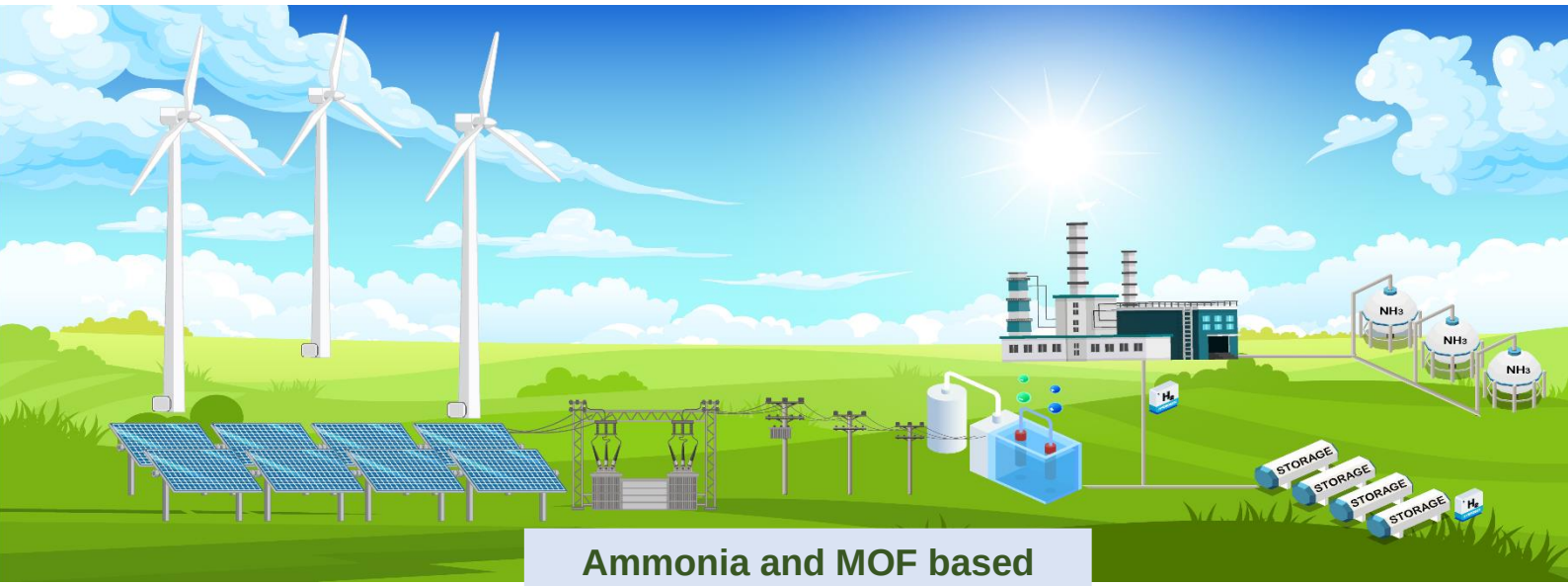

Ammonia and MOF based Hydrogen storage for Europe

Welcome to this second AMBHER newsletter. AMBHER is a four-year project targeting the development of high-performance, cost-effective hydrogen storage technologies. Two different technologies are addressed: novel nanoporous Metal Organic Frameworks (MOFs) for the short time hydrogen storage in vessels for transport applications and membrane reactors integrating new catalysts and membranes for ammonia synthesis for long term hydrogen storage media.

The present newsletter is the second release of the biannual letter that will be published by AMBHER presenting the progress on the project and highlighting information related to the R&D fields addressed. Hope you will find the info in this newsletter interesting. On our website www.ambherproject.eu you will find public presentations, all the public deliverables of the project and many other interesting news. Stay tuned!

In this number

Funded by the European Union

Ezgi Onur Sahin from the Max-Planck-Institut für Kohlenforschung (MPI KOFO) is working as a postdoctoral researcher in the Department of Diffraction and Spectroscopy where she also worked during her Ph.D. She completed her Ph.D. as a member of the International Max Planck Research School (IMPRS) SurMat doctoral program in 2021 on local structure analysis of non-crystalline photocatalysts by X-ray total scattering mainly by synchrotron radiation. She obtained her bachelor's and master´s degrees in 2013 and 2016 from the Metallurgical and Materials Engineering Department at Middle East Technical University in Ankara where she worked as a teaching assistant. She has a previous background in the industry working as an R&D leader in the ceramics and advanced materials department. She has a broad range of interest areas extending from alloys as battery materials to ceramic semiconductors, whereas the structure-performance relationship stays in the focus. In the context of the project, she will be involved in key materials and components for long-term H2 storage and will be working on the development of non-ambient sample environments for in situ/operando materials characterization by diffraction and spectroscopic techniques.

