

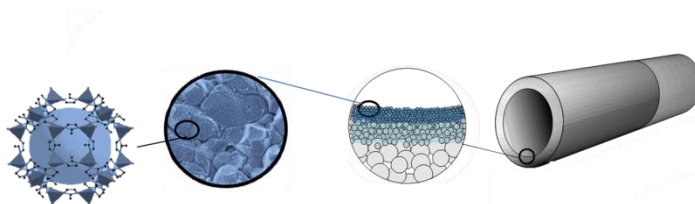
1- Rational design of porous ceramic and hybrid materials and membranes

An innovative Approach for the Preparation of Confined ZIF-8 Membranes by Conversion of ZnO ALD Layers

Journal of Membrane Science 475 (2015) 39-46

Involved MCP researchers: Anne Julbe, Martin Drobek

An innovative eco-friendly approach has been developed for the synthesis of ZIF-8-based nanocomposite membranes. The method involves the Atomic Layer Deposition (ALD) of ZnO thin films on the grains of a macroporous ceramic support and their subsequent conversion to ZIF-8 using a 2-methylimidazole/methanol solution and solvothermal conditions.



Despite of applying extremely low quantity of chemicals, reproducible and good quality ZIF-8-based membranes have been obtained, in which the ZIF-8 material was fully confined within the ceramic support macropores, thus leading to enhanced thermo-mechanical strength. A judicious choice of both the deposition conditions of ZnO layers and the solvothermal treatment parameters for their subsequent conversion to ZIF-8 were the key points for validation of this original protocol and evaluation of its potential for up-scaling on tubular industrial supports. The physico-chemical characterization of the ZIF-8/ZnO/ α -Al₂O₃ nanocomposite membranes was completed by a study of their gas transport properties. Reproducible ZIF-8/ZnO/ α -Al₂O₃ nanocomposite membranes were produced and tested in the separation of binary gas mixtures: membranes were found to extract H₂ from H₂/CO₂ and H₂/CH₄ equimolar gas mixtures with selectivities of about 7.8 and 12.5 respectively, measured at 100°C.

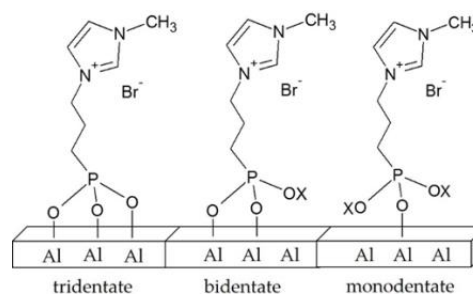
Design of Phosphonated Imidazolium-Based Ionic Liquids Grafted on γ -alumina: Potential Model for Hybrid Membranes

Int. J. Mol. Sci. 17 (2016) 1212

Collaborations: University of Montpellier - ICGM

Involved MCP researchers: Martin Drobek, André Ayrat, Anne Julbe

Imidazolium bromide-based ionic liquids bearing phosphonyl groups on the cationic part were synthesized and grafted on γ -alumina powders. These powders were prepared as companion samples of conventional mesoporous γ -alumina membranes, in order to favor a possible transfer of the results to supported membrane materials. Effective grafting was demonstrated using EDX, N₂ adsorption measurements, FTIR spectroscopy and a special attention was paid to ³¹P and ¹³C solid state NMR spectroscopy.



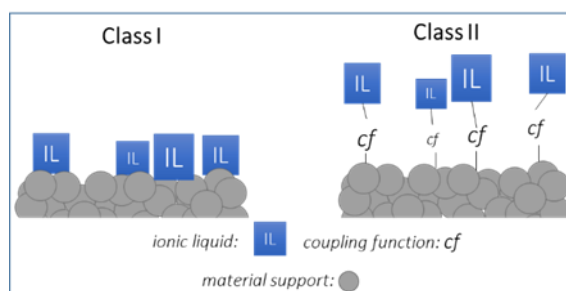
Controlled grafting of dialkylphosphonate-based ionic liquids on γ -alumina: design of hybrid materials with high potential for CO₂ separation applications

RSC Advances 9 (2019) 19882-19894.

Collaborations: ICGM- University of Montpellier ; IRCELyon- Villeurbanne

Involved MCP researchers: Martin Drobek, Anne Julbe

This work provides a detailed study on grafting reactions of various dialkylphosphonate-based ILs. A special attention has been devoted to a comprehensive investigation on how the nature of the anion, and the organic spacer composition (hydrophilic or hydrophobic groups) could impact on the grafting densities and bonding modes of phosphonate-based ILs anchored to γ -alumina (γ -Al₂O₃) powders. For the first time, the bonding of phosphonate-based ILs with only surface hexacoordinated aluminum nuclei was established using both solid-state ³¹P-²⁷Al D HMQC and ³¹P NMR experiments. It has been demonstrated that the grafting of dialkylphosphonate-based ILs is competing with a hydrolysis and/or precipitation process which could be attractively hindered by changing the anion nature: bis(trifluoromethane) sulfonylimide anion instead of bromide. In addition, independently of the chosen spacer, similar reaction conditions led to equivalent grafting densities with different bonding modes configuration. The CO₂ physisorption analysis on both pure ILs and grafted ILs on alumina powders confirmed that the initial sorption properties of ILs do not change upon grafting, thus confirming the attractive potential of as-grafted ILs for the preparation of hybrid materials in a form of selective adsorbers or membranes for CO₂ separation applications.



