LA-UR-12-25227
Approved for public release; distribution is unlimited.

Title: Combined experimental and theoretical study of the nitrogen reduction on novel Mo-N catalyst material

Author(s): Gonzales, Ivana
Armstrong, Karen
Daemen, Luc L.
Eckert, Juergen
Garzon, Fernando H.
Mueller, Alexander H.
Henson, Neil J.

Intended for: 222nd Electrochemical Society Meeting, 2012-10-07/2012-10-12 (Honolulu, Hawaii, United States)

Combined Experimental and Theoretical Study of Nitrogen Reduction on Novel Mo-N Catalyst Material

Ivana Matanovic, K. Armstrong, L. Daemon, J. Eckert, F. Garzon,
A. Muller and N. Henson
Physics and Chemistry of Materials
Los Alamos National Laboratory
Los Alamos, USA

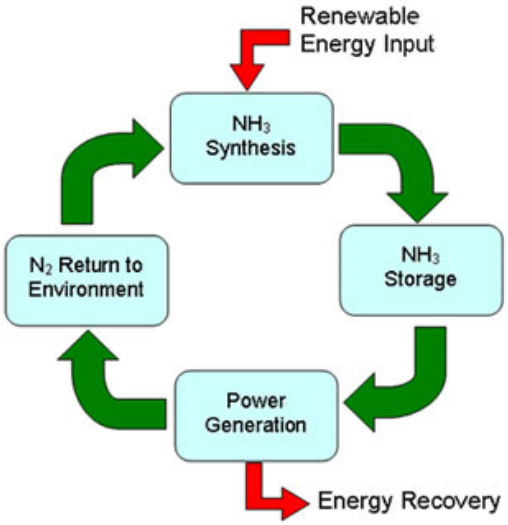
abstract

The conversion and efficient storage of electrical energy ranks among the most critical problems for modern technology and energy use in general. A potential new means for energy storage may rest with the chemical bonds of an abundant element, such as the N-H bonds of liquid ammonia. This approach, however, requires the development of molecular catalysts, which will reduce the energy requirements needed for artificial nitrogen fixation. Our newly synthesized, high surface Mo-N material may be such a candidate catalyst for the electroreduction of nitrogen into ammonia. We have therefore undertaken a combined computational and *in-situ* inelastic neutron scattering (INS) study to investigate its catalytic properties.

The vibrational spectra of the reactants, intermediates and products upon quenching the reaction between hydrogen and nitrogen at several different temperatures were obtained by INS, and interpreted on the basis of frequency calculations from the electronic structure models of the various species. Different types of active sites of this new material were modeled in our calculations, and used to study the binding of various species considered to be intermediates in the synthesis of ammonia, namely H, N and NH_x, NNH_x, x=1-3. We were able to demonstrate in this manner that different surfaces structures of the Mo-N material give rise to a large variation of chemical reactivity for H_2 and N_2 and that defects are critical in enhancing this activity. The vibrational frequencies for the various surface bonded intermediate species provide significant insights into the details of this reaction, as comparison with the INS spectra shows, for example, the prevalence of NNH_x intermediate species.

Introduction

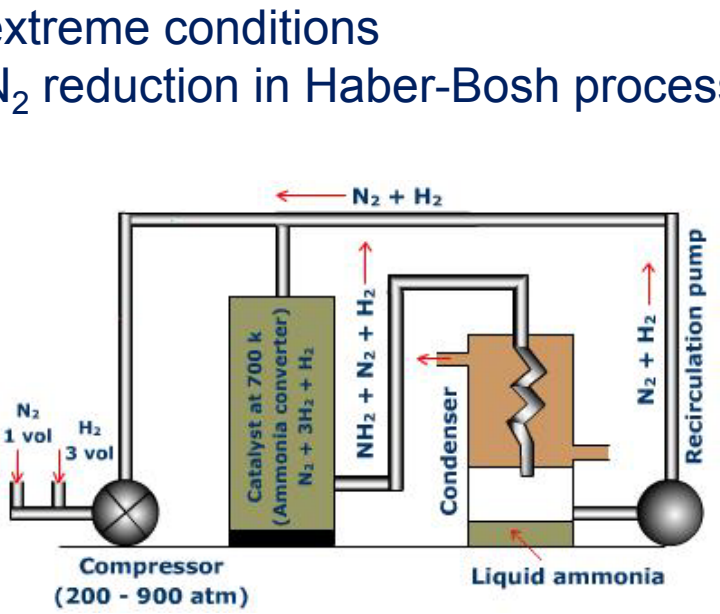
- one of the most important problems in modern technology: converting and efficiently storing electrical energy
- solution: storing electrons in the form of an abundant element, for instance N-H bonds of ammonia



- problems: high capital costs, low moderate efficiency of current production methods

Motivation

extreme conditions
N_2 reduction in Haber-Bosh process



- ammonia is difficult to produce on an industrial scale (high pressure, high temperature, catalysts required: Fe and Ru)