Hello new AMBHER colleagues, I am Iolanda Gargiulo and I come from the southern part of Italy, Napoli. I have just started to fill the role of PhD student at TU/e after I got my MSc degree in chemical engineering last May at University of Salerno. The place where I am working now (Eindhoven University of Technology) is not new for me, since I have spent my training period for the master thesis in the same department (SPE group) last year, during my period of Erasmus exchange, where I found a friendly, kind and serious environment!

I am very happy to be part of the new European Project, AMBHER, that will be a new challenge for me, since it will test my abilities and my skills. Particularly I will be focus on one part of all the project, namely the development of long-term Hydrogen storage technologies through the generation of Ammonia. I will be involved with the testing of new innovative carbon membranes as well as the testing of new friendly catalyst materials with the final aim to be integrated into a membrane reactor for the synthesis of Ammonia. Indeed, I will be involved in the design and fabrication of the reactor with the final aim of testing for ammonia production. This architecture will allow an effective operation at much lower temperatures and pressures compared to the ongoing Haber-Bosch process.

Elena Vicente Cayuela (chemist) is a PhD student in the Energy Conversion and Storage group at ITQ-CSIC. She received a B.Sc. in Chemistry from the University of Murcia in 2020, including a 5 month Erasmus scholarship stay in the Ghent University, and a M.Sc. in Sustainable Chemistry from Universitat Politècnica de València in 2022. She joined the Energy Conversion and Storage group in 2022 to develop her master thesis, that focused on heterogenous catalysis using electrocatalytic membrane reactors for the RWGS reaction. Her current work as a PhD student is focused on the heterogeneous catalysis and the use of electrocatalytic membrane reactors for diverse reactions. She has a previous background of one and a half years working as an R&D consultant in various topics.

Margot Anabell Llosa Tanco is researcher at TECNALIA Membrane Technology. In January of 2017 she obtained her second doctorate in Chemical and Biological Engineering awarded by the University of Porto-Portugal, with the thesis titled “Preparation and Characterization of phenolic-resin based composite-Carbon Molecular Sieve Membranes for the separation of gases”. In 1996, she obtained her first doctorate in Chemistry awarded by the University of Surrey-England, with the thesis titled “Thermodynamics of Complexation of Macrocyclic ligands-Crown ethers with alkali metal cations “. For 10 years (1998-2008) she has been working as a researcher at the Institute of Advanced Science and Research (AIST) in Japan, in the separation and detection of harmful compounds of water and in the development of inorganic membranes for the separation of gases especially in the membranes of Palladium for the separation of hydrogen. In February 2014 she joined TECNALIA Research & Innovation as principal investigator in "Membrane Technology & Process Intensification" area. She is the co-author of 45 articles in top-level journals, 15 patents, she has contributed to numerous international conferences.

Dr. Alfredo Pacheco Tanaka from TECNALIA Membrane Technology group obtained his PhD in Chemistry at the University of Surrey, UK (1996). From 1997, he was researcher at AIST (Japan) for 11 years working in a) materials for capture and detection of harmful compounds, and b) preparation Pd-based membranes for gas separation. In 2008, he moved to Portugal to do research on carbon membranes synthesis of nanoparticles and development of new catalysts, graphene for catalyst, solar cells and composites containing graphene. From 2012 he is at TECNALIA Research & Innovation being responsible of the preparation of inorganic membranes for gas separation. Dr Pacheco has more than 110 research papers and 20 patents.

On Catalysts

Introduction

AMBHER project aims to develop innovative environmentally friendly catalyst materials that can be used in a membrane reactor for ammonia synthesis at much lower pressures and temperatures compared to the Haber-Bosch (H-B) process. The catalysts developed will be capable to overcome the rate limiting step for the process, identified as the activation of the stable N≡N bond (945 kJ mol^{-1}). Ambitious and extremely challenging key targets are: (1) to develop catalysts capable of operating at pressures below 20 bar and temperatures below 250 °C with NH_3 production rates superior to 8 mmol $NH_3 g^{-1} h^{-1}$ offered by state-of-the-art catalysts; (2) to scale-up the synthesis method ensuring the necessary quantity of catalyst for the validation of the AMBHER at TRL5. Moreover, conductive Periodic Open Cellular Structures (POCS) will be activated, by coating techniques, with the most promising catalyst for integration with selective ammonia membranes in a membrane reactor. Conductive POCS fit well in the membrane reactor concept as it is a way to improve mass transfer toward the membranes and heat transfer for a more uniform temperature operation reducing risk of hot spot and improving efficiency of the conversion. Several research teams are involved in the framework of WP3 (Key materials and components for long-term hydrogen storage) to achieve the objectives of the AMBHER project.