Lanthanum manganite perovskite ceramic powders for CO₂ splitting: Influence of Pechini synthesis parameters on sinterability and reactivity
Ceramic international 45(2019) 15636-15648

Collaborations: CNRS-PROMES

Involved MCP researchers: Martin Drobek, André Ayrál, Anne Julbe

Solar-driven thermochemical splitting of CO₂ and H₂O using the redox properties of ceramic oxides is a promising option for the massive production of synthetic fuels without greenhouse gas emission and with complete recycling of chemical intermediates. The development of relevant redox oxide pairs with optimum formulation and design is a real challenge for the implementation of this attractive energy production technology. Redox oxide pairs offering both high redox properties and easy shaping ability have thus to be identified. In this work a series of (La,Sr)(Mn,X)O₃ and (La,Ca)(Mn,X)O₃ powders with X= Al, Mg, Ga or Cr have been prepared by Pechini-derived methods. In particular, the impact of the synthesis parameters and type of dopant (X) on the physicochemical characteristics and reactivity of the powders (sinterability and redox properties) has been investigated. The results offer a relevant control over the synthesis / structure / properties relationships of the perovskite powders as crucial parameters targeting both the best perovskite formulations and design to be possibly integrated in solar thermochemical reactors.

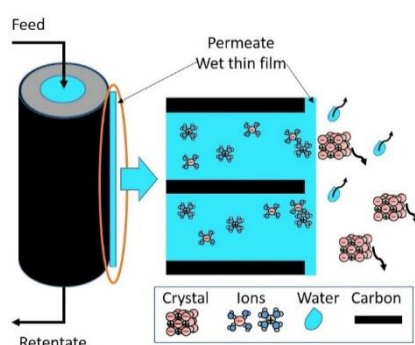
Fine Control of NaCl Crystal Size and Particle Size in Percrystallisation by Tuning the Morphology of Carbonised Sucrose Membranes
J. Membr. Sci. 567 (2018) 157-165

Collaborations: The University of Queensland-Australia

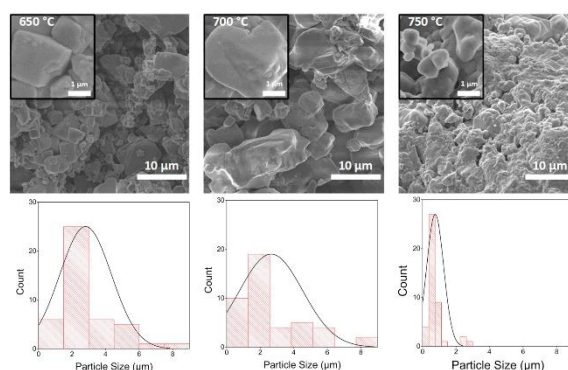
Involved MCP researchers: Anne Julbe

This work investigates the morphological features of porous carbon membranes and operation effects for the percrystallisation of NaCl. The carbon membranes were prepared by dip coating of α -alumina tubes in a sucrose solution, followed by a post vacuum-assisted impregnation and carbonisation in an inert gas atmosphere. The carbonisation temperature played an important role,

as the highest pore volume and wet contact angle were achieved at the highest carbonisation temperature of 750 °C. In turn, this created hydrophobic carbon membranes delivering the highest water flux of 33 L m⁻² h⁻¹ (NaCl 17.5 wt%) and NaCl flux of 6.9 kg m⁻² h⁻¹. The solvent (water) and the solute (NaCl) crystals were separated in a single-step in a wet thin-film formed on the permeate face of the membrane under pervaporation conditions, delivering almost pure water (> 99%) and dry NaCl crystals. The carbon membrane with the highest water flux delivered the smallest NaCl crystallite sizes, the smaller particle sizes, and the narrowest particle size distribution (< 2 μm). This was attributed to the fast water evaporation rate from the wet thin-film, as crystal growth rate was reduced and NaCl particle aggregation was restricted. A finer control of NaCl crystallite and particle size was achieved by tailoring the morphological features of the carbon membranes and operating at the lowest vacuum pressure.