mild conditions
N_2 reduction in biological systems

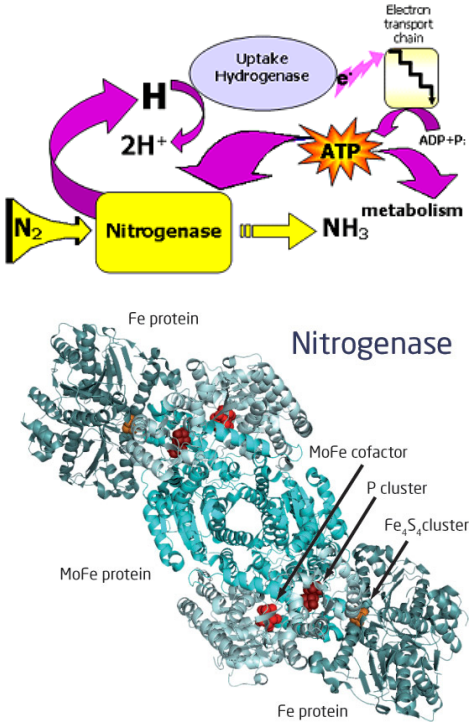


Figure: Nitrogenase - enzyme used by some organisms to fix atmospheric nitrogen

Electro-reduction of nitrogen

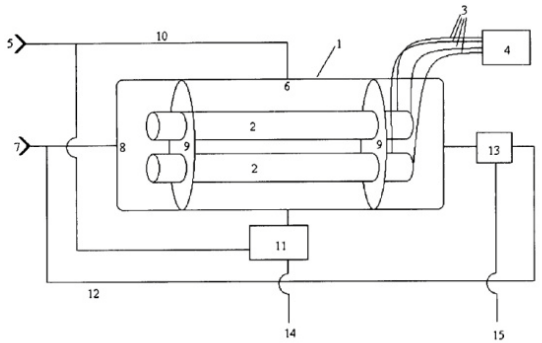
- ammonia can be obtained by electro-reduction of nitrogen

$$N_2 + 6e^- + 6H^+ \rightarrow 2NH_3$$

protons are supplied from electro-oxidation of hydrogen or water

Marnellos et al. Science 282 (5386) 98-100

Holbrook and Ganley, US patent 7811442 (2010): electrochemical synthesis of ammonia using high temperature proton conductors at atmospheric pressures

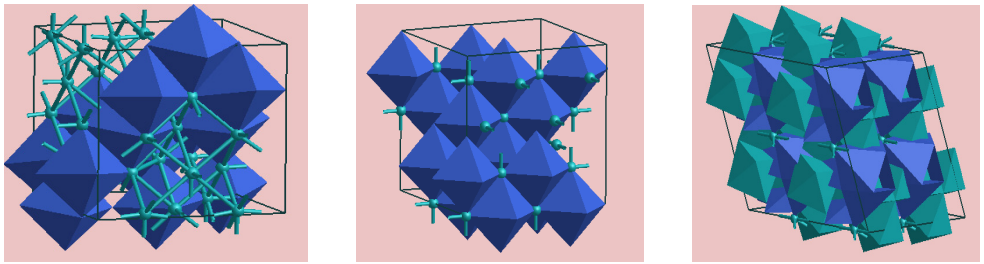


- challenges: development, characterization and optimization of **new electrocatalysts** for ammonia electrosythesis and stable anhydrous **proton conducting electrolytes**

Ammonia synthesis on MoN “foam”

- **early transition metal nitrides** - possible replacements for platinum-group metal catalysts - demonstrated catalytic activity for isomerisation, dehydrogenation, hydrogenation, water gas shift and amination reactions with competitive rates

- molybdenum nitride

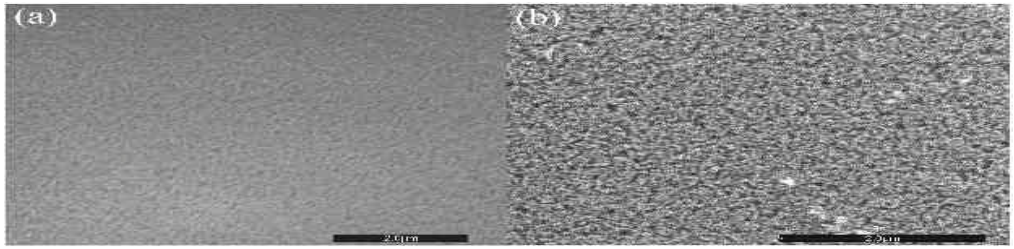


Structure of molybdenum nitride (i) tetragonal β-$Mo_{16}N_7$, (ii) hexagonal δ-MoN, and (iii) cubic γ-Mo_2N

Ammonia synthesis on MoN “foam”

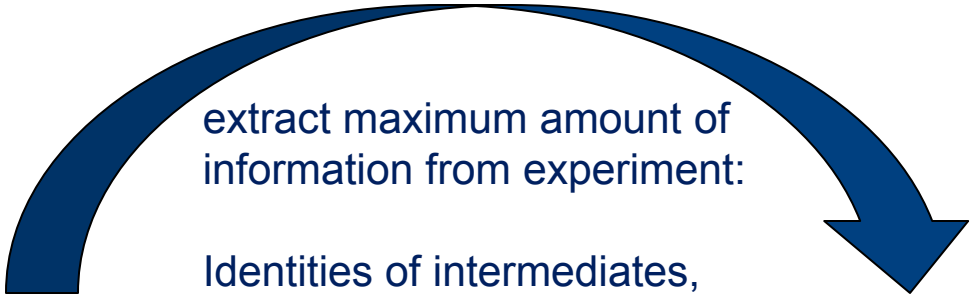
- **early transition metal nitrides** - possible replacements for platinum-group metal catalysts - demonstrated catalytic activity for isomerisation, dehydrogenation, hydrogenation, water gas shift and amination reactions with competitive rates

- molybdenum nitride - high surface area films synthesized at LANL



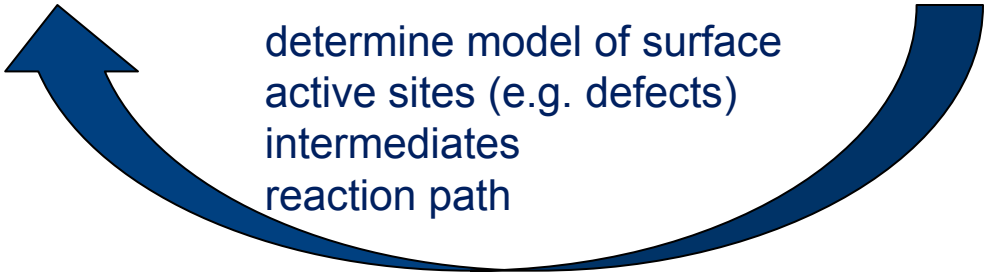
Field emission scanning electron microscope (FESEM) images

