



AIZ Day 2022

International Workshop on Zeolites Science and Technology



24th - 25th of November 2022, Torino (Italy)

The Italian Zeolite Association (AIZ) and the Politecnico of Torino extend to the zeolites community a cordial invitation to attend the AIZ Day 2022 - Workshop on Zeolites Science and Technology, which will be held in Torino (Italy).

Venue

First Day (h 14:00 – 18:00): Dipartimento di Scienza Applicata e Tecnologia - DISAT, Politecnico di Torino, Corso Duca degli Abruzzi, 24 – 10129 Torino (TO)

Second Day (h 09:00 – 14:00): Dipartimento di Scienza Applicata e Tecnologia - DISAT, Politecnico di Torino, Corso Duca degli Abruzzi, 24 – 10129 Torino (TO)

Contributions to the Workshop

All interested authors are invited to submit a 1-page abstract regarding zeolite and related materials, prepared in accordance with the template available on AIZ website (www.aizeta.it).

www.aizeta.it

Invited Speakers

Giuseppe Cruciani, *Università di Ferrara*
Roberto Millini, *ENI*

Scientific Committee

Domenico Caputo (*AIZ President*)
Paola Lanzafame (*AIZ Secretary-Treasurer*)
Annalisa Martucci
Raffaele Pirone
Marco Piumetti
Stefano Zanardi

Local Organizing Committee

Raffaele Pirone
Marco Piumetti
Clarissa Cocuzza
Andrea Rizzetto

Secretariat

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Registration and Payment

All information regarding Registration and Payment are available on AIZ web site (www.aizeta.it).

Registration fees:

Full Delegates 120 euro (including Social Dinner Ticket and AIZ Membership Fee 2022)

Students 80 euro (including Social Dinner Ticket and AIZ Membership Fee 2022)

Accompanying persons 40 euro (including Social Dinner Ticket)

Accommodation

Details for accommodation are available on AIZ web site (www.aizeta.it) together with a list of the hotels located in the neighborhoods of Conference venue.

Key-dates

20/10/2022 Call for Abstracts

06/11/2022 Deadline for Abstract submission **[Extended to 11/11/2022]**

10/11/2022 Acceptance of contributions **[Extended to 14/11/2022]**

15/11/2022 Deadline for Payment of Registration Fee **[Extended to 16/11/2022]**

20/11/2022 Final Programme



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BOOK OF ABSTRACTS

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November 24th, Thursday

14:30-16:00 **Registration (BURDESE)**

15:10-15:30 **Opening Ceremony (AULA A1)**

15:30-17:15 **Session 1: Chair Domenico Caputo (AULA A1)**

15:30-16:15 **IL1 – Beyond TS-1: Synthesis of Ti-containing zeolites, Dr. Roberto Millini**

16:15 **01 - Surface modification in zeolite-templated carbons: a promising electrocatalyst for CO₂ reduction**

G. PAPANIKOLAOU, D. CHILLÈ, S. PERATHONER, G. CENTI, D. COZZA, M. MIGLIORI, G. GIORDANO, P. LANZAFAME

16:35 **02 - ZSM-5 surface modification via secondary SIL-1 synthesis and chemical etching**

GIORGIA FERRARELLI, ENRICO CATIZZONE, MASSIMO MIGLIORI, GIROLAMO GIORDANO

16:55 **S01 – Dual Function Materials for CO₂ capture and conversion**

ANDREA RIZZETTO, RAFFAELE PIRONE, SAMIR BENSaid, MARCO PIUMETTI

17:05 **S02 - Mesoporous silica used as support for lactate dehydrogenase enzyme: a strategy to obtain a prototype biosensor**

CLARISSA COCUZZA, VALENTINA CAUDA, CARMINNA OTTONE, MARCO PIUMETTI

17:15-18:00 **Coffee Break and Poster Session (RIGAMONTI)**

18:00-19:00 **AIZ Business**

20:00 **Social Dinner – Ristorante La Capannina**

November 25th, Friday

9:00-10:45 **Session 2: Chair Marco Piumetti (AULA A1)**

9:00-9:45 **IL2 - Zeolites as Sustainable Energy Materials, Prof. Giuseppe Cruciani**

9:45 **O3 - Complete engineering of the administration of a drug: mesoporous silica-based nanodevices for smart chemotherapy**

MARZIA DE SANTO, CATIA MORELLI, ANTONELLA LEGGIO, LUIGI PASQUA

10:05 **O4 - p-induced crystal-fluid interaction in natural zeolites with eri and off topologies**

TOMMASO BATTISTON, DAVIDE COMBONI, PAOLO LOTTI, G. DIEGO GATTA

10:25 **S03 - Design of 13X zeolite-based materials for 3D printing by direct ink writing**

ENRICA LUZZI, MARTINA SALZANO DE LUNA, GIOVANNI FILIPPONE, DOMENICO CAPUTO, PAOLO APREA

10:35 **S04 - Study on the oxygen content of BEA and BEA@SIL zeolite templated carbon reduction**

PAOLO BRUNO, GIORGIA FERRARELLI, DANIELA COZZA, ENRICO CATIZZONE, MASSIMO MIGLIORI, GIROLAMO GIORDANO

10:45-11:10 **Coffee Break (RIGAMONTI)**

11:10-13:10 **Session 3: Chair Luigi Pasqua (AULA A1)**

11:10 **O5 – Insight on MWW silicates: from the 2D precursors to the 3D calcined zeolites**

FRANCESCA ROSSO, ALESSIA AIRI, MATTEO SIGNORILE, EDDY DIB, SILVIA BORDIGA, SVETLANA MINTOVA, VALENTINA CROCELLÀ, FRANCESCA BONINO

11:30 **O6 – Moving towards circular economy: REE recovery from spent fluorescent lamps exploiting NH₄-13X zeolite cation exchange properties**

FRANCESCO COLOMBO, GIORGIA CONFALONIERI, MATTIA SISTI, GIANLUCA MALAVASI, ROSSELLA ARLETTI

11:50 **O7 – Exploring the possibility to use Li-exchanged zeolite as catalyst for CO₂ hydrogenation**

ELISABETTA M. CEPOLLARO, STEFANO CIMINO, LUCIANA LISI

12:10 **O8 – From powder to 3D shaped LTA zeolite for carbon dioxide capture**

MARGHERITA CAVALLO, MARCO D'AGOSTINI, NATALE G. PORCARO, MARCO PIUMETTI, GIORGIA FRANCHIN, PAOLO COLOMBO, FRANCESCA BONINO, VALENTINA CROCELLÀ

- 12:30** **09 - Zeolitic pigments in Capodimonte porcelain production**
- ASSUNTA CAMPANILE, BARBARA LIGUORI, DOMENICO CAPUTO, PAOLO APREA
- 12:50** **S05 – Self-standing nanoporous zeolite/cellulose deposits prepared with ultrafiltration for energy storage applications**
- LORENZO METILLI, HÉLOÏSE UGO, CYRIL PICARD, WILLIAM CHÈVREMONT, AND FRÉDÉRIC PIGNON
- 13:00** **S06 – Intensification effect on catalytic CO₂ hydrogenation to DME prompted by water-adsorbent systems**
- SERENA TODARO, FRANCESCO FRUSTERI, VESNA MIDDELKOOP, YORAN DE VOS, ERIK ABBENHUIS, GIJSBERT GERRITSEN, CATIA CANNILLA, GIUSEPPE BONURA