Idealized illustration of the membrane percrystallisation mechanism



Morphology and size of NaCl particles produced by percrystallisation vs. membrane carbonisation temperature. (Percrystallisation conditions: 18 mbar permeate pressure, feed solution T°= 37 °C and [NaCl]=17.5 wt%)

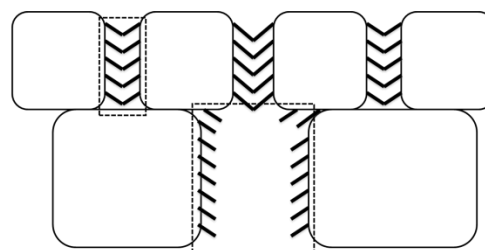
Novel concept for the preparation of gas selective nanocomposite membranes

Eur. Phys. J. Special Topics 224 (2015) 1923–1935

Collaborations: CTI SA, Specific Polymers

Involved MCP researchers: Anne Julbe, Martin Drobek, André Ayrál

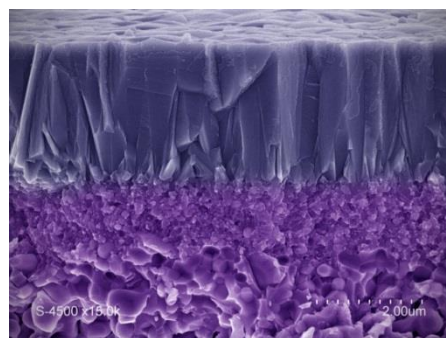
In this work we report on a novel concept for the preparation of gas selective composite membranes by a simple and robust synthesis protocol involving a controlled in-situ polycondensation of functional alkoxysilanes within the pores of a mesoporous ceramic matrix. This innovative approach targets the manufacture of thin nanocomposite membranes, allowing good compromise between permeability, selectivity and thermomechanical strength. Compared to simple infiltration, the synthesis protocol allows a controlled formation of gas separation membranes from size-adjusted functional alkoxysilanes by a chemical reaction within the mesopores of a ceramic support, without any formation of a thick and continuous layer on the support top-surface. Membrane permeability can thus be effectively controlled by the thickness and pore size of the mesoporous layer, and by the oligomers chain length. The as-prepared composite membranes are expected to possess a good mechanical and thermomechanical resistance and exhibit a thermally activated transport of He and H₂ up to 150°C, resulting in enhanced separation factors for specific gas mixtures e.g. FH₂/CO~10; FH₂/CO₂~3; FH₂/CH₄~62.



Coupling microwave-assisted and classical heating methods for scaling-up MFI zeolite membrane synthesis

Collaborations: Hyflux-Ceparation-The Netherlands
Involved MCP researchers: Anne Julbe, Martin Drobek

Silicalite-1 (S-1) nano-seeds obtained by microwave-assisted (MW) heating have been used to coat industrial supports and to up-scale the synthesis of MFI zeolite membranes synthesis by secondary growth applying classical heating (CH) method. The MW-assisted method was adapted/optimized for fast synthesis and high yield of uniform and non-aggregated S-1 nano-seeds suspensions which were directly used for seeding macroporous industrial $\alpha\text{-Al}_2\text{O}_3$ based supports by dip-coating. The CH secondary growth yielded uniform MFI membranes, by applying optimal reaction conditions while minimizing the reaction time and consumption of chemicals. The protocol coupling MW-assisted and classical heating in zeolite membrane synthesis revealed high reproducibility and has been validated on various industrial ceramic supports: single tubes (Pall-Exekia, Atech, Inocermic, CTI) and also single capillaries and capillary bundles, from Hyflux CEPARation Technologies, providing a higher surface/volume ratio (typically $S/V > 100 \text{ m}^2/\text{m}^3$). Membrane homogeneity has been validated by both SEM and single gas permeation measurements with N_2 and SF_6 . The N_2/SF_6 ideal selectivity was used to predict the ethanol/water separation factor of the prepared MFI membranes.

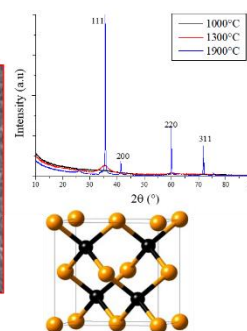
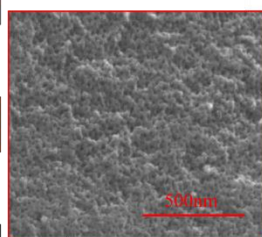
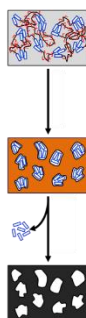


Highly crystalline silicon carbide of controlled mesoporosity

Mater. Chem. Phys. 250 (2019) 123208

Collaborations: Institut de Chimie Séparative de Marcoule
Involved MCP researchers: Julien Cambedouzou

The control of porosity in silicon carbide (SiC) at the mesoporous scale is a major concern for a range of separation applications. It was recently reported that mesoporous amorphous SiC could be synthesized by templating polycarbosilane precursors around polymeric templates, and after pyrolysis at 1000°C under inert atmosphere. In this publication, we report the synthesis of highly crystalline mesoporous $\beta\text{-SiC}$ based on the same approach, but involving much higher temperature pyrolyses (up to 1900°C).



The structure evolution with regards to the pyrolysis temperature is carefully studied by means of various analytical tools. Finally, the influence of different synthesis parameters on the control of the mesoporous structure is also discussed. It is shown for the first time that pure mesoporous $\beta\text{-SiC}$ with 10 nm pore diameter and a specific surface area larger than $50 \text{ m}^2/\text{g}$ can be obtained with a very high degree of crystallinity.