Carbon Molecular Sieves (CMSM) for gas separation and membrane reactors

Pacheco-Tanaka D.A[1,2*], Llosa-Tanco M.A.[1,2*], Gallucci F[2].

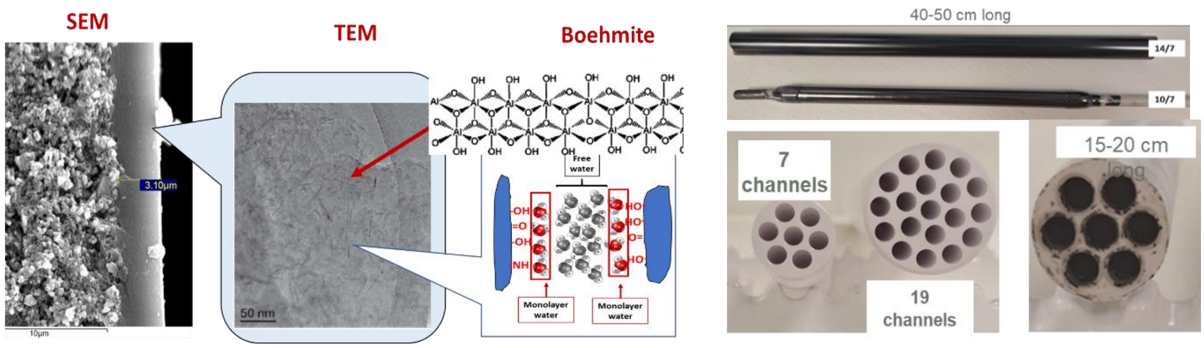
[1] *TECNALIA, Basque Research and Technology Alliance (BRTA), Mikeletegi Pasealekua 2, 20009, Donostia-San Sebastian, Spain*
[2] *Inorganic Membranes and Membrane Reactors, Sustainable Process Engineering, Department of Chemical Engineering and Chemistry, Eindhoven University of Technology, De Rondom 70, 5612 AP, Eindhoven, The Netherlands*
Email: alfredo.pacheco@tecnalia.com

Keywords: gas separation, membrane reactor, carbon molecular sieves membranes

Abstract:
Carbon Molecular Sieves membranes (CMSM) are microporous membranes product of the carbonization of thermosetting polymers. Comparing with polymeric membranes, CMSM have better thermal and chemical stability, higher selectivity and permeance and can be used in membrane reactors. The permeation mechanism is a combination of molecular sieving (size separation) and adsorption diffusion; the permeation properties of CMSM can be tailored by changing the polymer, carbonization conditions, and the presence of additives. The research carried out by Tecnalia and TUE in CMSM for gas separation and membrane reactors in various projects sponsored by the European Commission (EC) will be presented.

Experimental.
Supported CMSM were prepared by dipping a porous asymmetric alumina support (from Rauschert GmbH) into a NMP solution containing phenolic resin oligomer, curing agents and fillers; the coated support is then heated to 90-95 °C to condensation of the oligomers and removal of the solvent, and finally, carbonized under N_2 [1].

Results and discussion
The goals in the development of membranes is to obtain membranes with: a) the highest selectivity and permeation, stability at separation conditions and c) low cost. Phenolic resins are produced from cheap resources are the product of condensation of phenol and formaldehyde; the structure of the phenolic resin can be modified with the synthesis conditions and the addition of other functional groups. During the carbonization, functional groups are removed, pores are formed and the pores gradually loss the hydrophilicity; at high temperatures, reaction of condensation are taking place leading to the formation of aromatic-aromatic links and at higher temperatures a char structure with coalesced rigs are formed, in this process, size and number of pores are reduced. [2][3].



