

Introduction

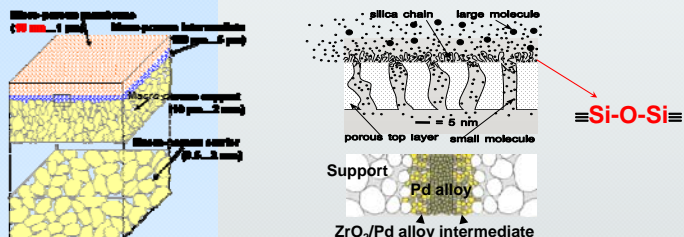
Micro-porous amorphous silica and dense Pd membranes are fabricated as thin films on strong and permeable porous ceramic supports. The silica membranes are suitable for separation of gases, such as H₂, He, CO₂, N₂, and O₂; the Pd membranes for H₂. These membranes will be applied in membrane reactors with permselective walls for conversion enhancement and improved space yield. It is important that the membranes survive operating conditions for several years.

Objectives

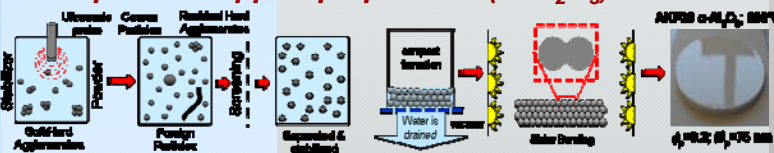
- H₂ molar permeance > 10⁻⁵ mol/(m² s Pa); separation factor >50
- Thermo-chemical stability for >1 year operation.
- Viable manufacturing possible
- Membrane reactor prototype

Methods

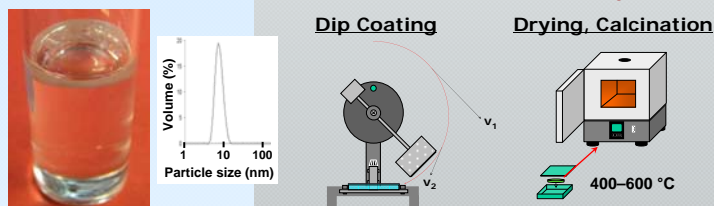
- Multi-layer structure by colloidal/electroless assembly
- Stable thin film Pd membranes on composite intermediate



Macroporous support preparation (α-Al₂O₃)



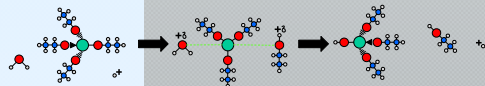
Mesoporous intermediate preparation (γ-Al₂O₃, ZrO₂)



Microporous amorphous silica preparation

Prepared by dip coating of partially hydrolyzed silica sol from TEOS and HNO₃ in EtOH, followed by drying and calcination.

- Hydrolysis: $\equiv\text{Si-OR} + \text{H}_2\text{O} \rightarrow \equiv\text{Si-OH} + \text{ROH}$



- Alcohol Condensation: $\equiv\text{Si-OR} + \text{HO-Si} \rightarrow \text{ROH} + \equiv\text{Si-O-Si}$
- Water Condensation: $\equiv\text{Si-OH} + \text{HO-Si} \rightarrow \text{H}_2\text{O} + \equiv\text{Si-O-Si}$



Dense Pd preparation

- AA3 carrier + AKP30 support, γ-Al₂O₃ intermediate layer
- Application of a Pd(O)-ZrO₂ seed layer
- Dip coating with a mixture of PVP and Pd(O)-ZrO₂ sol
- Palladium deposition by electroless plating with hydrazine reduction

Conclusions

- Promising results for silica and Pd membranes.
- ZrO₂ (composite) intermediate layer for improved stability.
- Rapid deposition methods, rapid thermal processing possible.
- Module constructed, leak tested, demonstrated for single gas.

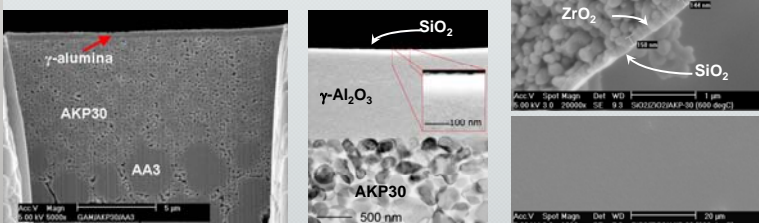
Results

SiO₂ membrane on 4-layer support



Dip solution:

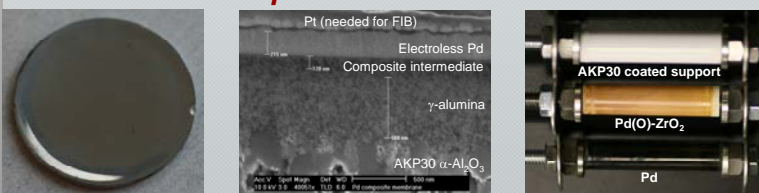
- PVA
- Boehmite sol
- PVP
- Zirconia sol



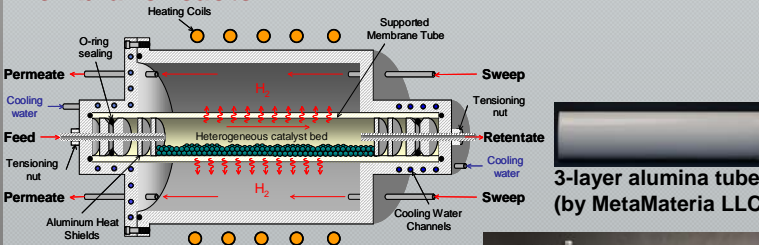
Three-layer alumina

supported SiO₂ with ZrO₂ intermediate

200 nm Pd on composite intermediate



Membrane reactor



- N₂ permeance tubes >10⁻⁵ mol/(m² s Pa)
- Temperature control within 0.5°C at 350°C using computer PID implementation

3-layer alumina tube (by MetaMateria LLC)



Stainless steel membrane reactor module (by Pall Corp.)

Acknowledgement

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