UNIVERSITEIT UTRECHT (UU) - Nanoconfined and highly dispersed Metal hydride-based catalysts.

UU has synthesized, characterized and tested several first-generation catalysts for ammonia synthesis which were based on intercalated potassium hydride (KH), sodium hydride (NaH) and lithium hydride (LiH). These catalysts have shown activities up to 1.5 mmol NH_3 g^{-1} h^{-1} at 10 bar pressure and 400°C. The focus will lie on further improvement of these catalysts towards an increased activity, mainly at lower temperatures (<300°C). X-ray powder diffraction has shown the effect of temperature on the degree of intercalation, which is expected to strongly affect the catalytic performance of such catalysts, and temperature programmed desorption has been used to track the hydrogen formation as a result of hydride decomposition, which is expected to coincide with the intercalation process.

THE UNIVERSITY OF BIRMINGHAM (UoB) - Metal-nitrogen-hydrogen (M-N-H) mixed anion catalysts.

At UoB, the focus has been on investigating catalysts for ammonia synthesis at low temperatures, with a particular emphasis on lithium hydride and lithium nitride hydride catalysts, as well as strontium lithium nitride hydride. A series of calcium nitride hydride catalysts with mixed imide-nitride-hydride composition were also developed. Complexes

of these catalysts with ruthenium displayed promising activities for ammonia synthesis, reaching up to 11 $mmol_{NH3}$ g^{-1} h^{-1} at 450°C and 2 bar of $3H_2$:N_2.

SPANISH NATIONAL RESEARCH COUNCIL (CSIC) - Transition metal (TM) nanocluster and nanoparticle-based catalysts.

CSIC have focused on two different approaches for the development of ammonia synthesis catalysts, both transition metal (TM) based: TM nanocerias and perovskites (e.g. Ru or Fe or Mo doped-$Ce_{0.91}Pr_{0.07}O_{2-\delta}$) and TM sulfide nanoclusters ($NH_4[Mo_3S_{13}]nH_2O$). Some of the synthesized catalysts were exposed to different treatments: exsolution for TM nanocerias and nitridation for TM nanoclusters. First catalytic tests have shown noticeable NH_3 synthesis activity for the TM nanocerias catalysts. More precisely, best performing catalyst, a Ru-doped ceria, has shown an NH_3 production of 3 $mmol_{NH3}$ g^{-1} h^{-1} at 400 ºC and 30 bar.

JOHNSON MATTHEY PLC (JM) - Novel Ru based catalysts.

JM has identified a ruthenium-based catalyst formulation. This catalyst can be shaped and is prepared by scalable routes which makes it a promising candidate for ammonia synthesis under conditions milder than typical Haber Bosch. Activity is very low at temperatures below 250°C, activity really starts to be significant at temperatures above 350°C. Work is currently under progress to improve this Ru-based catalyst by adjusting the metal loadings especially the dopant contents and optimizing the preparation route.

MAX PLANCK INSTITUT FUER KOHLENFORSCHUNG (PMI) & UNITED KINGDOM RESEARCH AND INNOVATION (UKRI) - In situ and operando catalyst characterization.

MPI and UKRI are working in close collaboration with the other institutions for an in-depth study of the property-performance relationship of the proposed catalysts using advanced in-situ and operando catalyst characterization techniques. UKRI have performed preliminary experiments to demonstrate the suitability of neutron techniques in studying catalysts from CSIC and UU. A preliminary neutron scattering experiment with KHC24 catalysts from UU has detected hydrogen mobility in the sample. Next hydrogen will be studied in the material using inelastic scattering. By high resolution XRD, ammonia synthesis conditions have been found to increase the unit cell volume of $CePrRuO_2$ catalysts from CSIC, whilst maintaining a fluorite symmetry in two distinct phases. A preliminary neutron diffraction study of the catalyst as received has resolved the oxygen stoichiometry of the material. An application has been made for a full day of ex-situ neutron diffraction experiments comparing samples before and after activation of various catalysts with differing catalytic activity, aiming to link oxygen stoichiometry to catalysis.

CONSIGLIO NAZIONALE DELLE RICERCHE (CNR-ITAE) & ENGIE - Thermal conductive Periodic Open Cellular Structures (POCS).

