Applications of hydrogen permeable membranes in ammonia synthesis and decomposition

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Sean-Thomas B. Lundin, Thomas F. Fuerst, Jason C. Ganley, Colin A. Wolden, J. Douglas Way

Chemical & Biological Engineering Department



Outline

- Ammonia Decomposition
 - Introduce membrane reactor concept w/ results
 - Discuss propensity of BCC metals to replace Pd
- Ammonia Synthesis
 - Explain similarities of hydrogen transport (PCCMs ~ Metals)
 - Show preliminary results (similar to PCCM studies)
 - Suggest method of looking for alternative catalysts



AMMONIA DECOMPOSITION



Ammonia Decomposition: Tubular Reactor Configuration



Zhang, et al. *J. Mem. Sci.* (2006) doi:10.1016/j.memsci.2005.10.014



Ammonia Decomposition: Pd Membrane Results

- At 500 °C, high conversion, recovery and good stability
- Low purity (~99%) due to defects in thin Pd films



Lundin et al. Sep. Pur. Tech. (2017) doi:10.1016/j.seppur.2016.07.041

Metals as Membrane Materials

- Traditional: Pd-alloy materials
 - Expensive, difficult to reduce thickness (cost)
- New focus: Group V (BCC) metals
 - Cheap, high flux potential



Dense BCC Metal/Pd Composite Membranes

V is over 70 times cheaper than Pd!



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MINES

Steward, S. A.; UCRL-53441, 5277693; Lawrence Livermore National Lab., CA (USA), 1983. Makrides USP 3,350,846, 1967

D. A. Cooney et al., *Int. J. of Hydrog. Energy* **39**, 19009 (2014).

Ammonia Decomposition: PdAg vs. Pd/Nb

Switch to planar geometry (foil restrictions)

- Pd coated Nb foil produces same values as PdAg except 200 °C lower!
- Issue: Pd alloys with Nb



New Concept: Dense BCC Metal/Carbide Composite Membranes



Gade, et al., *Advanced Materials, 2011.* **23(31)**: *p.* **3585–3589.** Way, J. D. and C. A. Wolden, U. S. Patent 8,623,121 B2, 2014.



Alternative Catalyst Coating for BCC Metals

- Mo₂C current research target
 - Reduced flux compared to PdAg
 - Improved thermal stability (do not alloy with BCC metals)



Gade, et al., Advanced Materials, 2011. 23(31): p. 3585-3589.

AMMONIA SYNTHESIS



Dense Metallic Membranes: Similarities to Electrochemical Cells



Left: Perry et al. doi:10.1016/j.jpowsour.2007.11.059 Right: Uemiya et al. doi:10.1023/B:TOCA.0000024930.45680.c7 Bottom: Wolden et al. doi:10.1016/j.memsci.2012.09.042

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NH₃ Synthesis: Pd/Nb/Ru



NH₃ conversion compared to equilibrium

- NH₃ concentration exceeded gas-phase equilibrium!
 - Similar to electrochemical studies



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Technology comparison

- PCCMs often limited by hydrogen flux
 - High conversion to NH₃, but limited room for improvement
- BCC metals have high flux
 - Catalytic improvements will allow vast increase in NH₃ synthesis rate



Catalytic Membrane Reactor: Proposed Configuration



Summary

- ▶ NH₃ Decomposition Membrane Reactor
 - Thin film Pd tested too costly, low purity
 - Pd/Nb proof of concept as viable alternative not durable
 - Alternative catalyst: Mo₂C
- NH₃ Synthesis Membrane Reactor
 - Ru/Nb interface comparable to PCCMs (~ 10^{-9} mol cm⁻² s⁻¹)
 - H₂ flux suggests high possibility for improvement
 - Alternative catalysts: Mo, Mo₂C, Zr, etc.