13:10-14:00 *Light lunch & Posters Session (RIGAMONTI)*

Poster (ATRIO)

P1 – Role of acid concentration in the chemical condensation of 2D MCM-22(P) precursor to 3D MWW zeolite

MARCO FABBIANI, AMINE MORSLI, GIORGIA CONFALONIERI, THOMAS CACCIAGUERRA, FRANÇOIS FAJULA, JULIEN HAINES, ABDELKADER BENGUEDDACH, ROSSELLA ARLETTI, FRANCESCO DI RENZO

P2 – Structural and computational study of zeolite-encapsulated UV filters

RICCARDO FANTINI, LORENZO MINO, MATTIA SISTI, MICHAEL FISCHER

P3 – Zeolite-rich composites for chromium removal from water

CARLO GRAVINO, BARBARA GALZERANO, ANTONIO PELUSO, DOMENICO CAPUTO, PAOLO APREA, BRUNO DE GENNARO

P4 – Electronic properties of neurotransmitters in a hybrid system with zeolite L

CRISTIANO INVERNIZZI, L. GRIMM, F. BIEDERMANN, G. TABACCHI, E. FOIS

P5 – From zeolite precursor to the moon: toxicological studies of simulated moon agglutinates

OLIMPIA TAMMARO, ANTONELLO MAROCCO, MICHELE PANSINI, GABRIELE BARRERA, PAOLA TIBERTO, PAOLO ALLIA, CHIARA BELLOMO, CRISTINA PAVANA, FRANCESCO TURCI, ROSSELLA ARLETTI, SERENA ESPOSITO

IL1

BEYOND TS-1: SYNTHESIS OF TI-CONTAINING ZEOLITES

Roberto Millini

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The discovery of Ti-Silicalite-1 (TS-1), claimed in the late 1970's, is a milestone in the long history of science and technology of zeolites. Its peculiar properties as an oxidation catalyst of various organic substrates with H₂O₂ under mild conditions, has allowed to improve, also from an environmental point of view, various processes, such as the hydroxylation of phenol to hydroquinone and pyrocatechol, the epoxidation of light olefins. (in particular, of propylene to the corresponding oxide), the ammoximation of cyclohexanone to cyclohexanone oxime. An extensive characterization of TS-1 allowed to unambiguously assess some important aspects (e.g., the effective incorporation of Ti in the silica **MFI** framework, the maximum heteroatom content, the local structure of the Ti sites, ...) necessary to fully understand the mechanisms of oxidation reactions [1].

As a medium-pore zeolite, the small size of the 10R pore openings imposes severe diffusion limitations when working with even relatively large molecules. To overcome this limitation and with the aim of expanding the use of zeolite oxidation catalysts to other substrates of industrial interest, an extensive research activity was soon undertaken with the aim of incorporating Ti into the framework of zeolites with different pore architecture and sizes. The focus was not only on the incorporation of Ti into the large pore (e.g., Beta, **MOR**, **ISV**, **IFR**, ...) and extra-large pore (e.g., **CFI**, **DON**, **SFH**, ...) zeolites, but also in exploiting the peculiar properties and versatility of 2D-zeolites, in particular of **MWW**-type structures, whose crystallization occurs through a layered precursor [2].

It is worth noting that, about 40 years after its discovery and despite the huge amount of work done, TS-1 remains the only zeolite catalyst employed in industrial oxidation processes. It is therefore important to understand the reasons that prevented the development of other Ti-containing zeolite industrial catalysts. In this regard, a careful analysis of the literature provides useful information on the different zeolite systems which, in the light of the deep knowledge accumulated on TS-1, can form the basis for the design of the future experimentation.

References:

[1] Bellussi, G., Millini, R., *Struct. Bond.* **2018**, 178, 1-52.

[2] Millini, R., Bellussi, G., Pollesel, P., Rizzo, C., Perego, G., *Microporous Mesoporous Mater.* **2022**, 346, 112286.

IL2

ZEOLITES AS SUSTAINABLE ENERGY MATERIALS

Giuseppe Cruciani

Department of Physics and Earth Sciences, University of Ferrara, Via Saragat 1, 44122, Ferrara, Italy

Projections for increase of global CO₂ emissions by 1% in 2022 were presented at the recent UN Climate Change Conference of the Parties (COP27). Forecasts predict 37.5 billion tonnes of carbon dioxide injected by humanity into the atmosphere, setting a new (negative) record. This is defining a trend for which the limit of 1.5 °C for the Earth warming above pre-industrial temperatures, as established by the 2015 Paris climate agreement, would be reached in just nine years [1]. In the next future years, measures are expected to be urgently adopted by governments and companies to cut planet-warming emissions. Increasingly more attention should be paid to energy from renewable sources. This will require a balance between the increasing energy demand and the environmental commitments to ensure a smooth energy transition. In this context, materials can play an important role in efficient and sustainable way. One feature common to several renewable energy sources is their intermittent nature (e.g., solar) or the need to relocate heat from places where it is generated to places where it is needed (e.g., waste heat or geothermal). As an example, one a visionary geothermal technology presented by the Clean Air Task Force (CATF) is the so called “Superhot rock energy” which encompasses drilling into rock that is highly pressurized and hotter than about 374°C (ideally as hot as 400°C or more). Once the hot rock is accessed, water is circulated through fractures or pipes to gather heat and then brought safely back to the surface [2]. Then systems to store and transport heat must be designed. These systems can take advantage of the well know ability of zeolites to store thermal energy through their adsorption properties. This is just an example of the many different applications in which natural and synthetic zeolites can be instrumental to avoid disastrous levels of climate change and allow the sustainable use of renewable energy resources.

References:

[1] Nature, NEWS 11 November 2022, DOI: 10.1038/d41586-022-03657-w

[2] <https://www.catf.us/2022/11/superhot-rock-energy-growing-needs-more-support-reach-full-potential>

SURFACE MODIFICATION IN ZEOLITE-TEMPLATED CARBONS: A PROMISING ELECTROCATALYST FOR CO₂ REDUCTION

G. Papanikolaou¹, D. Chillè¹, S. Perathoner¹, G. Centi¹, D. Cozza², M. Migliori², G. Giordano², P. Lanzafame¹

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² Laboratory of Chemical Engineering, Catalysis and Sustainable Processes CECaSP_Lab, University of Calabria, Via P. Bucci, 87036, Rende (CS), Italy