CNR-ITAE and ENGIE are collaborating to develop conductive Periodic Open Cellular Structures (POCS). The samples have been designed in a cylindrical shape with different sizes (diameter = 1cm – 2,66cm, Length = 1.5 -10cm) and with various structural characteristics (cell type, density, strut diameter...). The POCSs have been manufactured by Laser Powder Bed Fusion (LPBF) at ENGIE Laborelec and delivered to the CNR-ITAE for

catalytic activation. From the manufacturability point of view, the 3D printed samples closely matched their CAD designs. Computational Fluid Dynamic (CFD) simulations have been also carried out at ENGIE Crigen to address theoretical pressure drop and heat/mass transfer. At CNR-ITAE a coating method based on a dip/spin technique has been developed and optimized to deposit thin, homogeneous and stable catalytic layers on POCS surface. The method was scaled up to prepare POCS with suitable geometry for the integration with ammonia selective CMS membranes.

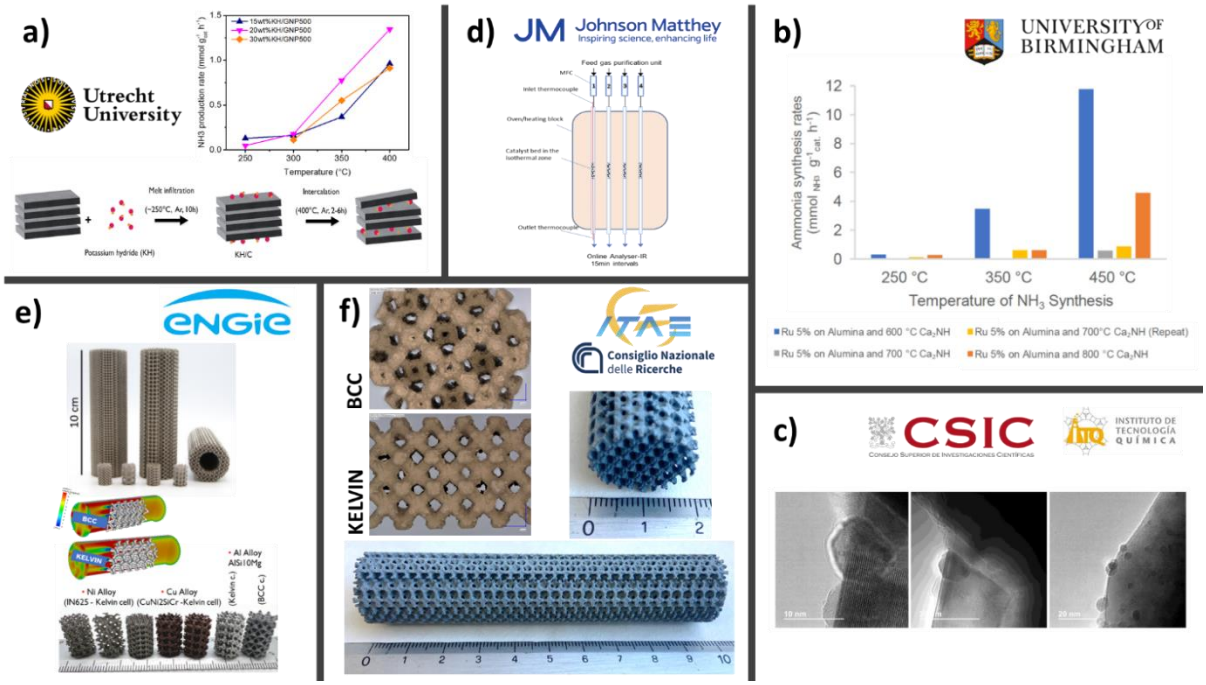

Figure 1. a) Intercalation process scheme and NH_3 production rate as a function of temperature for KH/GNP500 showing the effect of metal weight loading on the catalytic performance of the alkali metal hydride carbide catalysts. Reaction conditions: 1MPa, 250-400°C and SV = 36,000 mL g_{cat}^{-1} h^{-1} N_2:H_2 1:3; b) NH_3 synthesis rate of Ca_2NH (synthesized between 600 – 800 °C) with Ru 5% on alumina (4:1) catalysts at different temperatures; c) TEM observations of Ru doped-$Ce_{0.91}Pr_{0.07}O_{2-\delta}$ after exsolution treatment at 700 °C at 10 nm (left), 20 (middle) and 20 nm (right) scale; d) Schematic of JMs ammonia synthesis multi-reactor; e) Several large and small POCS printed in different metallic materials (Al, Ni and Cu alloys) and CFD calculations about pressure drop through BCC and Kelvin cells; f) BCC and KELVIN POCS activated by dip/spin coating method.