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Ammonia Synthesis: Catalyst Selection

- Ru is good due to relatively even binding energies of H and N atoms
 - Zr is poor because H coverage limited by strong N binding
 - Pd is poor because N coverage limited by strong H binding
- Zr could be much better than Ru
 - High N coverage and low rate of hydrogenation causes low TOF
 - Reduction in N coverage would cause rate to increase
 - Can we substitute low N coverage with high H supply via a membrane?





Ammonia Synthesis: Catalyst Selection



Skúlason E. et al. *Phys. Chem. Chem. Phys.* (2012) doi:10.1039/c1cp22271f

FCC Pd & alloys vs. BCC metal membranes

Pros:

- 50-1000x less costly than palladium
- BCC crystal structure promotes higher permeability, $\geq 10x$ more than Pd
- Free-standing planar foils or tubular membranes with 100-300 micron thickness have adequate H_2 flux and perfect selectivity

Cons:

- Prone to hydrogen embrittlement at low temperatures below 350 °C
- Cannot self-catalyze hydrogen dissociation reaction and require active catalyst (usually Pd)
- Lose Pd catalyst by intermetallic diffusion at T \geq 400 °C
- Narrow operating temperature window for pure metals



Ammonia Decomposition: Equilibrium

- Decomposition highly favored at higher temperatures
 - Pd membranes easily operate at 673 K to 773 K
- Increasing pressure decreases equilibrium in traditional reactor configuration
 - Membrane reactors can change this dynamic



Ammonia Decomposition: Kinetics

- Itoh et al. showed increase in performance using membrane reactor configuration
 - Due to kinetic enhancement when H₂ removed from products
- Model indicates vast improvements for thin membranes
 - Does not account for concentration polarization effects
 - · Actual benefit less, but should still be significant



Ammonia Synthesis: Traditional Reactor is Equilibrium Limited



Traditional Reactors: Very high pressures to overcome kinetic/ thermo limitations

Problem:

 H_2 / N_2 compete for active sites on catalyst

Solution:

Decouple H_2 / N_2 activation and independently control flux of each



100 nm Pd on 100 μm Nb at 500 °C and 0.34 bar

Atomic Hydrogen as ultra-reactive species: Verification of Hydrogen as Reactive Species



$\frac{2.4 \ \mu\text{m}}{\text{Exposed to N}_2 \text{ at 700}^{\circ} \text{ C}}$

Observed: No evidence of Mg when annealed under N2

Conclusion/Hypothesis:

-MgO only reduced under presence of H₂

$\frac{2.5 \ \mu\text{m}}{\text{Exposed to H}_2 \text{ at } 700^{\circ} \text{ C}}$

Observed: Mg and O peaks clearly visible

Conclusion/Hypothesis:

-Mg present on surface, quickly forms oxide when removed from shell

Atomic Hydrogen as ultra-reactive species: Permeation Required for Reactivity







As-fabricated membrane surface

Environment: Dried in air at 120 C Peaks: Pd, O

Post-tested: Non-permeation H₂ soak

Environment: soaked (non-permeation) in H_2 at ~7 psi and 700 C for 45 h

Peaks: Pd

Post-tested: Permeation H₂ soak

Environment: Operated in permeation mode under H₂ at ~7 psi and 700 C for 45 h

Peaks: Pd, O, Mg



Ammonia Synthesis: Benefits of Proton Conducting Ceramics

- Marnellos et al. used proton conducting ceramic to produce NH₃ at low pressure
 - Ceramic = $SrCe_{0.95}Yb_{0.05}O_3$
 - Catalyst = Pd
 - H_2 conversion ~70%
 - NH_3 reaction rate increased with increasing H_2 driving force
 - Reaction rate ~10⁴ times higher than conventional reactor
 - Production exceeded equilibrium (CCR rate)





SSPC NH₃ synthesis rates from Amar (2011)