(a) (b)

Figure 1 a) Supported CMSM containing nanoplatelets of boehmite b) Scaling up the production of membranes from tubular (50 cm long) to multichannel (***HERMES*** project)

The pores of CMSM containing nanoplatelets of boehmite (AlO(OH)) (Al-CMSM) carbonized at < 600 °C are hydrophilic and water molecules can be adsorbed in the pores (Figure 1a); most of the pores of the hydrated membrane are below 0.36nm. Since the kinetic diameter of H_2 and CH_4 are 0.29 and 0.38 nm respectively, these membranes were used for the separation of H_2 from a mixture containing H_2 10% and 90 % CH_4 [4], at 30 °C, the purity of H_2 in the permeated obtained was 99.4% (***Hygrid*** EU Project). In the Power to Methane process, CH_4 is produced from CO_2 and H_2; to increase the concentration of CH_4 to be injected in the gas grid, the EU ***MEASURED*** project study the use of Al-CMSM to remove H_2 and CH_4 leaving in the retentate CH_4 at high pressure. At ***Hygrid*** tubular CMSM 15-20 cm long 10/7 (outer/inner (mm)) were used; in ***MEASURED***, 40-50 long 14/7 (o.d/id.) membranes are being prepared; in the project ***HERMES***, the production of membranes is scaled up by developing CMSM in multichannel tubes (Figure 1b)

The reaction of CO_2 and H_2 is a very important process in the production of fuels and chemicals such as CH_4, methanol (MeOH) and dimethylether (DME, CH_3-O-CH_3) (i.e. $2CO_2 + 6H_2 \leftrightarrow CH_4 + 2\ H_2O$). Water vapour is a product of the reaction which can reduce the activity of the catalyst, compete with the active sites and H_2O can condensate shifting the equilibrium to the reactants reducing the conversion. The reaction can be improved if water vapor is removed during the reaction by water selective membranes. Hydrophylic Al-CMSM were used for the synthesis of DME (***C2FUEL*** Project) and methanol (***GICO*** Project).

Ammonia is an attractive compound to store and transport H_2. Technologies for small ammonia plants are becoming increasingly important as ammonia production from green hydrogen ($N_2 + 3H_2 \leftrightarrow 2NH_3$), the reaction is promoted at low temperature and high pressure; the aim of the project ***AMBHER*** is produce NH_3 selective membranes to increase the yield at lower temperatures. At the end user, NH_3 need to be cracked to recover H_2; thus, in ***ANDREAH project***, CMSM selective to H_2 stable at 450-500 °C are being developed.

Conclusions

CMSM are promising alternatives to conventional membranes for gas separation and membrane rectors, starting from small and short membranes at ***Hygrid,*** the process or production are being scaled to a multitubular structures for industrial production at ***HERMES.***

References

[1] M.A. Llosa Tanco, D.A. Pacheco Tanaka, S.C. Rodrigues, M. Texeira, A. Mendes, *Int. J. Hydrogen Energy* 40 (2015) 5653–5663.

[2] L. Forster, C. D'Agostino, M.A. Llosa-Tanco, V. Spallina, C. Brencio, F. Gallucci, M. Lindley, S.J. Haigh, D.A. Pacheco-Tanaka, *Chem. Eng. J.* 424 (2021) 129313..

[3] S. Poto, A. Aguirre, F. Huigh, M.A. Llosa-Tanco, D.A. Pacheco-Tanaka, F. Gallucci, M.F. Neira d'Angelo. *J. Memb. Sci*. 677 (2023) 121613.

[4] M.A. Llosa Tanco, J.A. Medrano, V. Cechetto, F. Gallucci, D.A. Pacheco Tanaka, *Int. J. Hydrogen Energy* 46 (2021) 19758–19767..

Acknowledgments

Funded by the European Union

This work has received funding by the European Commission projects: HaDEA: MEASURED (grant agreement N° 101091887), AMBHER (gran agreement101058565) Horizon-JTI-CLEANH2, ANDREAH (grant agreement N° 101112118), HERMES (gran agreement 101192352)

"Views and opinions expressed are however those of the author(s) only and do not necessarily reflect those of the European Union or HaDEA or JTI-CLEANH2. Neitherthe European Union nor the granting authority can be held responsible for them."