The carbon replica of Zeolite (Zeolite templated carbons - ZTCs) is a new featured carbon materials with ordered structure (from the Zeolite scaffold) and the characteristic properties (gas adsorption and electric conductivity) of Carbon-base materials. Because of their peculiar characteristics, those materials are now being explored for a wide range of applications both in the field of storage and also of energy conversion, [1]. In particular, the 3D microporous carbon nanostructure with a high surface area, high conductivity and chemical stability, make these materials ideal candidates as electrocatalysts for the CO₂ reduction reaction (CO₂RR). Moreover, the oxygen content on the ZTC surface could represent an important aspect to take into account, as the nature and the amount of C-O bond can affect surface polarity, conductivity, and in turn electrocatalytic behaviour consequently. We report here the synthesis of ZTCs, using two different Na-BEA zeolites, through Chemical Vapour Depositions using ethylene as a carbon source at high temperature. The nature and the amount of the surface-oxygen functionalities on the ZTCs were modified by a combination of chemical (sodium borohydride - NaBH₄) and thermal treatment and their effect was studied by a depth characterization using multiple techniques. The analysis of BET results revealed a progressive reduction of the surface area as the effect of post- synthesis treatment, while the reduction of oxygen functionalities was observed from FT-IR spectra. Raman spectroscopy data evidenced an increasing trend of order degree for both treated samples highlighting the conversion of the amorphous phase into a “graphene-like” ordered one [2]. From the analysis of the CO₂RR results it was possible to ascertain that the surface modification of the ZTC through the combination of chemical/thermal treatments led to an increase in the electrocatalytic activity and selectivity to formic acid with a quadrupled Faradaic efficiency compared to the untreated ZTCs samples.

References

- [1] P. Sazama, J. Pastvova, C. Rizescu, A. Tirsoaga, V.I. Parvulescu, H. Garcia, L. Kobera, J. Seidel, J. Rathousky, P. Klein, I. Jirka, J. Moravkova, and V. Blechta, *ACS Catal.*, **8**, 1779-1789 (2018).
- [2] G. Papanikolaou, D. Chillè, S. Abate, S. Perathoner, G. Centi, G. Giorgianni, D. Cozza, F. Dalena, M. Migliori, G. Giordano, and P. Lanzafame, *Applied Materials Today*, **26**, 101383 (2022).

O2

ZSM-5 SURFACE MODIFICATION VIA SECONDARY SIL-1 SYNTHESIS AND CHEMICAL ETCHING

Giorgia Ferrarelli¹, Enrico Catizzone², Massimo Migliori², Girolamo Giordano²

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2. *CECaSP_Lab - University of Calabria, Via P. Bucci -87036 Rende (CS), Italy*

The properties and the usage of internal and external acid sites of zeolites might be significantly different, as acid sites located in the internal channels allow the reactions to be directed towards the desired products, owing to the zeolites shape-selectivity. On the other hand, external acid sites did not offer the possibility to exploit such unique option to control the size of the molecules involved in the reaction and generally this leads to a decrease of products selectivity. Coating zeolites with an inert Silicalite-1 layer represents a recognised technique for passivating the catalysts surface acidity responsible for onset of unwanted reactions and for coke formation. However, chemical etching is an efficient method to improve intracrystalline transport and reduce diffusion barriers. To combine these effects, in this contribution, a zeolite with an MFI structure (ZSM5_P, Si/Al=25) was synthesized and coated with a layer of Silicalite-1 before and after having treated it with chemical etching with fluoride ions. NH₄F was dissolved in a HF aqueous solution (0,2 M), and then 0.5 g of the parent ZSM-5 zeolite (in as made form) was dispersed in the mixed solution and react at 298 K for 6 min under stirring [1] The untreated (ZSM5_P) and treated zeolites (ZSM5_F) were then passivated with a layer of Silicalite-1 following a procedure already published [2]: ZSM-5 crystals were added to the Silicalite-1 synthesis gel and coating procedure lasted 24h at 180°C under hydrothermal conditions. The products (ZSM5_P_X and ZSM5_F_X) were rinsed repeatedly by deionized water and dried at 363 K overnight. Samples were studied by X-ray diffraction (XRD), N₂ adsorption isotherms and temperature-programmed desorption of ammonia (NH₃-TPD). To investigate the effect of surface passivation combined with chemical etching, catalysts were tested for the reaction of methanol dehydration to DME in a packed bed reactor operating at atmospheric pressure. XRD spectra confirmed that the passivation and etching treatments did not affect the crystallinity of the samples. Porosimetric results showed that both the etching and passivation treatment improved the physical properties of the starting zeolite (such as BET surface area, micropore area). The catalytic results showed that, despite a decrease in total acidity for the treated catalysts, they exhibited conversions comparable to the parent zeolite with a higher stability and selectivity towards DME even at high temperatures. In conclusion characterization data together with catalytic results are promising.

References:

- [1] Qin, Z., Lakiss, L., Gilson, J.P., Thomas, K., Goupil, J.-M., Fernandez, C., Valtchev, V., *Chemistry of Materials* **2013**, 25, 2759–2766.
- [2] Ferrarelli, G., Giordano, G., Migliori, M., *Catalysis Today* **2022**, 390–391, 176–184.

COMPLETE ENGINEERING OF THE ADMINISTRATION OF A DRUG: MESOPOROUS SILICA-BASED NANODEVICES FOR SMART CHEMOTHERAPY

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In the nanotechnology era, the materials scientist is obliged to adopt a new, broader, concept of material including the detail of its design at the nanoscale to the aim of obtaining the desired nanostructures and, consequently, the expected performance. Mesoporous silica offers the most intriguing opportunities as starting architecture in the development of nanodevices for bionanotechnology applications [1]. Adverse reactions, toxicity and poor patients' compliance still represent major challenges for conventional chemotherapies. Localized drug delivery would ideally improve the therapeutic efficacy, minimizing side effects. A MSU-type mesoporous silica-based nanodevice (FOL-MSN-BTZ), able to selectively deliver the antineoplastic drug bortezomib (BTZ) to folate receptor over-expressing multiple myeloma (FR+ MM) cells is described [2]. The receptor-specific ligand, folic acid, grafted on the external surface of the nanosystem, allows tumor recognition and cell internalization while BTZ, mainly linked to pore internal surface through a covalent pH-sensitive bond, is released in acidic tumor environment. A detailed investigation showed that only the fine balancing of the different functionalities of the nanodevice around the external and internal surface of the MSN particles shows absence of toxicity towards healthy cells in vitro and negligible BTZ-release at physiological pH, suitable features for applicative purposes in the engineering of the therapies. After complete characterization in vitro, an accurate suspendability assessment that considered the sedimentation process that reduces particles amount and, consequently, drug content in the suspensions, allowed developing an injectable formulation of FOL-MSN-BTZ that showed a higher antitumor efficacy and an overall tendency to a lower toxicity in a MM mice model, if compared to conventional bortezomib chemotherapy.