Table 2. Summary of the SSPC electrolytes and the rates of ammonia formation

Proton Conductor	Electrolytic Cell	Temperature	NH3 Formation rate	Structure Type F	Reference # from Amar
		°C	(mol/s/cm^2)		
SCV	Steam H2O, Pd ISCVI Ru-based catalyst N2	650	9 10E-14	nerovskite	[57]
SZV	H2 Ag ISZVI Eq catalyst, N2,	450	6 20E-12	perovskite	[37]
100	H2 Ag_Pd II CCI Ag_Pd N2 NH3	520	1 30E-00	pyrochlore	[70]
BCN18	H2 Δq Pd IBCN18 Δq Pd N2 NH3	620	1 42E-09	pyrochiore	[07]
SCV	H2 Pd ISCVI Pd N2 NH3 Ha	570	1.60E-09	perovskite	[33]
LCGM	H2 Ag_Pd II CGMI Ag_Pd N2 NH3	520	1.63E-09	perovskite	[79]
BCZN	H2 Ag_Pd IBCZNI Ag_Pd N2 NH3	620	1.82E-09	perovskite	[75]
LBGM	H2 Aq_Pd II BGMI Aq_Pd N2 NH3	520	1 89E-09	perovskite	[78]
LCZ	H2 Ag_Pd II C7I Ag_Pd N2 NH3	520	2 00E-00	pyrochlore	[70]
102	H2 Ag-Pd II CZOLAg-Pd N2 NH3	520	2.00E-09	pyrochlore	[34]
LBGM	H2 Aq_Pd II BGMI Aq_Pd N2 NH3	520	2.00E-09	perovskite	[79]
BCY	H2 Aq_Pd IBCYI Aq_Pd N2 NH3	500	2 10E-09	perovskite	[66]
BCNN	H2 Ag-Pd IBCNNI Ag-Pd N2 NH3	620	2.16E-09	perovskite	[55]
LSGM	H2 Ag-Pd II SGMI Ag-Pd N2 NH3	520	2.53E-09	perovskite	[79]
BCC	H2 Aq-Pd IBCCI Aq-Pd N2 NH3	480	2.69E-09	perovskite	[68]
BCGO	H2 Ag-Pd IBCGOI Ag-Pd N2 NH3	480	3.09E-09	perovskite	[63]
LSGM	H2 Ag-Pd II SGMI Ag-Pd N2 NH3	550	3.37E-09	perovskite	[53]
BCD	H2, Ag-Pd IBCDI Ag-Pd, N2, NH3	530	3.50E-09	perovskite	[61]
BCY	H2, Ni-BCY IBCYI BSCF, N2, NH3	530	4.10E-09	perovskite	[67]
SCY	H2. Pd ISCYI Pd. N2. NH3. He	570	4.50E-09	perovskite	[12]
BCGO	H2. Ni-BCGO IBCGOI Aq-Pd. N2. NH3	480	4.63E-09	perovskite	[64]
BCS	H2, Aq-Pd IBCSI Aq-Pd, N2, NH3	620	5.23E-09	perovskite	[65]
BCGS	H2. Aq-Pd IBCGSI Aq-Pd. N2. NH3	650	5.82E-09	perovskite	[65]
YDC	H2, Aq-Pd IYDCI Aq-Pd, N2, NH3	650	6.50E-09	fluorite	[111]
LDC	H2, Aq-Pd ILDCI Aq-Pd, N2, NH3	650	7.20E-09	fluorite	[97]
LDC	H2, Aq-Pd I LDCI Aq-Pd, N2, N H3	650	7.20E-09	fluorite	[98]
YDC	H2, Ag-Pd IYDCI Ag-Pd, N2, NH3	650	7.50E-09	fluorite	[97]
CLC	H2, Aq-Pd ICLCI Aq-Pd,N2, NH3	650	7.50E-09	fluorite	[98]
GDC	H2, Ag-Pd IGDCI Ag-Pd, N2, NH3	650	7.70E-09	fluorite	[97]
SDC	H2, Ag-Pd ISDCI Ag-Pd, N2, NH3	650	8.20E-09	fluorite	[97]