On Membranes

One of the objectives of AMBHER is the development of innovative membranes for selective separation of NH_3 during production process: Carbon microporous membranes, product of the carbonization of thermosetting polymers. The mechanism of gas permeation is the combination of molecular sieving (the gases smaller that the pores will pass, diameter of the pores are < 0.5 nm) and adsorption diffusion based on the interaction between the gas and the pores of the membrane (diameter of pores 0.5 – 0.9 nm). Tecnalia prepared supported Alumina-Carbon Molecular Sieve Membranes (Al-CMSMs) by the one dip-dry-carbonization method. A porous asymmetric alumina support was dipped in a dipping solution containing novolac phenolic resin (carbon precursor),

boehmite (AlO-OH) as Al source and curing agents. After drying at 95 °C the membranes are carbonized under N_2 environment. The pore size and presence of functional groups in the carbon structure can be modified with the carbonization temperature. During the carbonization, functional groups are gradually removed making the membrane more hydrophobic [1-3]. Two Al-CMSM were prepared using equal dipping solution composition and carbonized at 500 and 700 °C to study the effect of the carbonization temperature on the permeation behaviour. At 500 °C, the membrane is hydrophilic because of the presence of oxygen containing groups in the carbon and boehmite structures which can form hydrogen bonds with NH_3 (N_2 and H_2 cannot do it). Single gas N_2, H_2 and NH_3 permeance at two bar pressure difference at temperatures relevant in AMBHER for Al-CMSM carbonized at 500 and 700 °C are shown in Figure 1. In both cases, N_2 and H_2 permeances increases with the temperature.

As far as NH_3 is concern for the hydrophilic membrane (500 °C), the permeance decrease with the temperature, however, for the hydrophobic membrane (700°C), the opposite is observed. In the hydrophilic membrane the main mechanism of transport seems to be adsorption diffusion due to the interaction with the functional groups in the membrane. For the hydrophobic membranes, the permeation is mainly by molecular sieving.

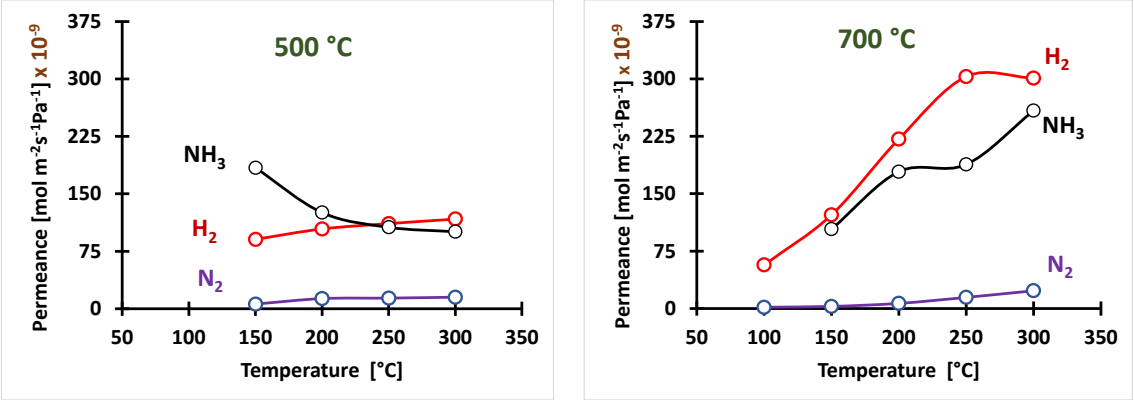

Figure 1.- Single gas permeation of membranes carbonized at 500 °C (left) and 700 °C (right) in function of the temperature of permeation at two bar pressure difference

The objective of AMBHER membranes are perm-selectivity NH_3/N_2 and NH_3/H_2 > 50 and >10 respectively with the Al-CMSM, these targets are not accomplished because the NH_3 adsorption at these temperatures is very low due to the weak hydrogen bond interaction between the functional groups of the membrane and NH_3. In the next period, permeation using relevant mix gases at higher pressures(< 20 bar) will be carried out. It is expected that the NH_3 selectivity will increase due to the higher content of NH_3 adsorbed as the pressure increases.

