Preparation of Si-rich LTA zeolite for membrane reactors in *e-methanol* synthesis

Lidia Castoldi[1], Luca Lietti[1*], Carlo Visconti[1], Nadia Cerone[2], Francesco Zimbardi[2]
[1]*Politecnico di Milano, Department of Energy, LCCP group, via La Masa 34, 20156 Milano, Italy.*
[2] *ENEA, Energy Technologies and Renewable Sources Department, ss 106, 75026 Rotondella, Italy.*
**luca.lietti@polimi.it*

Significance and Relevance

Membrane technology has attracted considerable interest in both academia and industry due to its benefits, including relatively low energy requirements, reduced operating and capital costs, compact design, and excellent selectivity and separation performance. These advantages have led to membranes increasingly replacing competing technologies across various industrial sectors. Moreover, membranes enable the integration of multiple processes within a single unit, promoting process intensification. For instance, a membrane reactor (MR) can combine chemical reactions and separation within one system. In this respect, zeolite-based catalytic membrane reactors have been successfully applied in overcoming the thermodynamic limitations of methanol synthesis.

Preferred and 2nd choice for the topic: CO_2 utilization and recycling
Preferred presentation: ORAL or SHORT ORAL preferred

Introduction and Motivations

Hydrogenation of CO_2 to methanol with hydrogen obtained from renewable energy (the so-called *e-methanol*), has been proposed as a way of solving two of the main problems that technology is currently facing: the need to reduce CO_2 emissions and the depletion of fossil fuels. One of the drawbacks of this reaction is the low conversion per pass due to the limitations posed by thermodynamic equilibrium. The use of membrane reactors, by removing H_2O and/or MeOH from the reaction environment, have been proposed as a way to improve the methanol per pass yield[1].
In this respect, zeolite membranes have a promising future for applications in membrane reactors (Zeolitic membrane Reactors, ZMRs) due to their selectivity, permeability, and stability concerning higher temperatures and chemically aggressive media. The development of these membranes has focused on the use of inorganic supports with a Si-rich LTA zeolite layer that selectively permeates the water produced by the CO_2 hydrogenation reaction. Indeed, due to the in situ and rapid removal of the produced water from the catalytic layer through the hydrophilic zeolite LTA membrane, it is effective to break the thermodynamic equilibrium limitation, thus significantly increasing the CO_2 conversion and methanol selectivity[2].
In this work the application of LTA zeolitic membranes in e-methanol synthesis has been investigated. Accordingly, a membrane reactor has been designed and ceramic tubes coated with a LTA zeolite layer have been synthesized and characterized in terms of morphology and permeation properties.

Materials and Methods

The synthesis of zeolites begins with the production of seeds through a process without organic structure-directing agents (OSDA), thereby increasing the Si/Al ratio and the resulting stability[2]. These seeds will then be used to create the desired membrane through a second growth step[3].
The zeolite seeds were prepared from a gel with a molar composition of 3.9 Al_2O_3 : 18 SiO_2 : 5 Na_2O : 173 H_2O. For a typical synthesis, $Na_2Al_2O_4$ is dissolved in H_2O and NaOH solution is added to obtain the final Na/Al ratio; the solution was mixed for 60 min. A 40% colloidal silica solution (LUDOX-40) is diluted in H_2O with vigorous stirring at 250 rpm for 60 min. Then, the two solutions were mixed and stirred at 350 rpm for 24 h at ambient temperature; finally, stirring was stopped and the temperature increased up to 67°C and maintained for 7 days. to obtain a uniform hydrogel. After the aging phase, the seeds are washed with H_2O and centrifuged three times, filtered and dried in ambient air[4].
α-alumina tubes are abraded with #4000 sandpaper and washed in boiling water three times to roughen the surface and promote membrane growth, then dried in an oven at 100°C overnight.

The seeds are crushed in a mortar and sieved with a 140-mesh sieve. After wetting the abraded tubes, the seeds are adhered to the surface and then dried for 4 hours at 80°C.
The growth gel is prepared from a solution with a molar composition 0.21 Al_2O_3 : SiO_2 : 0.27 Na_2O : 38 H_2O, using the same procedure of seeds synthesis with 6 hours of stirring. The seeded supports, 10 - 15 cm length, were subsequently immersed into a Teflon-lined stainless-steel autoclave filled with the synthesis gel for the hydrothermal reaction. The autoclave was placed horizontally in the oven at 120°C at different times. The obtained membranes were washed in H_2O and dried overnight at 80°C.