Synergy of Inelastic Neutron Scattering and Computation: Ammonia synthesis on MoN "foam"



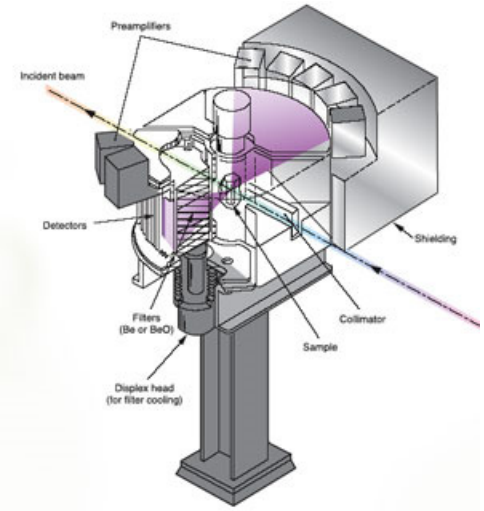
INS Experiments
observe frequencies for intermediates

Computational Studies
calculate frequencies for intermediates



Inelastic neutron scattering experiment

The Filter Difference Spectrometer (FDS) at LANL



- used for molecular vibrational spectroscopy by **inelastic neutron scattering**
- most useful for measurements requiring high sensitivity; for example, very dilute systems or molecules adsorbed on surfaces such as in catalysts

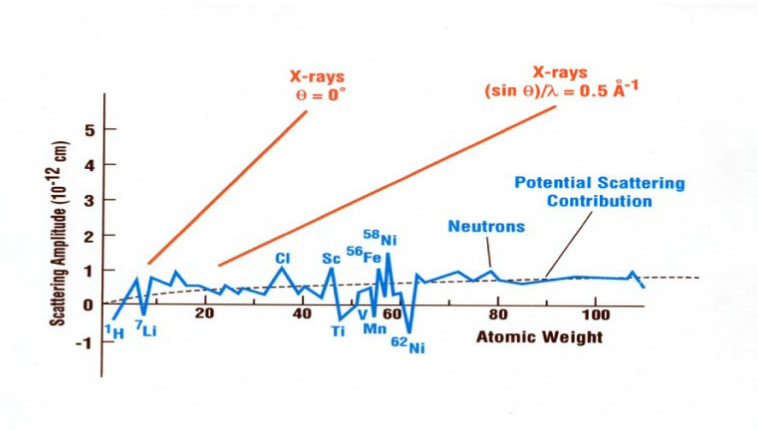
Why Neutrons ?

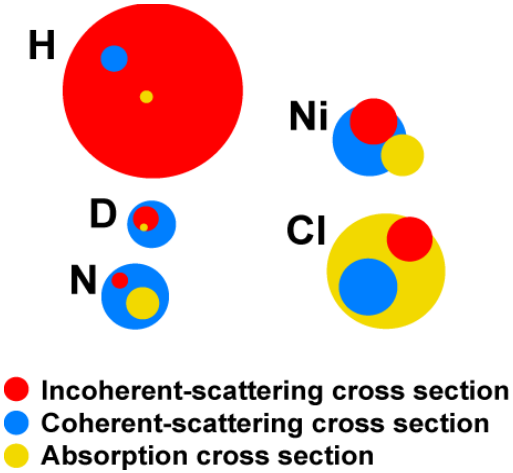
Light

atomic scattering lengths based on atomic number (electrons)

Neutrons

scattering cross-section is a complex function of nuclear properties –hydrogen very sensitive





vibrational spectra measured on FDS

- < 1g sample of catalyst adsorb in-situ H_2, then add N_2
- heat stepwise to increasing T
- collect INS spectrum at each step

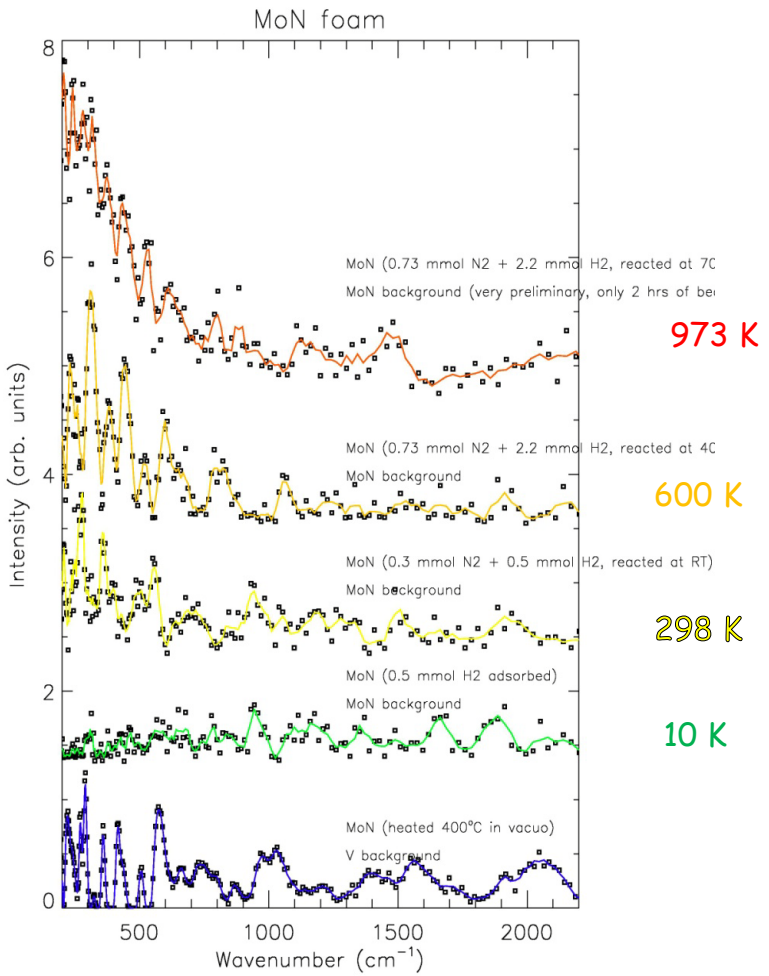
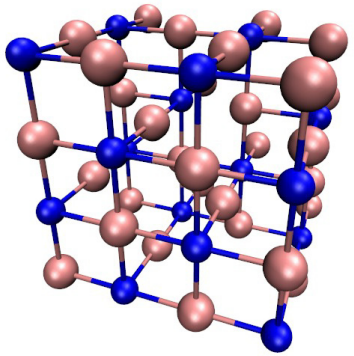