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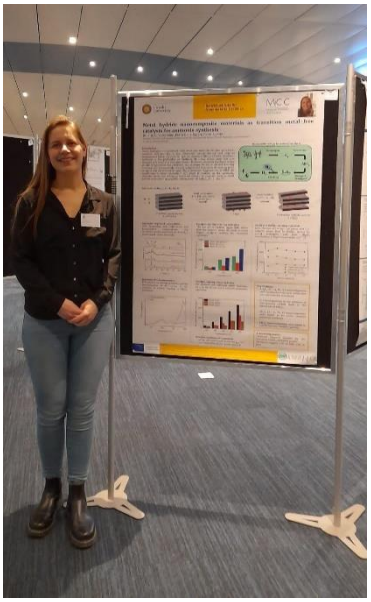
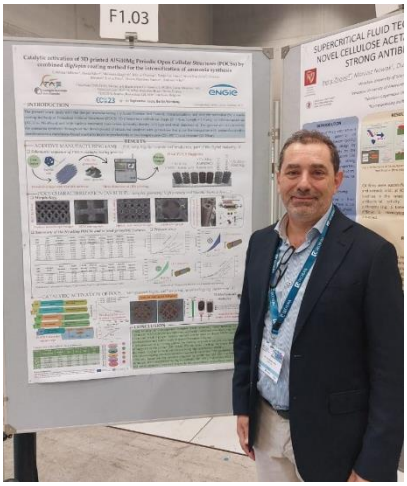
Dissemination and events

The AMBHER project was presented at the 24th edition of the Netherlands' Catalysis and Chemistry Conference (NCCC) in Noordwijkerhout. The NCCC offers a unique and international forum to discuss and exchange innovative ideas with both academic and industrial scientists in a broad area of catalysis and chemistry research.

PhD candidate Juliette Verschoor from Utrecht University, one of the institutes responsible for work package 3, presented a poster on their progress on the development of transition metal free ammonia catalysts. On the topic of Heterogeneous Catalysis, there were multiple interesting discussions on the subject of ammonia synthesis and its use as an alternative hydrogen carrier.

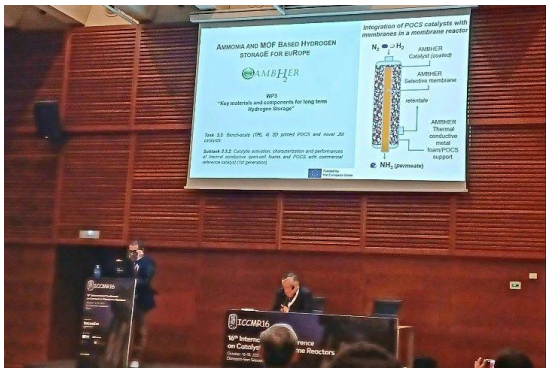


The AMBHER project has been presented by Iolanda Gargiulo, PhD student of the TU/e Chemical Engineering and Chemistry, at two conferences, the 18th edition of the Netherlands Process technology Symposium Enschede, and at the 2nd Symposium on Ammonia Energy in France. in both cases she presented the modeling of membrane reactors for ammonia production. The presentation is available in the website of the project together with other material



AMBHER project is being presented at the 14th European Congress of Chemical Engineering #ECCE2023 in Berlin. Antonio Vita is presenting a work on catalytic activation of 3D printed #POCs for #ammonia production.

