter-support 7^{th} ionization energy m.a.d., Promoter-support 7^{th} ionization energy mean, Promoter-support 8^{th} ionization energy m.a.d., Promoter-support 8^{th} ionization energy mean, Promoter-support log electrical conductivity m.a.d., Promoter-support melting temperature m.a.d., Promoter-support Mendeleev number m.a.d., Promoter-support Mendeleev number mean, Promoter-support molar volume m.a.d., Promoter-support num. of valence electrons m.a.d., Promoter-support num. of valence electrons mean, Promoter-support num. of d valence electrons m.a.d., Promoter-support num. of d valence electrons mean, Promoter-support num. of f valence electrons m.a.d., Promoter-support num. of s valence electrons m.a.d., Promoter-support num. of s valence electrons mean, Promoter-support polarizability m.a.d., Promoter-support polarizability mean, Promoter-support row number m.a.d., Promoter-support shear modulus m.a.d., Promoter-support shear modulus mean, Promoter-support thermal conductivity m.a.d., Promoter-support work function m.a.d., Promoter-support cohesive energy m.a.d.

s.t.d.: standard deviation, HOMO: Highest occupied molecular orbital, m.a.d.: mean absolute deviation

Table S8. Ammonia synthesis activity dataset (Experimentally measured) of the Ru, Promoter (M), Cs/Pr_2O_3 catalysts used for active learning. Reaction Conditions (3 MPa, 673 K, 36000 mL h^{-1} g_{cat}^{-1}, H_2 to N_2 ratio of 1:1)

Promoter (M)	**Precursor**	**Ammonia Synthesis Rate (mmol g^{-1}_{Ru} h^{-1})**
Ga	nitrate	0.001
Sm	nitrate	24.3
Y	nitrate	27.6
Yb	nitrate	26.6
Nd	nitrate	21.1
Ca	nitrate	23.7
Hf	acetylacetonate	30.1
Mg	nitrate	24.5
Ba	nitrate	48.8
K	acetate	33.2
Rb	acetate	30.2
Na	acetate	6.7
Sn	acetate	3.3
Sr	nitrate	32.6
Li	acetate	2.6
Eu	nitrate	34.3
Mn	nitrate	3
Sc	acetate	31.4
In	nitrate	2.6
Al	nitrate	11.1
V	acetylacetonate	6.3
Cr	nitrate	16.8
Lu	nitrate	39.4
Tb	nitrate	24.6
Tm	nitrate	22.5
Fe	nitrate	6
Ir	acetate	17.2
Ag	nitrate	21.1
Ho	nitrate	26.6
Zn	acetate	0.001
La	nitrate	21.1
Ce	nitrate	22.3
Co	nitrate	24.6
Gd	nitrate	35.7
Cd	nitrate	27.4
Ni	nitrate	11.5
Er	nitrate	24.9
Pb	nitrate	0.001
Zr	oxynitrate	19.1
Re	perrhenate	23.2
Bi	nitrate	0.001
Dy	nitrate	44.5

Cu	nitrate	12.3

Table S9. Comparison of the activity of the best catalysts found in this study with some state-of-the-art catalysts in the literature.

Catalyst	**Ru (wt %)**	**T (K)**	**P (MPa)**	**Space velocity ($ml\ g^{-1}_{cat}\ h^{-1}$)**	**H_2/N_2**	**NH_3 synthesis rate ($mmol\ g^{-1}_{Ru}\ h^{-1}$)**	**Reference**
Ru, Ba, Cs/Pr_2O_3	1	673	3	36000	1	4880	This work
Ru, Dy, Cs/Pr_2O_3	1	673	3	36000	1	4450	This work
Ru/Pr_2O_3	5	673	3	72000	1	1820	[12]
Ru/$C_{12}A_7$:e–	0.3	673	1	18000	3	1229	[18]
Ba, Ru/BN	4.5	673	10	-	3	4147	[19]
Ru-Co DSAC	0.92	673	1	60000	3	2598	[20]
Ru/$BaTiO_{2.5}H_{0.5}$	0.9	673	5	59400	3	3133	[21]
Ru/3LaN/ZrH_2	2	673	1	60000	3	625	[22]
Ru, Cs/$BaCeO_3$	1.25	723	3	24000	3	2240	[11]
Ru/$La_{0.5}Ce_{0.5}O_{1.75}$	5	673	1	72000	3	1286	[23]
Ba/Ce/Ru ACC	2	673	1	60000	3	2808	[24]
Ru-Fe/CNT	1.67	673	1	24000	3	361	[25]

