Vanadium As a Potential Catalytic Membrane Reactor Material for NH_3 Production

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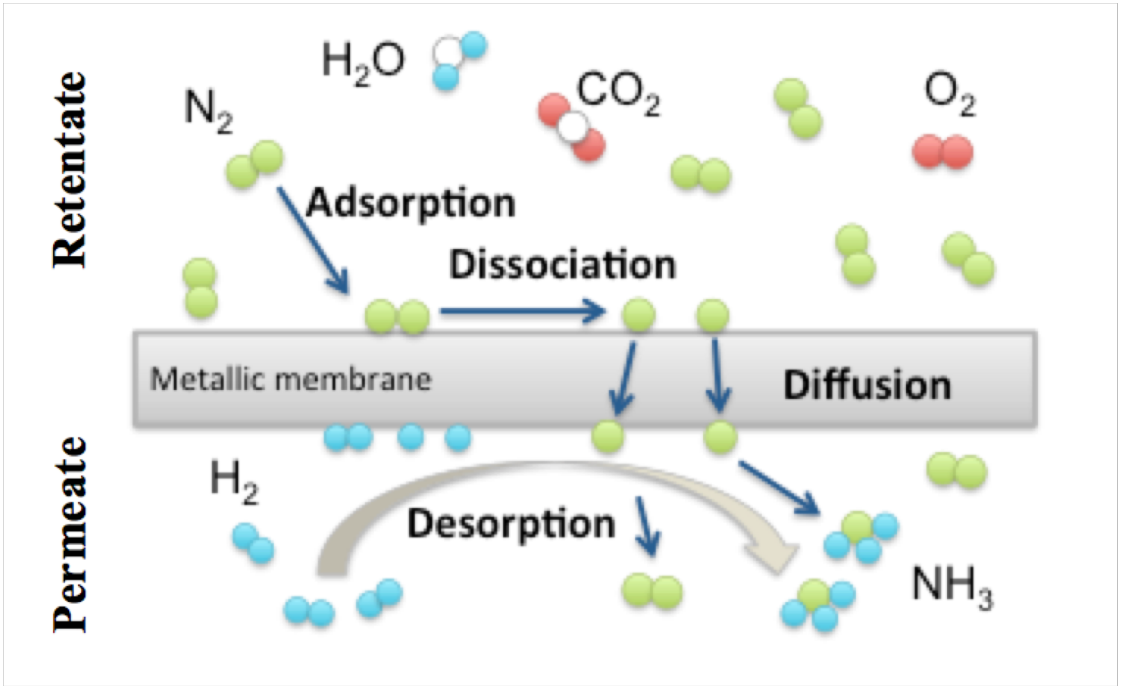
Aim

Ammonia production through a catalytic membrane reactor configuration using Earth-abundant metals for the N_2-selective membrane reactor at low pressure, up to 30 bar and low temperature 400 C, instead of the typical conditions used in the Haber-Bosch process.



N_2 Selectivity Metallic Membranes – Low pressure

400 °C

N_2 Permeating Flux [L/m^2/day]

Δp [bar]	Nb	Ta	V
2	34	28	40
3	45	40	57
4	62	45	62
5	68	57	73

- Metallic membranes (V, Nb, Ta) are entirely selective for N_2 over He and CO_2 ($\alpha = \infty$)
- Fluxes are low
- Metallic thin films, an order of magnitude thinner than foils, may lead to significantly higher fluxes

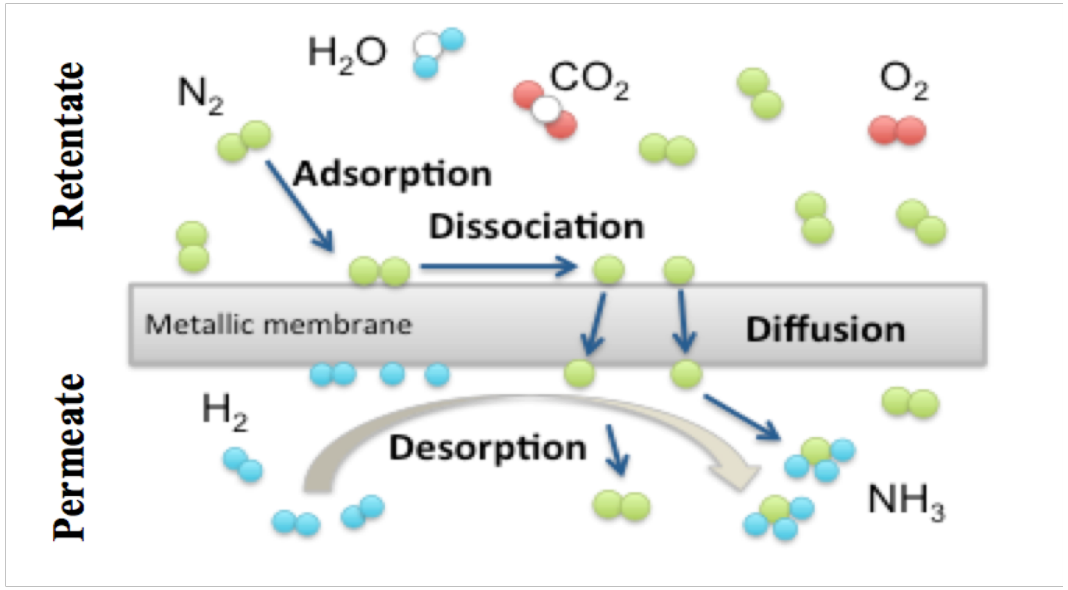
N_2 Selectivity Metallic Membranes – High pressure