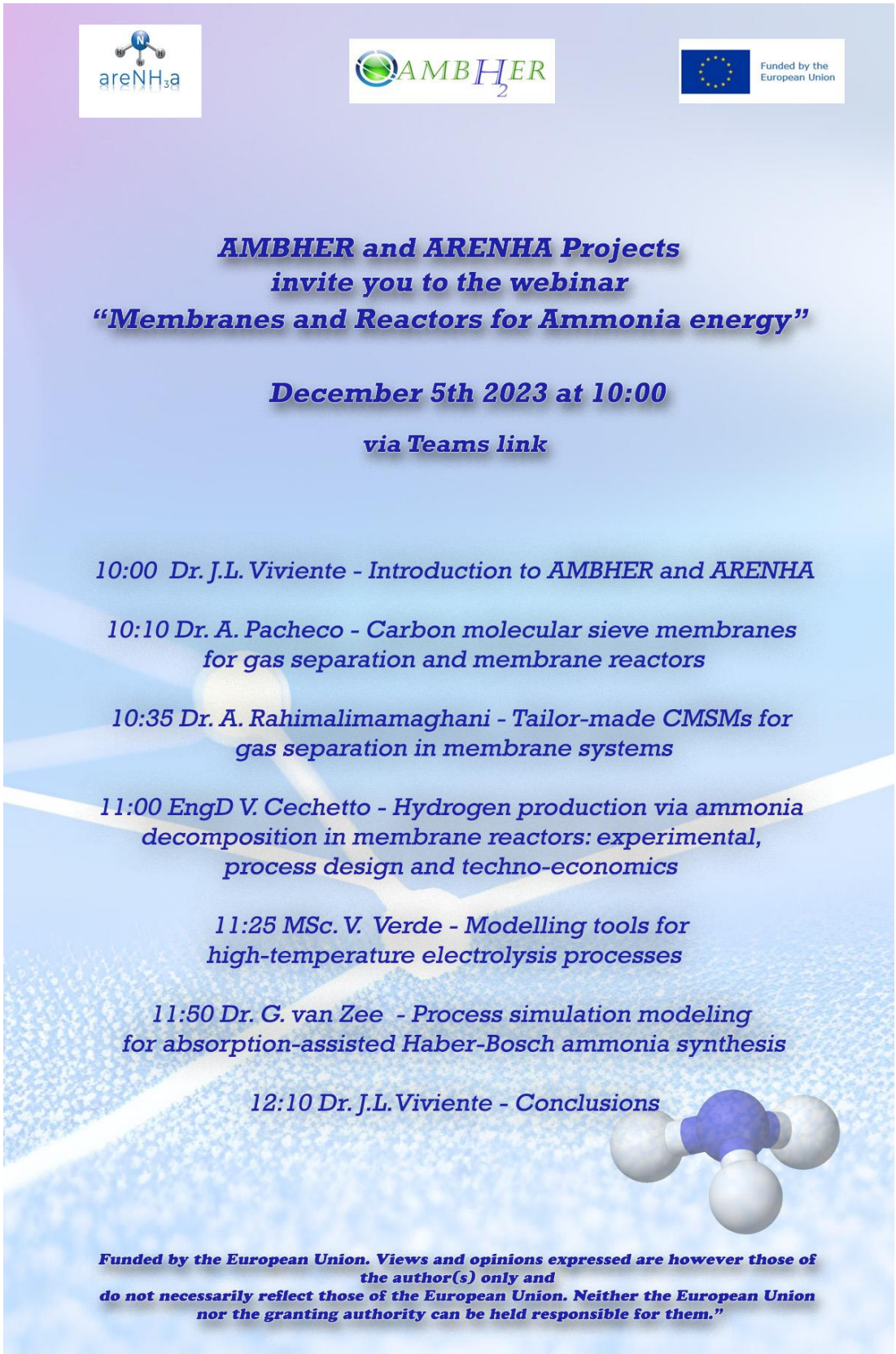
The AMBHER project has been presented by Antonio Vita, Angela Mary Thomas and Iolanda Gargiulo at the 16th International Conference on Catalysis in Membrane reactors, organized by TECNALIA in San Sebastian, October 2023. Below a few pictures



AMBHER First webinar

The AMBHER project has organized a first webinar on Catalysis for ammonia production. The webinar has been followed by a number of people with nice discussions with the speakers. The recordings of the webinar are available on the website of AMBHER.

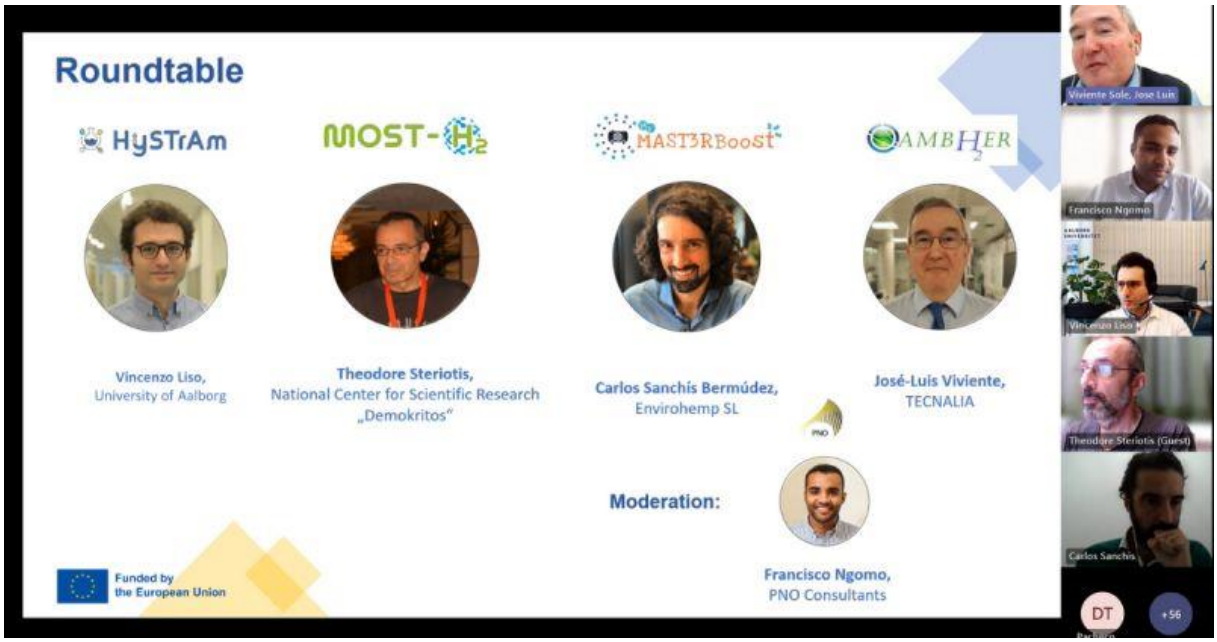
A second webinar on AMBHER project, related to membranes is organized for December 5th. The flyer is attached below.