References:

- [1] Mazzotta E., De Santo M., Lombardo D., Leggio A., Pasqua L., *Materials Today Bio* **2022**, 17, 100472
- [2] De Santo M., Giovinazzo A., Fava M., Mazzotta E., De Napoli I.E., Greco M., Comandé A., Nigro A., Argurio P., Perrotta I., Davoli M., Tagarelli A., Elliani R., Nicolini G., Chiorazzic, Semperboni S., Ballarini E., Crocamo C., Cavaletti, G. Lombardo D., Sisci D., Morelli C., A. Leggio A., L. Pasqua L. *Mat. Chem. Fron.*, **2022**, in press, DOI: 10.1039/D2QM01009G

P-INDUCED CRYSTAL-FLUID INTERACTION IN NATURAL ZEOLITES WITH ERI AND OFF TOPOLOGIES

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2. *European Synchrotron Radiation Facility, Grenoble, France*

The pressure-mediated intrusion of molecules (and solvated ions) into the nanocavities of open-framework minerals, such as zeolites, represent an interesting phenomenon with a potential exploitability in creating new functional materials or boosting industrial catalytic process [1,2]. In addition, this phenomenon has potential implications in Earth Sciences: zeolites, which are commonly spread in the upper oceanic crust, might act as volatiles and fluid carriers in early stage of subduction, also with potential over-hydration induced by the changes in physical-chemical conditions (i.e., increase of P-T). The aim of this study is to describe the high-P behavior, and in particular the P-induced crystal-fluid interaction, of the natural zeolites offretite and erionite (with OFF and ERI framework topologies, respectively). Both members of the ABC-6 family, these zeolites share a similar framework sequence (AABAAC for erionite and AAB for offretite). Stacking faults between the B and the C positions, which are very common in natural samples, lead to the intergrowth of the two species. Erionite, the most abundant in nature, was described in volcanoclastic deep-sea sediments collected in the framework of the Oceanic Drilling Program (ODP) [3]. Investigations have been performed via in-situ high-P synchrotron X-ray diffraction, using a diamond anvil cell (DAC), at the ID15b beamline of ESRF (Grenoble, France) and P02.2 of PETRA-III (Hamburg, Germany). Hydrostatic compression was provided using different fluids, both non-penetrating (e.g., daphne oil 7575 and silicone oil) and potentially penetrating (methanol:ethanol:water 16:3:1, ethanol:water 1:1 and distilled H₂O). A further experiment using Ne as P-transmitting fluid was also conducted on offretite. The P-V patterns showed different trends according to the nature of the P-fluids, which reflect the different ability of the diverse molecules to intrude the framework, in response to the applied pressure. A correlation between the magnitude of the intrusion and the H₂O content of the mixtures was observed. The structure refinements allowed the description of the deformation mechanisms at the atomic scale, as well as the location of the absorbed molecules. The intrusion of Ne atoms was observed in natural offretite, which forms weak Van der Waals type interaction with the extra-framework population.

References:

- [1] Comboni D., Pagliaro F., Lotti P., Gatta G.D., Merlini M., Milani S., Migliori M., Giordano G., Catizzone E., Collings I.E. & Hanfland M., *Catal. Today* **2020**, 345, 88-96
- [2] Gatta, G.D., Lotti, P., Tabacchi, G., *Phys. Chem. Miner.* **2018**, 45, 115-138
- [3] Vitali, F., Blanc, G., Larque, P., *Clays and Clay Miner.* **1995**, 43, 92-104

INSIGHT ON MWW SILICATES: FROM THE 2D PRECURSORS TO THE 3D CALCINED ZEOLITE

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The family of MWW zeolites is composed by silicates, borosilicates and aluminosilicates. [1] They consist of by a layered structure in which two parallel non-interconnected 10 Member-Ring (MR) channel systems run one intra- and one inter-layer. Thus, 18.2×7.1 Å inter-layer supercages are formed upon the Organic Structure Directing Agents (OSDAs) removal and are connected by the inter-layer channel system. [2,3] The formation of the purely siliceous zeolite requires two OSDAs: the hexamethyleneimine and the N,N,N-trimethyl-adamantammonium hydroxide. [2,3] In this work, the composition of the hydrothermally treated gel and the calcination procedure (the OSDAs removal) are shown to influence the properties of the synthesized MWW silicates. The calcined and as-synthesized samples were deeply characterized to understand the obtained properties. The crystallinity, the structural order and the particle size distribution of both the as-synthesized and the calcined samples were determined by means of Powder X-Rays Diffraction (PXRD), ²⁹Si Magic Angle Spinning Nuclear Magnetic Resonance (MAS-NMR) spectroscopy and Scanning Electron Microscopy (SEM) images respectively (Figure 1). The calcined samples were further characterized by (1) N₂ physisorption at 77 K, to determine the Specific Surface Area and the porosity, and (2) in-situ transmission infrared (IR) and ²⁹Si{¹H} Cross Polarization (CP) ²⁹Si MAS-NMR spectroscopy to explore the nature of silanols present. The proportions of the OSDAs present inside the as-synthesized samples were estimated using ¹³C MAS-NMR and ¹³C{¹H} CP-MAS-NMR and their degradation (i.e., the calcination) by transmission IR operando spectroscopy on the pelletized as-synthesized samples, coupled with a gas phase IR analyzer, to detect the degradation products of the OSDAs.

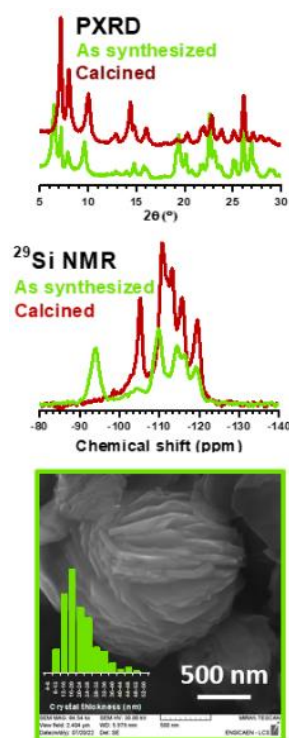


Figure 1

References:

- [1] Ostroumova, V. A., Maksimov, A. L., *Pet. Chem.* **2019**, 59, 788-801.
- [2] Cambor, M. A., Corma, A., Díaz-Cabañas, M. J., *J. Phys. Chem. B*, **1998**, 102, 44-51.
- [3] Xu, H., Guan, Y., Lu, X., Yin, J., Li, X. Zhou, D. Wu, P. *ACS Catal.* **2020**, 10, 4813-4819.

MOVING TOWARD CIRCULAR ECONOMY: REE RECOVERY FROM SPENT FLUORESCENT LAMPS EXPLOITING NH₄-13X ZEOLITE CATION EXCHANGE PROPERTIES

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Rare Earth Elements (REEs) are considered strategic resources [1] due to their extensive use in many technological fields. The current political scenario, the monopoly of only a few countries, the so-called balance problem between demand and natural abundance, and the need to limit the environmental costs of their mining [2], stress the necessity of a recycling policy of these elements. Different recovery methods have been tested but despite the well-known ion-exchange properties of zeolites, just few preliminary works investigated their application for REE separation and recycle. In this work we present a double ion exchange experiment on a NH₄-13X zeolite, aimed at the recovery of different Rare Earths from solutions mimicking the composition of liquors obtained from a two-step leaching procedure of spent fluorescent lamps [3]. Preliminary experiments were aimed at the evaluation of the cation exchange capacity of the zeolite. NH₄-13X zeolite was put in contact with four different mono-elemental solutions: Ce 0.03M, La 0.04M, Eu 0.006M and Y 0.17M. Three different solid/liquid ratio (g/ml), 1/10, 1/50 and 1/100 were tested for each solution. The results from SEM-EDS, TG, EA (on the powders) and ICP (on the solutions) analysis show that the zeolite was able to exchange all the REEs tested. We observed that the higher the amount of REE in the starting solution, the higher the amount exchanged. The exchange capacity of the zeolite is different for the different REEs: despite Y being the more concentrated REE in the solutions, the cation exchange is lower than less concentrated ones (16 atoms p.u.c. vs 21 atoms for Ce and La solutions). This suggests a possible selectivity towards REE. In order to exchange back REEs from the zeolite and recover them, a second exchange with an ammonium solution was performed. The preliminary results obtained (only for Ce and La) show that almost all of Ce remains in the zeolite, while half of La is released. This once again suggests a possible selective release of REE and open the possibility for a recovery process in which Rare Earths can be effectively separated.