Figure: INS spectra of reactive species on MoN

molybdenum nitride

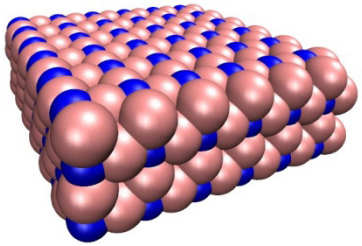
γ-Mo_2N – rock salt structure with 50% less nitrogen atoms



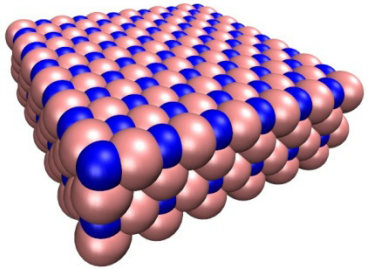
- model the surface
- model the reaction on the surface – identify the intermediates
- model the INS spectra – compare with the experiment

modeling active sites

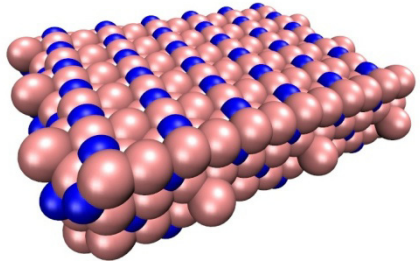
(100/010)



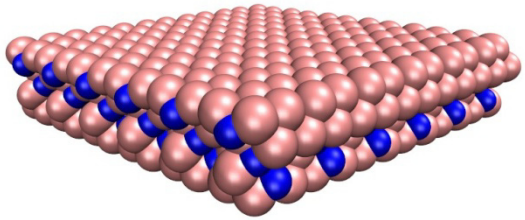
(001)



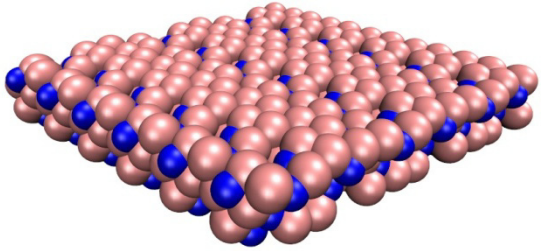
(110)



(111)



(111) + defects



reactivity of γ-Mo_2N

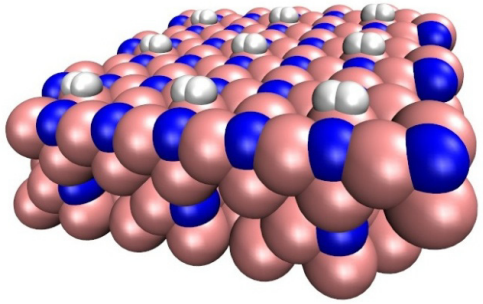
	(001)/eV	(100/010)/eV	(111)/eV	(111)*	(101)/eV
$\Delta E(H_2)$	does not bind	-0.46	-0.81	dissociates	dissociates
ΔE(H) terminal1	-2.34	-2.53			
ΔE(H) terminal2		-2.40			
ΔE(H) bridging	-2.03	-2.69		-3.28	-3.80
ΔE(H) fcc			-3.48	-3.22	

$*$ surface with defects introduced

different surfaces – very different reactivity: (001) does NOT adsorb H_2, (101) and (111) + defects dissociates H_2

molecular chemisorption (Kubas dihydrogen complex)

d(Mo-H_2) = 1.86 Å
d(H-H) = 0.85 Å (activated H-H bond)



reactivity of γ-Mo_2N

	$(001)/cm^{-1}$	$(100/010)/cm^{-1}$	$(111)/cm^{-1}$	$(111)^*/cm^{-1}$	$(101)/cm^{-1}$
H terminal1	1745, 739	1732, 727			
H terminal2	n/a	1675, 731			
H bridging	1208, 910	829, 701		1280, 1157	1339, 1231
H fcc			1233, 951, 823	1260, 1013	

- intensities calculated from DFT vibrational frequencies ω_k and amplitudes C^k

double differential cross section

$$\frac{d^2\sigma}{d\Omega dE} = \frac{\mathbf{k}}{\mathbf{k}_0}\sum_i \frac{\sigma_i^{\text{inc}}}{4\pi} S_i^{inc}(\mathbf{Q},\omega)$$

incoherent cross section for atom *i*

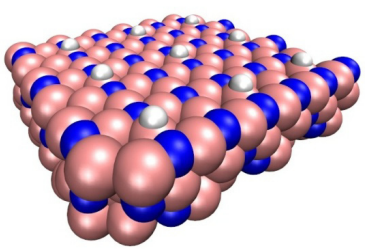
$$S_i^{\text{inc}}(\mathbf{Q},\omega) = \exp(-Q^2\langle \mathbf{u}_i^2 \rangle)\frac{\hbar|Q\cdot C_i^k|}{2\omega_k}\delta(\omega-\omega_k)$$