Results and Discussion

As-synthetized Si-rich LTA shows a typical type IV N_2 adsorption-desorption isotherm (Fig. 1A). The average mesopore size results of 39 nm and BET surface area 30 m^2/g_{cat}.
The characterization of the seeds was performed through XRD analysis (Fig.1B), which shows patterns consistent with the desired LTA zeolite, and no sodalite (SOD) phase is observed[4]. The Fig. 1C shows characteristic FT-IR[5] bands of as-synthesized LTA zeolite: i) the 3378 cm^{-1} broad band is assigned to the stretching of H bridges attributed to the interaction between physically adsorbed water and surface oxygen; ii) vibrations around 1641 cm^{-1} are attributed to the bending of the OH group in adsorbed water; iii) vibrations reflected at 1000 cm^{-1} are assigned to the asymmetric stretching vibrations characteristic of Si–O (Si) and Si-O (Al) bridge bonds in TO_4 tetrahedra belonging to aluminosilicates; iv) the 665 cm^{-1} band is assigned to the symmetrical stretching vibrations of the Si-O-Al bond bridges.
SEM image of LTA zeolite deposited over the alumina tubes for different maturation times (Fig. 2) shows the crystallization habits of the as-synthesized zeolite. In general, the sample consists of particles aggregates and isolated ones with well-developed faces and defined edges showing cubic and, in some cases, cubic-octahedral shapes. The crystal shape observed is consistent with the assigned space group *Fm3c* for LTA zeolite. Increasing the maturation time increases the homogeneity of the zeolite layer. Experiments are on-going to characterize the permeability of the prepared membranes towards methanol/water mixtures.

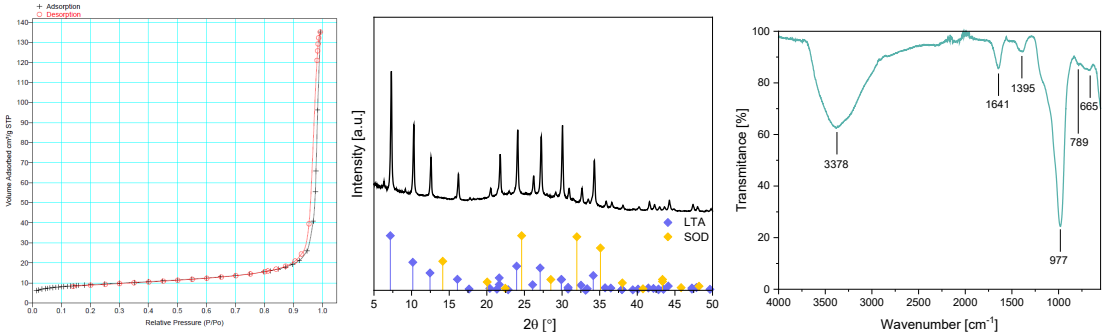

Figure 1 - A) N_2 adsorption-desorption isotherm; B) XRD analysis; C) FT-IR analysis

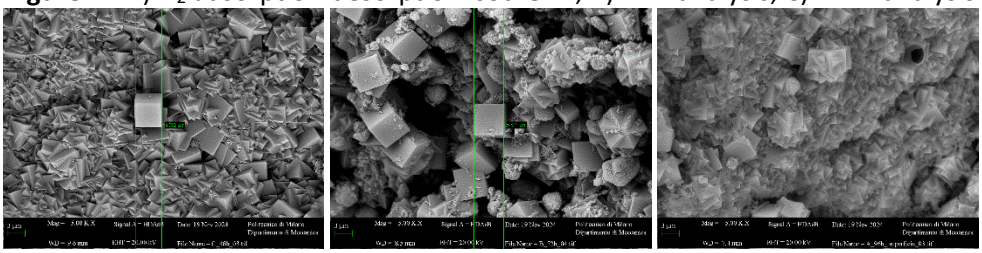

Figure 2 - SEM images of alumina coated tubes at different maturation times: 48h, 72h, 96h (5.00kX)

References

1. M. Seshimo, B. Liu, H. Ryeon Lee, K. Yogo, Y. Yamaguchi, N. Shigaki, Y. Mogi, H. Kita, S. Nakao, *Membrane* **2021**, *11*, 505
2. W. Yue, Y. Li, W. Wei, J. Jiang, J. Caro, A. Huang *Angewandte Chemie - International Edition* **2021**, *60*, 18289
3. B. Liu, H. Kitaa, K. Yogo, *Sep Purif Technol* **2020,** *239*, 116533
4. A. Jacas-Rodríguez, P. Rodríguez-Pascual, D. Franco-Manzano, L. Contreras, C. Polop, M.A. Rodriguez, *Sci Eng Compos Mater* **2020**, *27*,236
5. W. Mozgawa, M. Król, K. Barczyk, K. *CHEMIK* **2011**, *65*, 667