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EXPLORING THE POSSIBILITY TO USE Li-EXCHANGED ZEOLITES AS CATALYST FOR CO₂ HYDROGENATION

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Converting CO₂ emissions from industrial processes into synthetic fuels, such methane, using green hydrogen represents an interesting tool to manage the surplus production of energy from intermittent renewable sources using a greenhouse gas [1]. The occurrence of CO₂ methanation, based on the Sabatier reaction, requires the use of a catalyst consisting in an active metal (generally Ni or Ru) supported on mesoporous or microporous materials, as alumina, SBA-15, MCM-41 and zeolites [2]. Addition of alkali, most of all to alumina, strongly improves the CO₂ adsorption capacity thus increasing the overall catalytic performances [3]. Alkali cations also modify the basicity of zeolites enhancing the CO₂ adsorption/activation [2]. Low silica type X zeolite (LSX) was found a promising CO₂ sorbent, Li-LSX showing excellent performance [4]. Dispersion of an active metal on the zeolite provides the catalytic functionality to produce methane from adsorbed CO₂ and H₂ [1, 2]. The alkali metal is generally exchanged whereas the active transition metal cation is more commonly introduced by impregnation. Nevertheless, the location of the active metal cation in the zeolite plays a crucial role in determining both activity and selectivity [5] and a close contact between adsorbed CO₂ and H₂ is a key factor for the catalytic reaction [3]. Attempts to exchange Ru in ZSM-5 have been reported using suitable precursors and the performance of the exchanged zeolite was found better than that of the Ru-impregnated counterpart even if for a reaction different from methanation [6]. In this work the CO₂ adsorption capacity of commercial Li-LSX pellets was explored in order to evaluate the possibility to use this material as support for methanation catalysts after the dispersion of Ru, investigating the possible routes to introduce the noble metal.

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O8

FROM POWDER TO 3D SHAPED LTA ZEOLITE FOR CARBON DIOXIDE CAPTURE

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To counter CO₂ emissions caused by anthropogenic activities, zeolites have been studied as adsorbent materials for carbon capture, storage and utilization (CCUS) technologies.¹ However, to increment their industrial applicability, they should meet different requirements as high CO₂ sorption capacity, weak regeneration conditions, availability into already shaped form and low costs.² This work focuses on the study of a low-cost LTA zeolite and on its applicability as potential CO₂ adsorbent. Firstly, the CO₂ adsorption capacity of powder NaLTA as such and after ion-exchange was evaluated in the medium-low temperature range (25-90°C). Subsequently, to facilitate its industrial applicability, the same materials in beads form were investigated in both static and dynamic conditions. Lastly, to further improve the adaptability to industrial conditions, a 3D printed NaLTA zeolite was investigated. Interestingly, the 3D printed material exhibits at 25°C a CO₂ adsorption capacity comparable to the commercial one (Figure 1).

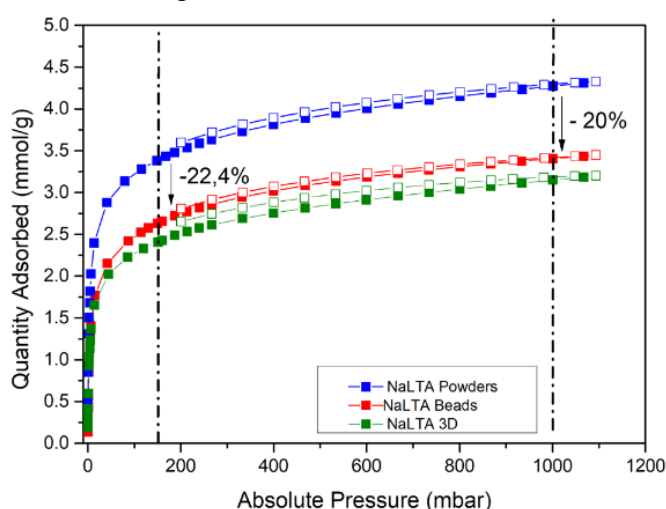


Figure 1. CO₂ adsorption/desorption isotherms at 25°C of NaLTA in powder (blue curve), beads (red curve) and 3D printed (green curve).

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09

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Currently, commercial blue pigments are obtained by heat treatment at high temperatures (1300 – 1400 °C) of cobalt silicates and aluminates, resulting in high energy costs and environmental impact issues. As an alternative, the use of zeolitic materials containing specific chromophores is proposed. The use of a microporous material (zeolite) allows the production of nanostructured pigments characterized by a high color yield. The production technology is based on ion exchange of synthetic zeolites. The obtained pigments are chemically and thermally stable in the firing range of ceramic materials. The reliability of these pigments in porcelain manufacture was tested in a research activity developed at the Federico II University of Napoli (Italy) in collaboration with Institute for the Capodimonte Porcelain “Giovanni Caselli”. The new cobalt pigments were firstly tested in the porcelain mixture to obtain a colored product.



Figure 1. Porcelain products after firing obtained by different artistic techniques

Then the efficacy, in term of color and aesthetic effect, was tested in some of the most common decoration methods such as ingobbio, colored glazes and “third fire decoration” (Figure 1).

SO1

DUAL FUNCTION MATERIALS FOR CO₂ CAPTURE AND CONVERSION

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To mitigate CO₂ emissions, carbon capture, utilization, and storage (CCUS) is considered a promising technology and it attracted the attention of scientists and researchers because of the simplicity of the approach which involves capturing, transporting, storing, and reconverting CO₂. Therefore, the research is focusing on the selection of an adsorbent material with suitable characteristics such that the capture process would be effective and reversible in terms of converting the adsorbed gas.¹ Dual-function materials create a favorable energy balance for CO₂ capture systems by eliminating the energy-intensive temperature swing CO₂ desorption and transportation steps necessary for conventional CO₂ capture units. This is achieved by directly hydrogenating captured CO₂ in the same reactor at the same temperature and pressure so that the final product being released from the reactor is a synthetic natural gas that can directly be used on-site as fuel or transported via existing natural gas pipelines. Dual-function materials consist of a catalyst and adsorbent component, both of which play a critical role in determining the methanation capacity of the final material.² In this work, cerium oxide was chosen as the CO₂ adsorbent phase because ceria-based catalysts have been found to possess higher activity and selectivity to methane. Ruthenium is the active transition metal selected since it presents optimum chemisorption energy, and a great capacity to activate H₂.³ The adsorbing properties of the supported cerium oxide were tested on two different materials with a high surface area, aluminum oxide, and commercial ZSM-5 zeolite. Three different nominal percentages of CeO₂ (10%, 20%, and 30%) were prepared through an impregnation method; the materials were characterized using the main chemical-physical characterization techniques, such as Powder-XRD, N₂ physisorption at -196 °C, TPDRO, ICP/MS, and XPS. Their adsorption capacities were tested in laboratory gas-adsorption implant at different temperatures (423, 473, and 523 K). Ru-supported catalysts (2 wt%) were prepared by adding dropwise a water solution of ruthenium precursor to 30%CeO₂/ZSM-5 and 30%CeO₂/Al₂O₃ samples. Methanation tests concerning both stability and cyclic experiments on ruthenium-impregnated materials were performed.