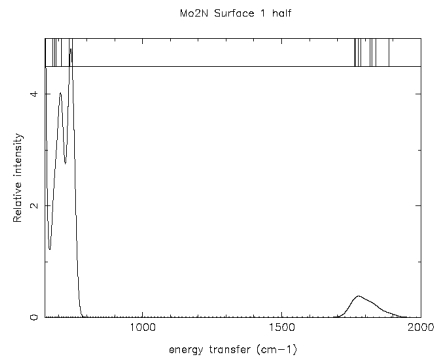
momentum transfer
experimental value: **Q = k – k_0**

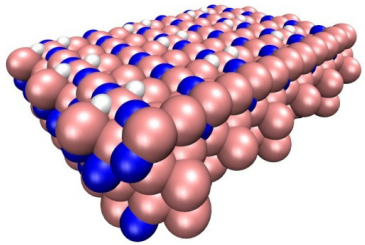
mean-square amplitude for atom *i*

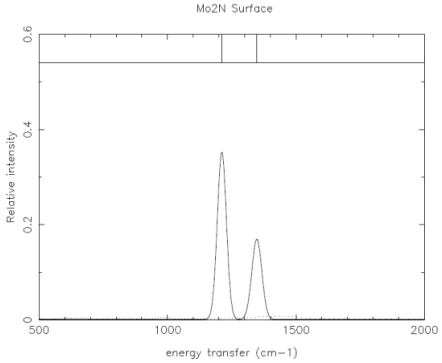
reactivity of γ-Mo_2N

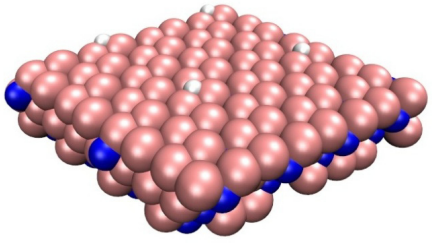
	$(001)/cm^{-1}$	$(100/010)/cm^{-1}$	$(111)/cm^{-1}$	$(111)^*/cm^{-1}$	$(101)/cm^{-1}$
H terminal1	1745, 739	1732, 727			
H terminal2	n/a	1675, 731			
H bridging	1208, 910	829, 701		1280, 1157	1339, 1231
H fcc			1233, 951, 823	1260, 1013	

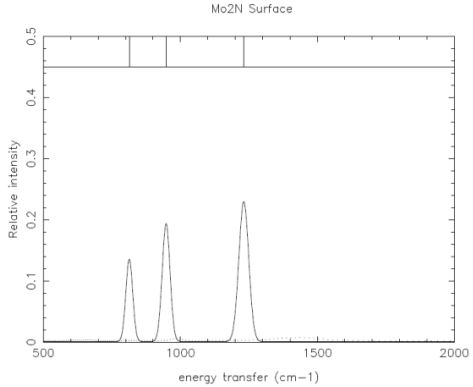












INS spectra assignment

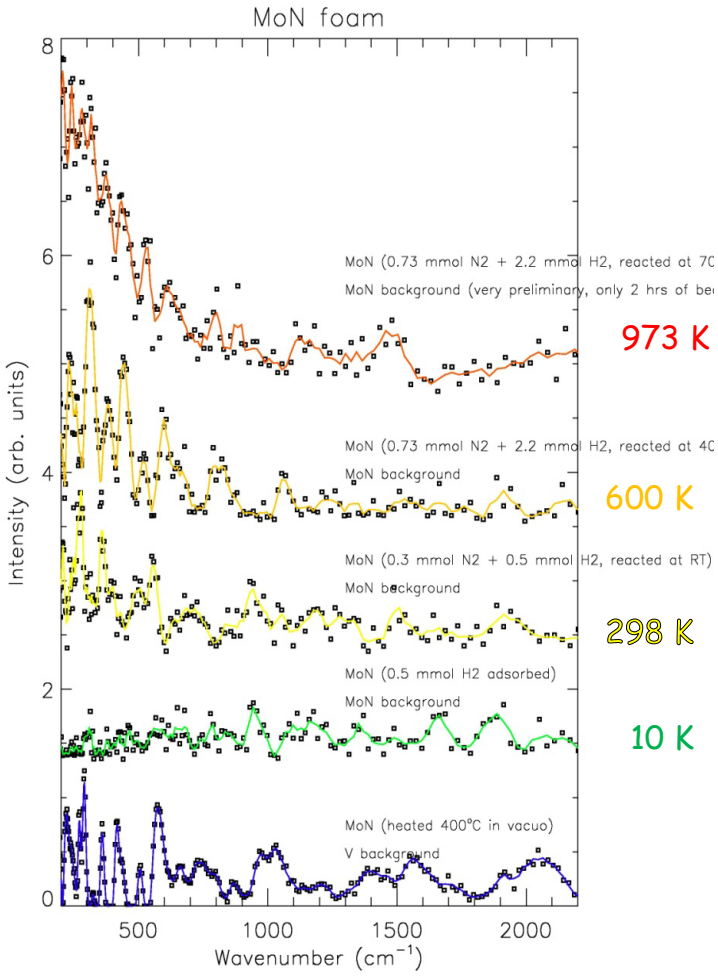
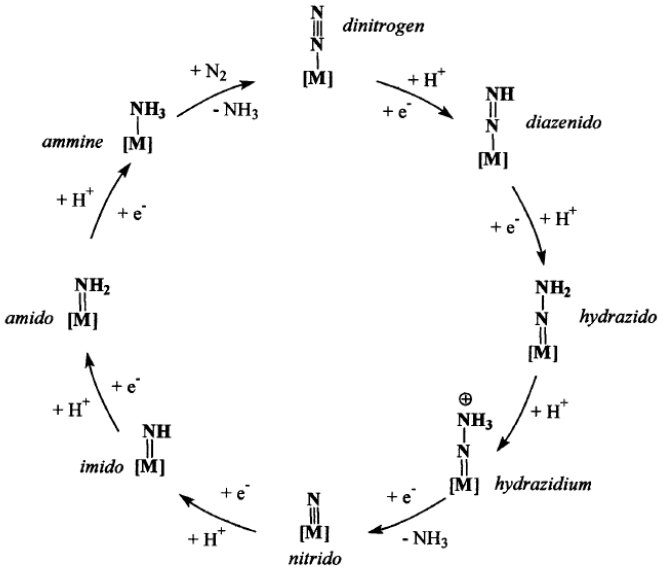