- At **each temperature**, no He and CH_4 were detected during the testing. Only N_2 permeated through the membrane.
- The following table shows the **comparison between V and Fe membranes** by performing permeation testing with pure N_2 at different temperature and pressure.

N_2 [L/m²/day]						
p [bar]	*T = 400 – V*	*T = 400 – Fe*	*T = 500 – V*	*T = 500 – Fe*	*T = 600 – V*	*T = 600 – Fe*
30	116	88	239	158	402	15
40	156	125	352	225	603	26
50	216	165	465	311	828	33
60	271	211	577	376	1079	45

- V membrane shows better performance in terms of N_2 permeation with respect to Fe membrane.
- *At 600 °C, the N_2 permeating flux dropped dramatically.*

Ammonia Synthesis by using V membrane



Data at 500 C and 60 bar – V membrane

	NH_3 [mol/cm² s]
Permeate side (1 bar)	3.91E-10
Retentate side (60 bar)	3.71E-10

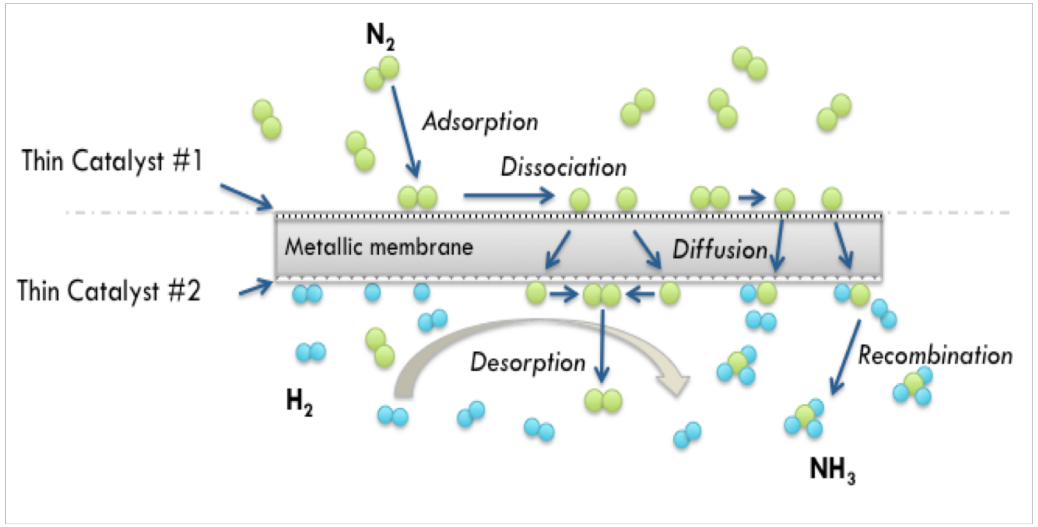
Only 5% of the permeate nitrogen reacts to form NH_3

Deposition of thin layer V-Ru on V membrane

A V-Ru thin layer(~150 nm) was sputtered on three V membranes.

V-Ru was sputtered on three different samples:

- Retentate side of the V membrane
- Permeate side of another V membrane
- Both sides of the V membranes



V-Ru thin layer on V membrane – retentate side

- The membrane was characterized by permeation tests with pure gases.
- With respect the pure V membrane v-Ru/V showed an improved permeated flux.
- The improvement was approximately of 5% at each condition.

Ammonia Synthesis by using V-Ru/V membrane

Data at 500 C and 60 bar – V-Ru/V membrane

	NH_3 [mol/cm² s]	NH_3 [mol/cm² s] (V membrane)
Permeate side (1 bar)	4.11E-10	3.91E-10
Retentate side (60 bar)	4.55E-10	3.71E-10

Work in progress on:

- V/V-Ru → where the thin layer of V-Ru is deposited on the permeate side
- V-Ru/V/V-Ru → where the thin layer is deposited on both sides of the membranes

Conclusion

- V, Nb, Ta, Fe show infinite ideal selectivity with respect to He, CO_2 and CH_4 → only N_2 can permeate through the membranes
- N_2 permeation flux through the membrane is extremely low
- NH_3 production strongly depends on the N_2 permeation and the presence of catalyst

Future Work

- Reduce the thickness of the metallic membrane
- Prepare defect-free inorganic membrane able to work for long periods
- Quantify ammonia production as a function of temperature, pressure gradient and membrane material

THANKS FOR
YOUR KIND ATTENTION