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SO2
MESOPOROUS SILICA USED AS SUPPORT FOR LACTATE DEHYDROGENASE
ENZYME: A STRATEGY TO OBTAIN A PROTOTYPE BIOSENSOR

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It has been shown that most cancer cells are subjected to a different metabolism: pyruvate is converted to lactate even in aerobic conditions. The responsible for this conversion is the lactate dehydrogenase (LDH) enzyme. The aberrant expression and activation of LDH are correlated to most types of cancer cells. LDH is therefore considered a promising target for anticancer drugs. This research aims to obtain a prototype of a biosensor to rapidly and economically evaluate anticancer drugs' performance. To recover and use again the enzyme, a possible strategy can be its immobilization on an inorganic support. In this scenario, mesoporous silica represents the most used support due to its properties¹. Commercial mesoporous silica (MCM-41) was selected as support for LDH. MCM-41 was functionalized with two organosilanes to provide the amino and glyoxyl groups necessary to covalently immobilize LDH². The functionalized mesoporous silicas had been characterized with complementary techniques (N₂ physisorption at 77 K, FT-IR spectroscopy, and HR-TEM) and compared with the untreated silica. The additional peaks present in the IR spectra demonstrated that the functionalization process was successful. The functionalized silicas obtained were used to immobilize LDH with two different procedures. The monofunctional MCM-41 was pre-activated with two different concentrations of glutaraldehyde, while the immobilizations with heterofunctional MCM-41 were carried out in presence of PEG or trehalose and compared with the case in absence of stabilizers. The immobilization yields are in the range of 77 – 99 % and the retained activity is 7 – 25 %. Although the low activity values, the immobilization of LDH on insoluble support seems a promising strategy to recycle the enzyme and obtain a prototype of biosensors.

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DESIGN OF 13X ZEOLITE-BASED MATERIALS FOR 3D PRINTING BY DIRECT INK WRITING

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Driven by the increasing diffusion of zeolites in industrial applications, growing efforts are being devoted in developing novel strategies to confer them a monolithic shape, while preserving their high adsorption, sieving, or catalytic properties. Most of the currently employed strategies (pelletization, granulation, extrusion) usually reduce at least in part the zeolites effectiveness. A promising solution is found to be 3D printing, as it allows for many degrees of freedom in materials design[1]. Among the possible additive manufacturing techniques, Direct Ink Writing (DIW) is considered one of the most versatile and suitable for the purpose. DIW consists in the extrusion at room temperature of a zeolite-containing “ink” through a moving nozzle. The desired object is obtained through a layer-by-layer deposition and is subsequently consolidated by controlled drying and sintering. In this process, the proper formulation of a printable ink with specific physicochemical properties is crucial. The ink usually consists of the active powder (zeolite particles), a solvent and a binder, the latter holding the particles together during printing and providing mechanical coherence to the printed object. Even though examples of 3D printed zeolite-based materials are reported in literature [2], there are still no reliable criteria for materials design, and the ink formulation is heavily dependent on the operator expertise. Here, 3D printed zeolite-based prototypes have been designed and produced with the aim of defining criteria to relate the properties of the produced specimens to the 3D printing operating parameters. Several inks have been formulated using 13X zeolite as active phase, water as solvent, and bentonite or sodium alginate as binding agents, the latter with the aim of providing mechanical coherence only during the printing process but being decomposed by the thermal treatment. Zeolite content was also varied to highlight the particles contribution to the ink properties. Rheology has been selected as the primary tool for assessing the printability of the ink, in terms of its ability to be extruded while retaining its shape. Preliminary tests gave encouraging results: X-Ray diffraction revealed that 13X particles are unaltered by the heat treatment, while Scanning Electron Microscopy proved the effectiveness of the sintering process. Print trials also confirmed the correlation between the rheological behavior of the inks and their printability, suggesting the possibility to develop empirical criteria and guidelines to optimize their design and printing process.

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SO4
**STUDY ON THE OXYGEN CONTENT OF BEA AND BEA@SIL-1 ZEOLITE
TEMPLATED CARBON**

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Zeolite templated carbons (ZTCs) are carbon-based materials with a well-defined and ordered nanoporous structure. The scientific, academic and industrial interest for this type of material is growing in the recent years due to the high specific surface area (2000-3000 m²/g), electrical conductivity, thermal and chemical stability that make this kind of material the perfect candidate for applications in electrochemistry. The presence of oxygen as main heteroatom in the ZTC structure is, nowadays, not well studied in the literature. Structural defects in the zeolite framework could be the cause of the introduction of some oxygen-containing functional groups inside the ZTC structure. In this paper, Silicalite-1 was used as passivating agent to cover the external surface of BEA zeolite crystals, in order to exclude the superficial defects of BEA zeolite from the chemical vapor deposition process. BEA@Sil-1 core-shell zeolites were synthesized with different passivating layer thickness via steam assisted crystallization and BEA core and BEA@Sil-1 core-shells were used as scaffolds in the production of BEA-structure type zeolite templated carbon via high-temperature continuous chemical vapor deposition of dilute ethylene gas [1]. The ZTCs were liberated from the zeolite framework by HF/HCl washing steps and oxygen content and physical properties were analyzed by X-Ray Diffraction technique (XRD), Porosimetric analysis, Thermogravimetric analysis and FT-IR spectroscopy. No structural differences arose from the use of BEA or BEA@Sil-1 core-shells as ZTC scaffolds. Porosimetric analysis showed that the overall BET surface area decreases when a passivated scaffold is used, but the ratio between micropore volume and total pore volume increases, suggesting that a more orderly structure is obtained. FT-IR spectroscopy was used to qualitatively measure the oxygen content in the various samples [2], showing that using a passivated scaffold can lower the overall oxygen content in the ZTC framework. FT-IR analysis was also used to measure the oxygen content in the BEA Zeolite-ZTC composite showing that some oxygen-containing functional groups are indeed introduced by the washing step with hydrofluoric acid. In conclusion, using a passivated zeolite as template may be a viable way to tune the ZTC oxygen content.