Figure: INS spectra of reactive species on MoN

(10 K) fcc H: 950, 1250 cm^{-1}
bridging H: ~ 600, ~800, 1140 cm^{-1}
terminal H: ~700, 1645 cm^{-1}

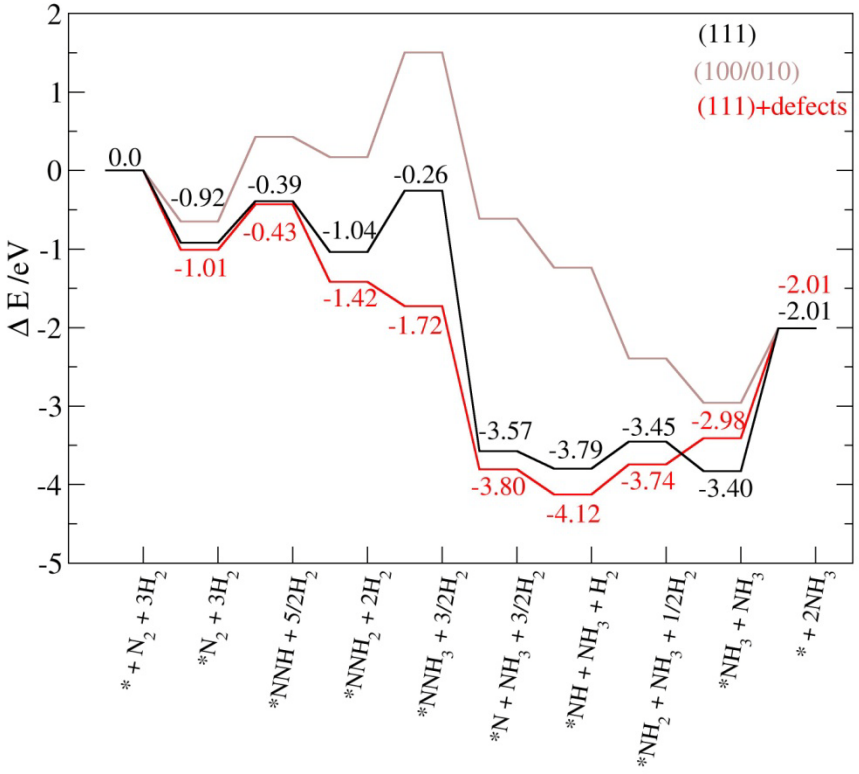
reactivity of γ-Mo_2N: adsorption energies

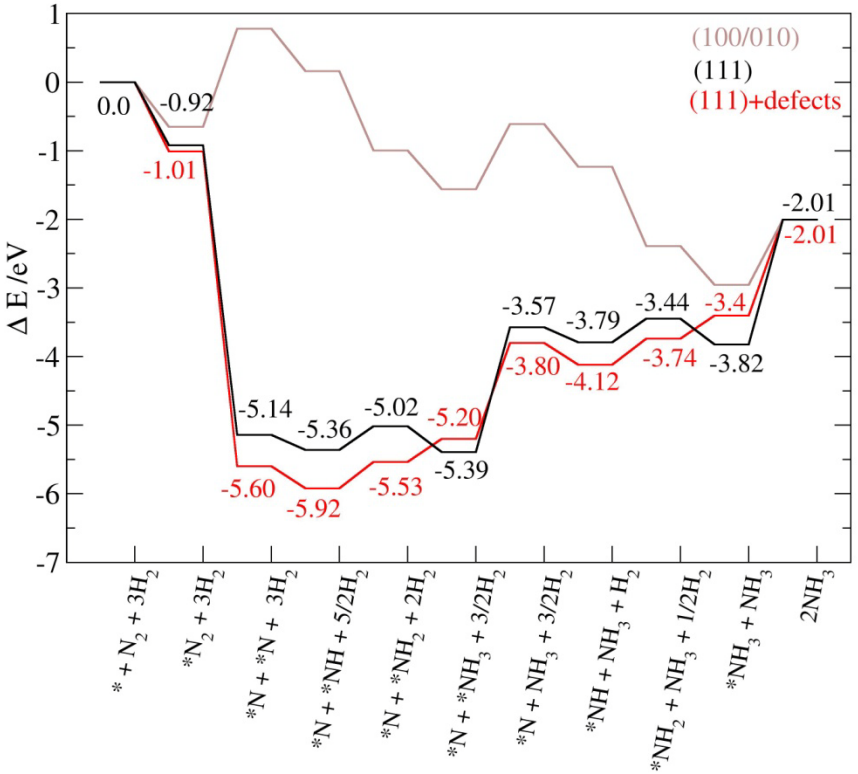


	$\Delta E_{(100/010)}$/eV	$\Delta E_{(111)}$/eV	$\Delta E_{(111*)}$/eV
N_2	-0.65	-0.92	-1.01
N	-4.88	-7.84	-8.07
NNH	-1.65	-2.42	-2.51
NNH_2	-2.94	-4.15	-4.34
NNH_3	-2.41	-4.17	-5.64
NH	-3.86	-6.42	-6.75
NH_2	-2.97	-4.03	-4.32
NH_3	-0.95	-1.82	-1.40