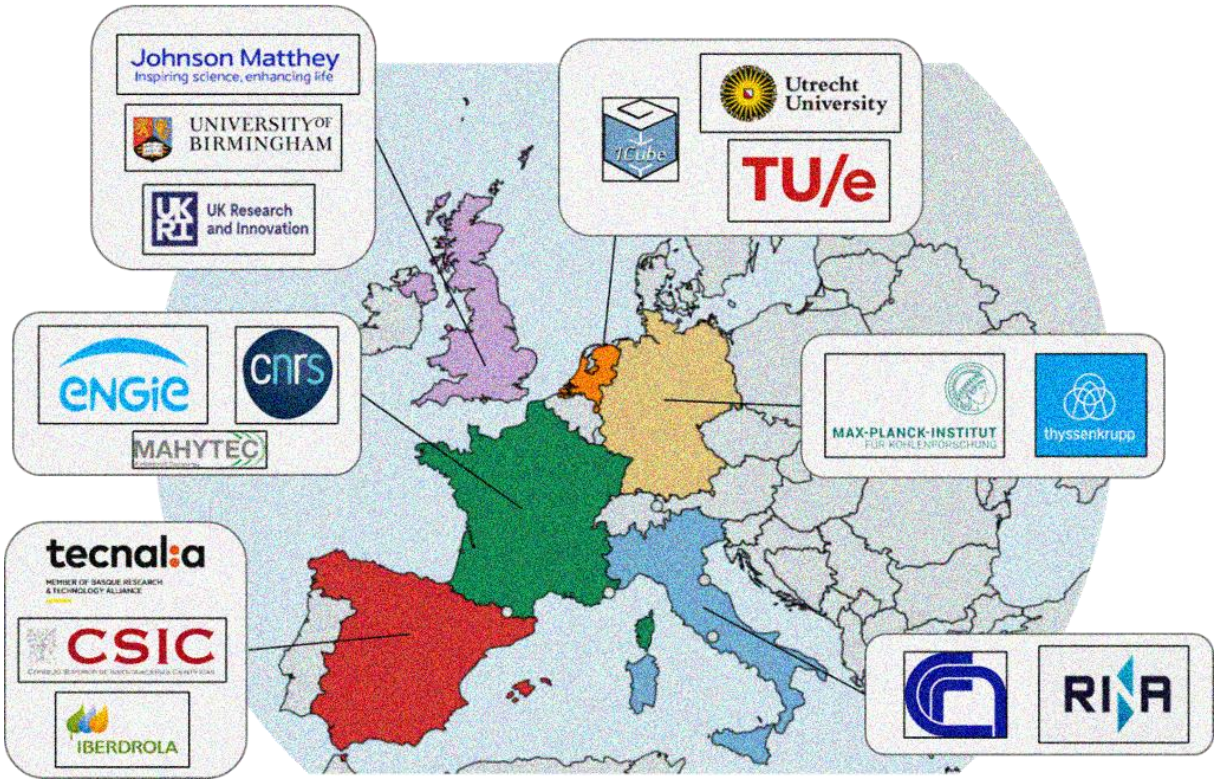


AMBHER Joint webinar

The AMBHER project participated in a joint webinar with 3 other European projects.

During the event HySTrAm, MOST-H2, AMBHER project and MAST3RBoost project explored the forefront of European innovation that is shaping #HydrogenEconomy.





Project details:
Project number: 101058565
Project name: Ammonia and MOF Based Hydrogen storagE for euRope
Project acronym: AMBHER
Call: HORIZON-CL4-2021-RESILIENCE-01
Topic: HORIZON-CL4-2021-RESILIENCE-01-17
Starting date: June 1st 2022
Duration: 48 months

UE funding: 4,915,870 Euro
COORDINATOR: Fundación Tecnalia Research & Innovation
Project Coordinator: José-Luis Viviente

Funded by the European Union

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