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SO5
**SELF-STANDING NANOPOROUS ZEOLITE/CELLULOSE DEPOSITS PREPARED
WITH ULTRAFILTRATION FOR ENERGY STORAGE APPLICATIONS**

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Metal-organic frameworks (MOFs) are a class of crystalline solids containing metal ions and organic ligands. Owing to their high porosity and tuneable selectivity, they have been intensively researched for their application in gas separation, filtration, catalysis, sensing and energy storage [1]. However, MOFs are typically produced in forms of powders, which require further processing before being applied on a larger, industrial scale. In the field of liquid separation, synthesis or deposition of MOFs on polymeric membranes has been regarded as a viable solution, however further research is needed to evaluate the microstructure-function relationship of these hybrid materials. The use of biopolymers-based membranes for supporting MOFs constitutes an attractive fabrication route, owing to their intrinsic physiochemical properties, sustainability and biocompatibility [2]. The present work focuses on the use of a hydrophobic MOF (ZIF-8), which exhibits energy storage capability through cycles of liquid intrusion/extrusion [3]. The ZIF-8 powder was mixed with crystalline nanocellulose (CNC) and used to fabricate a hybrid deposit by means of ultrafiltration. The flow behavior of the ZIF-8/CNC suspensions was probed using oscillatory rheology. The effect of the composition of the feed solution on the deposit formation has been also investigated, and the deposit was characterized with optical and electron microscopy, and ultra-small angle X-ray scattering. Results show that low amounts of CNC enable formation of a homogeneous and resistant ZIF-8/CNC composite material which maintains its performance as an energy storage system, with intruding pressures up to 250 bar.

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INTENSIFICATION EFFECT ON CATALYTIC CO₂ HYDROGENATION TO DME PROMPTED BY WATER-ADSORBENT SYSTEMS

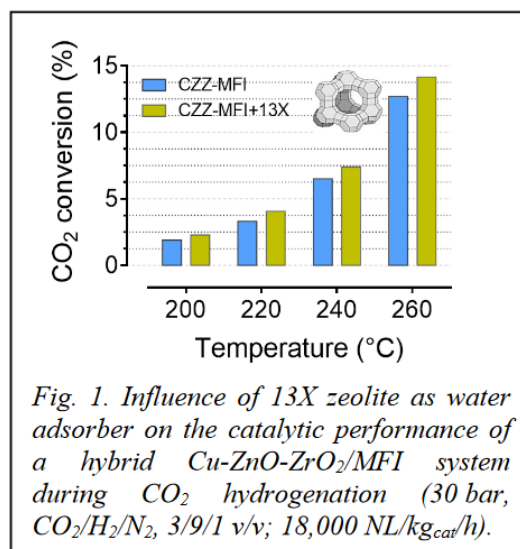
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In recent years numerous R&D strategies have been proposed for the establishment of sustainable CCU technology chains, so to boost an effective recycle of carbon dioxide in presence of green hydrogen for the production of bulk chemicals or fuels [1]. In this framework, particular interest has been addressed to the catalytic hydrogenation of CO₂ into dimethyl ether (DME), requiring a hybrid catalyst for the direct DME synthesis in one step, wherein a methanol-synthesis phase (CuO-ZnO-Al₂O₃ or CuO-ZnO-ZrO₂) and a methanol dehydration phase (typically zeolites) are closely integrated [2]. Nevertheless, the catalyst performance and its lifetime are strongly limited by water formed during the process, so that the efforts on novel system architectures, nature and location of active sites, even probed in a large set of experimental conditions, do not allow to overcome the equilibrium restrictions preventing their industrial scale-up [3]. In this work, we investigated the intensification effect prompted by the combination of *in situ* water adsorbent agents (like zeolites) with a previously optimized hybrid Cu-ZnO-ZrO₂/MFI system [2,3], so to demonstrate how the effective removal of water from the reaction medium can shift the equilibrium of CO₂ conversion to more favourable values, also determining a higher DME productivity (Fig. 1). This work has received funding from the European Union's Horizon 2020 research and innovation programme under GA No. 838061.



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ROLE OF ACID CONCENTRATION IN THE CHEMICAL CONDENSATION OF 2D MCM-22(P) PRECURSOR TO 3D MWW ZEOLITE

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The ADOR (assembly-disassembly–organization–reassembly) method of zeolite synthesis by 2D-3D transformations presents several critical steps. Two of them are (a) the use of appropriate mild conditions of solvolysis-condensation of bonds between structural tetrahedra; (b) the control of the orientation of 2D structures in the condensation into 3D structures. Useful information on these steps can be provided by the study of the 2D-3D condensation of layered zeolite precursors. MWW zeolites are an appropriate testbed, as their two non-interconnected two-dimensional networks made of 10MR channel systems are formed by calcination of a layered precursor MWW(P). In this work, we show that a combined organic solvent-acid treatment in mild conditions allows to remove the organic template from one of the most accessible porous systems and brings in the meantime to the condensation of the zeolite network by dehydration of opposing silanols of the layered precursor [1].

An HMI-synthesized MCM-22(P) with Si/Al 23 was treated at 30°C by a 20% w/w 1,4-dioxane aqueous solution acidified at pH 1 by HNO₃. This treatment allowed to extract 40% of HMI, representative of the template in the interlayer space, and reduced the c cell parameter from 26.8 to 25.0 Å. Q3 Si(OAl)₃OH ²⁹Si MAS-NMR signals are not affected by the treatment, suggesting that extraction of HMI and shrinkage of the c parameter have not been accompanied by any significant dehydration-condensation of silanols.

A more severe acid treatment of MCM-22(P) was performed by 70% HNO₃ at reflux temperature. The treatment led to the shrinkage of the c parameter to 25.1 Å and to the extraction of 55% of HMI and early 40% Al of the sample, whose Si/Al became 49. ²⁹Si MAS-NMR indicated the presence of less than 5% Q3 Si(OAl)₃OH signals, an amount corresponding to the silanol nests formed by dealumination of the material. The decrease of the amount of silanols indicates an increased connection between the layers, as expected in the 3D MWW structure.

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P2

STRUCTURAL AND COMPUTATIONAL STUDY OF ZEOLITE-ENCAPSULATED UV FILTERS

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In the last decades, the growing UV irradiance at the Earth's surface has led to enhanced human UV exposure, with a consequent increase in skin cancer incidence.

Organic and inorganic UV filters (UVfs) play a major role in health protection. Unfortunately, several issues are still linked to the stability and safety of UV filters for both human health and the environment. Thus, the development of new, safer, and more effective UV filters is of paramount importance.

Our group encapsulated two organic UV filters (octinoxate, OMC, and avobenzone, AVO) into zeolites of LTL, MOR, FAU, and MFI topology, in both their high- and low-silica forms [1]. The obtained hybrid materials (ZEOfilters) showed diverse filtering properties depending on the UV filter-zeolite combination, with LTL- and 13X-FAU-based ZEOfilters being the most efficient UV absorbers.