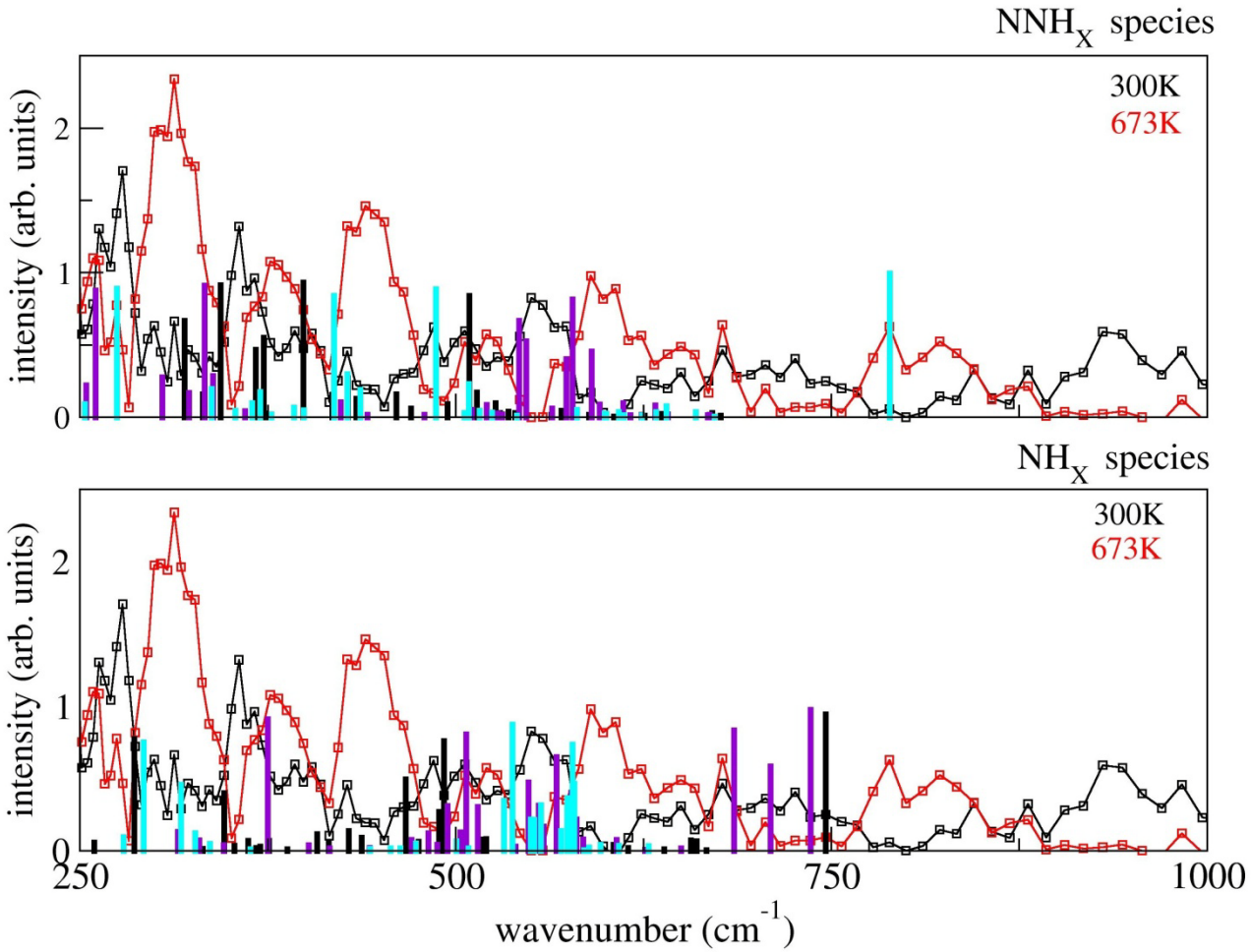
$*$ surface with defects introduced

reactivity of γ-Mo_2N: energetics



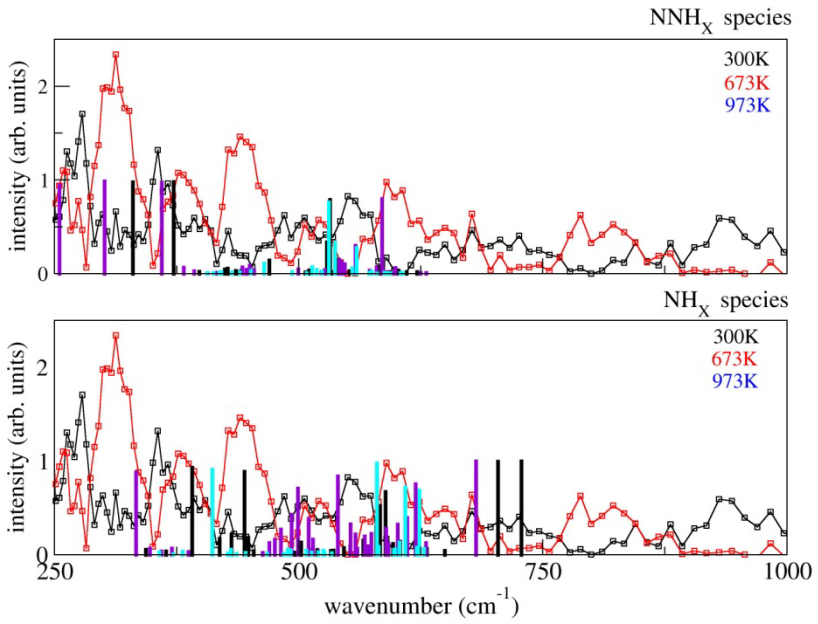


INS spectra: (111) with defects

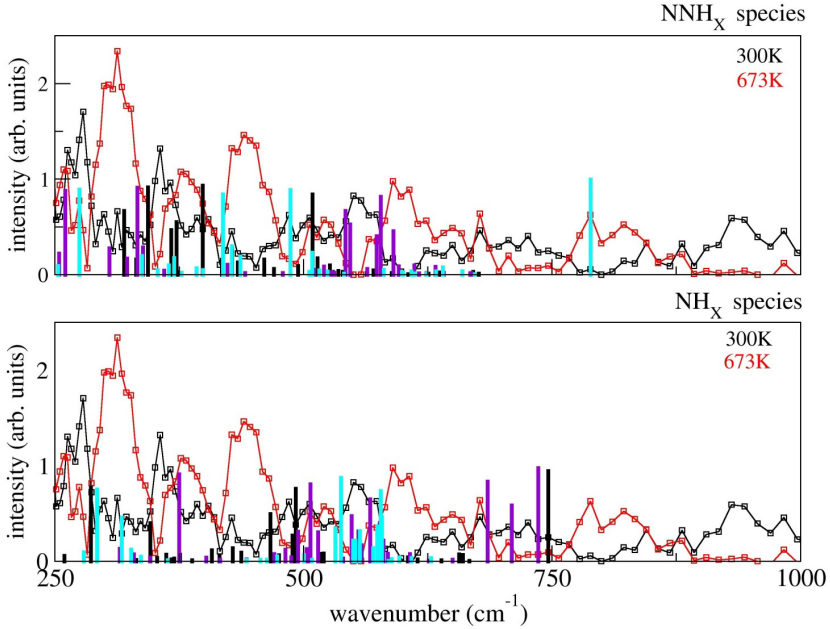


INS spectra: (111) perfect surface

(111) perfect surface



(111) surface with defects



assignment

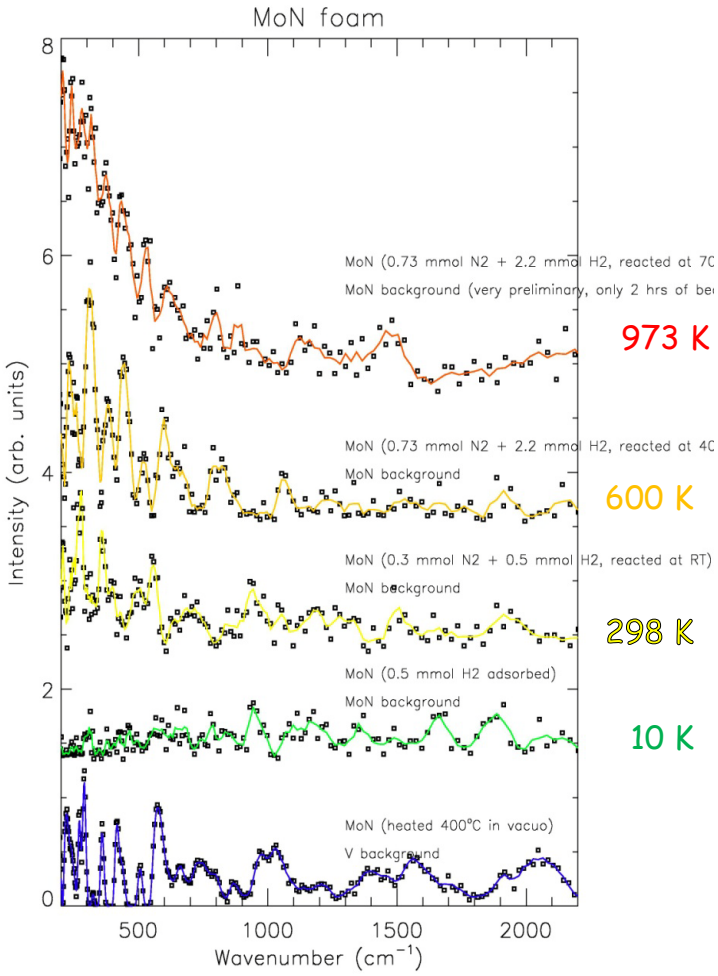


Figure: INS spectra of reactive species on MoN

(973 K) NNH_x species gone; mainly NH_x species left.
ammonia phonon DOS states below 400 cm^{-1}
Mo-(NH_3) complex, incl. (NH_3) torsion at 120 cm^{-1} !!
Peaks at ~ 600, 800, 900, 1150 and 1475 cm^{-1}

(600 K) H species gone; peaks at 425, 510, 600, 660, 725, 1070, (weak: *1240*, *1550*), 1900 cm^{-1}:
mainly NNH and NNH_2;
plus more strong peaks below 400 cm^{-1}:

(298 K) Similar to (10 K), but fewer H species,
new peaks at ~500, 700 and 1550cm^{-1}: NNH

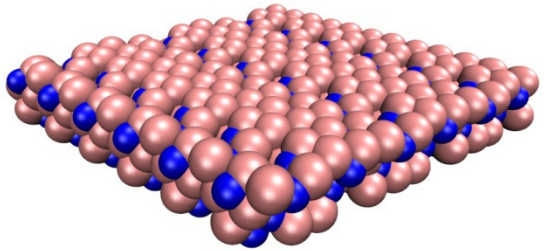