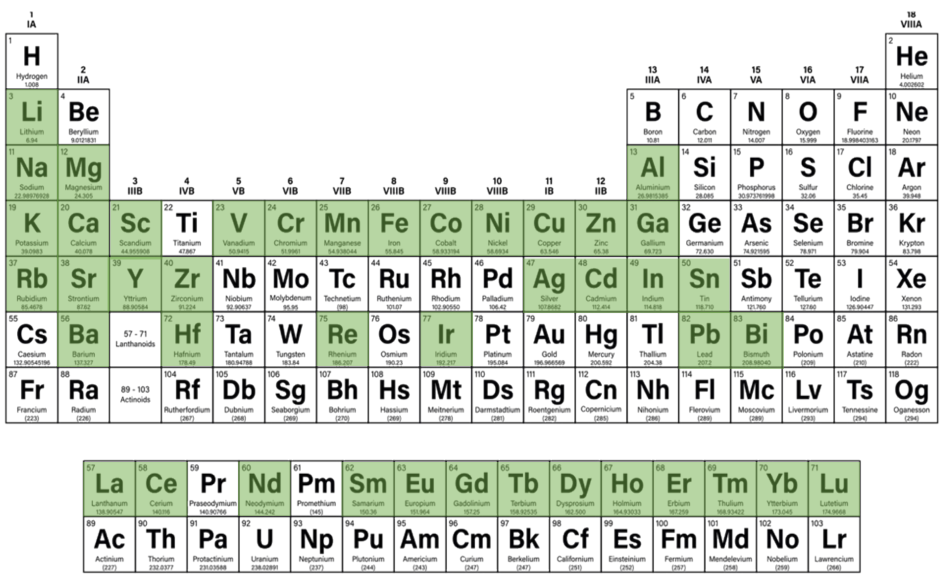

Fig. S1. Selected secondary promoters in the search space.

1. Details of experimental methods

1.1 Catalyst preparation

The praseodymium oxide support was prepared by precipitation of 0.5 M praseodymium nitrate (Sigma Aldrich) dissolved in DI water into ammonium hydroxide solution (Sigma Aldrich). Precipitate was stirred, washed with DI water, dried at room temperature over 4 days, and calcined at 973 K in static air for 5 h.

Promotion of the catalysts was conducted using incipient wetness impregnation of precursors dissolved in DI water. Cobalt nitrate, copper nitrate and lithium acetate were sourced from Acros Organics (Geel, Belgium); nitrates of aluminum, barium, calcium, europium, gallium, gadolinium, holmium, indium, lanthanum, lutetium, nickel, samarium, yttrium, ytterbium and zinc, potassium acetate and scandium acetate were sourced from Alfa Aesar (Ward Hill, MA); nitrates of bismuth, cadmium, dysprosium, erbium, lead, strontium and terbium, acetates of cesium, iridium and sodium, hafnium acetylacetonate, vanadium acetylacetonate and zirconium dinitrate oxide were sources from Fisher Scientific (Waltham. MA); nitrates of silver, cerium, chromium, iron, magnesium, manganese neodymium and thulium, ammonium perrhenate, and tin acetate were sourced from Sigma Aldrich (St Louis, MO); and rubidium acetate was sourced from Strem Chemicals (Newburyport, MA). Catalysts were produced in 2 g samples, before being dried at 393 K and calcined for 1 h at 923 K to remove all ligands.

Ruthenium was added using a triruthenium dodecacarbonyl (Sigma Aldrich) precursor. The ruthenium was dissolved in tetrahydrofuran (Fisher Scientific) and stirred vigorously before the promoted support was added. Once the tetrahydrofuran was evaporated, the samples were transferred to a Lindberg Blue furnace, which was heated under argon (Airgas) to 623 K and held for 3 h to decompose the ruthenium precursor.

1.2 Catalyst testing

About 0.2 g of each catalyst were tested in a four-channel parallel reactor, with K-type thermocouples measuring the temperature in each reactor. Each catalyst was tested following a one-hour reduction at 773 K before being cooled under the reaction mixture of hydrogen (Airgas) and nitrogen (Airgas). Hydrogen (60 mL/min) and nitrogen (60 mL/min) were flowed at a 1:1 ratio. Each reactor was independently pressurized to 30 bar and heated between 573 K and 703 K. Effluent was analyzed with Shimadzu GC-2014 fitted with a Restek RTX-VolatileAmine column.

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