Recently, we investigated the relationship between the crystal structure of ZEOfilters and their properties, using X-ray diffraction, UV-vis and IR spectroscopies, and DFT calculations. After the study of LTL/OMC ZEOfilter [2], we are now focusing on the two UV filters encapsulated in high-silica (HS) and 13X FAU-type zeolites

The DFT investigations consisted of structure optimization of HS-FAU and 13X-FAU with adsorbed different isomers of OMC and AVO. Both low loadings (1 molecule per unit cell) and experimentally observed saturation loadings (4-6 molecules p.u.c.) were considered. Low-energy configurations were analyzed for the diverse isomer-zeolite combinations. Calculations displayed several differences in the computed adsorption energies among the different isomers of a given UV filter in the two zeolites. However, as the isomerization may be hindered by steric constraints, a more negative adsorption energy does not necessarily mean that one isomer is indeed present in the zeolite. This point can only be resolved through a comparison of vibrational spectroscopy and DFT calculations. Here we report results from this ongoing investigation.

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ZEOLITE-RICH COMPOSITES FOR CHROMIUM REMOVAL FROM WATER

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Chromium is a harmful pollutant of particular concern, being difficult to remove with a single process, as it can occur both as cationic Cr(III) or anionic Cr(VI). Among the different strategies that can be employed for its removal from water, the use of natural zeolites is still a promising technique [1]. Unfortunately, zeolites are good cation exchangers, but cannot be anion exchangers, removing only Cr(III). To overcome this intrinsic limitation, their behavior can be enhanced by several chemical treatments aimed at making them active towards more classes of pollutants, like anions or organics [2]. In fact, as previously reported [3], it is possible to modify the external surface of a zeolite by grafting with a proper surfactant, thus obtaining a Surface Modified Natural Zeolite (SMNZ), suitable for anion exchange, even if with a limited exchange capacity. In this work, a SMNZ was produced by modifying a phillipsite-rich tuff (belonging to the Neapolitan yellow tuff) with the cationic surfactant HDTMA-Br. To overcome the limitation arising from the low anionic exchange capacity, the SMNZ was also coupled with zero-valent iron (ZVI), which, promoting the conversion of Cr(VI) to Cr(III), also allows to exploit the high cation exchange capacity of the zeolite. Four SMNZ/ZVI mixtures were prepared at 1/1, 3/1, 4/1, 7/1 zeolite/iron ratio. Kinetic tests were carried out by contacting 4 g of sample with 1 L of 100 mg/L Cr(VI) solution. On the basis of the collected results, dynamic tests were also performed in fixed beds loaded with the ZVI fraction stacked on top of the SMNZ, to first activate the Cr(VI) - Cr(III) conversion and then the cation exchange. The results of both tests demonstrated that the best performing sample was the SMNZ/ZVI 4/1 composite, which showed a Cr removal percentage of 47% and an exchange capacity of 2.4 mg/g, a noticeably better performance than that of mere SMNZ (Cr removal percentage = 17%; exchange capacity = 0.18 mg/g).

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ELECTRONIC PROPERTIES OF NEUROTRANSMITTERS IN A HYBRID SYSTEM WITH ZEOLITE L

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The hybrid compound Zeolite L + 2,7-dimethyldiazapyrenium (MDAP, photosensitive dye, charged + 2) is an artificial receptor with high affinity for small neurotransmitter molecules. The efficacy of this system as nanosensor has been shown in the literature by the significant change of its optical spectra after titration with Serotonin (having a +1 charge in water) [1]. More specifically, the association of the neurotransmitter with the dye causes the onset of a long-wavelength signal in the UV-vis absorption spectrum, which was absent in the spectrum of the Zeolite L + MDAP receptor. We analyzed by ab initio methods the electronic excitations of the following model systems: a) Zeolite L + H₂O + MDAP; b) Zeolite L + H₂O + MDAP + Serotonin. Our goal was to identify the nature of the long-wavelength signal in the experimental spectrum, and to understand the molecular-level factors that influence the position and intensity of this band. To this purpose, electronic excitations were calculated at the CAM-B3LYP/6-311++G(df,pd) level on different configurations of the MDAP + Serotonin aggregate. These configurations were sampled from an ab initio molecular dynamics trajectory, conducted at 298 K on the Zeolite L + H₂O + MDAP + Serotonin system. The simulated absorption spectrum of the aggregate, averaged over the considered configurations, shows a similar trend to that found in the experimental one. Furthermore, comparison with the spectrum similarly calculated for the Zeolite L + H₂O + MDAP system indicates that the association of the neurotransmitter with MDAP causes a reduction in the intensity of the MDAP-related peaks - in agreement with experimental observations, [1] and the appearance of a new signal, assigned to a charge-transfer transition from Serotonin to MDAP. The overall data analysis shows that the charge-transfer transition, regardless from the Serotonin conformation, exhibits higher wavelength and oscillator strength in configurations having the π -systems of Serotonin and MDAP perpendicular to each other, a not excessively distorted MDAP geometry and a smaller Serotonin-MDAP distance. The latter depends on both the number and the position of water molecules around the aggregate: these can be located between MDAP and Serotonin, preventing them from coming any closer, or in positions that allow a closer contact between MDAP and Serotonin. Finally, this insight, which is not accessible experimentally, represents a fundamental basis for the improvement of artificial zeolite-based sensors for diagnostics and other biomedical applications.

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FROM ZEOLITE PRECURSOR TO THE MOON: TOXICOLOGICAL STUDIES OF SIMULATED MOON AGGLUTINATES

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Curiosity about the space around us has increasingly driven the pursuit of space missions to the moon for both public and private entities. This behaviour, however, has highlighted the problem of the possible toxicity of lunar dust. This dust is the result of continuous bombardment by micro-meteorites, solar wind, irradiation, and sputtering of cosmic and galactic rays. The combination of all these events in absence of an oxidative atmosphere creates freshly-fractured surfaces highly reactivity and peculiar magnetic behaviour. It must be noted that in agglutinated dust, iron occurs as Fe⁰ or Fe²⁺ species, and not as Fe³⁺ species, like in terrestrial minerals. Not only the intriguing chemical composition but also the size distribution can affect the toxicological properties. Despite the missions carried out so far, the lunar dust that has returned to Earth turns out to be in quantities too low to be efficiently analysed by the scientific community, highlighting the need to conduct the necessary tests for studies using lunar simulants. With this in mind, we propose lunar simulants obtained thorough a smart, high output and highly controlled process using as starting material two commercial zeolites (i.e., Na-A and Na-X). The precursors were Fe-exchanged and thermally treated in a reducing atmosphere in order to obtain two nanocomposites, formed by the dispersion of Fe nanoparticles in a ceramic matrix. The nanocomposites produced were subjected to a highly controlled and efficient milling under inert atmosphere to mimic some of the Moon environmental conditions with the dual purpose of reducing the particle size to the respirable range and activating the reactivity through the creation of freshly formed reactive moieties. The milled dusts were studied in terms of particle size distribution, morphology, presence of surface radicals and reactive centers (EPR), oxidative properties (terephthalate assay/fluorimetry), and the capability to induce in vitro cell membrane damage.



CERTIFICATE OF ATTENDANCE

This certificate is presented to **Andrea Rizzetto** from **Polytechnic of Torino**

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