(10 K) fcc H: 950, 1250 cm^{-1}
bridging H: ~ 600, ~800, 1140 cm^{-1}
terminal H: ~700, 1645 cm^{-1}

Conclusions

- we have investigated the catalytic mechanism and the active sites of newly synthesized material using inelastic scattering of neutrons and DFT calculations

- different surfaces have very different reactivity towards N_2, H_2 and NNH_x, NH_x species

- active sites: (111) defect sites with under-coordinated Mo



- synthesis of ammonia proceeds through the formation of both NNH_x and NH_x species

Acknowledgements

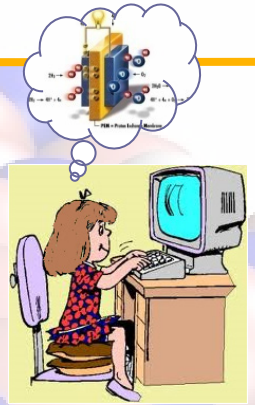
For $$$

LANL LDRD program for postdoctoral fellowship
U.S. Department of Energy, Energy Efficiency and Renewable Energy for financial support

for computational resources:

National Energy Research Scientific Computer Center, Pacific Northwest National Laboratory Advanced Computing Center and Center for Nanophase Materials Science

Tony Burrell



Thank you for you attention