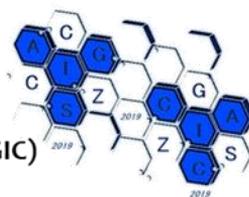


Jointly Meeting of the
Italian Zeolite Association (AIZ)
Czech-Italian-Spanish (CIS) Conference
Italian Interdivisional Catalysis Group (GIC)



AIZ-CIS-GIC Jointly Meeting 2019, 11th - 14th June, 2019



PROGRAM & BOOK OF SUMMARY



XVI National Congress of Zeolites Science and Technology



8th Czech-Italian Spanish Conference on Molecular Sieves and Catalysis



XXI National Congress of Catalysis

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Prof. Cruciani Giuseppe University of Ferrara, Italy
Prof. Martucci Annalisa University of Ferrara, Italy

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Book of Summaries

Editing

Dr. Ardit Matteo	University of Ferrara, Italy
Dr. Rodeghero Elisa	University of Ferrara, Italy
Prof. Giuseppe Cruciani	University of Ferrara, Italy

Cover

Prof. Martucci Annalisa	University of Ferrara, Italy
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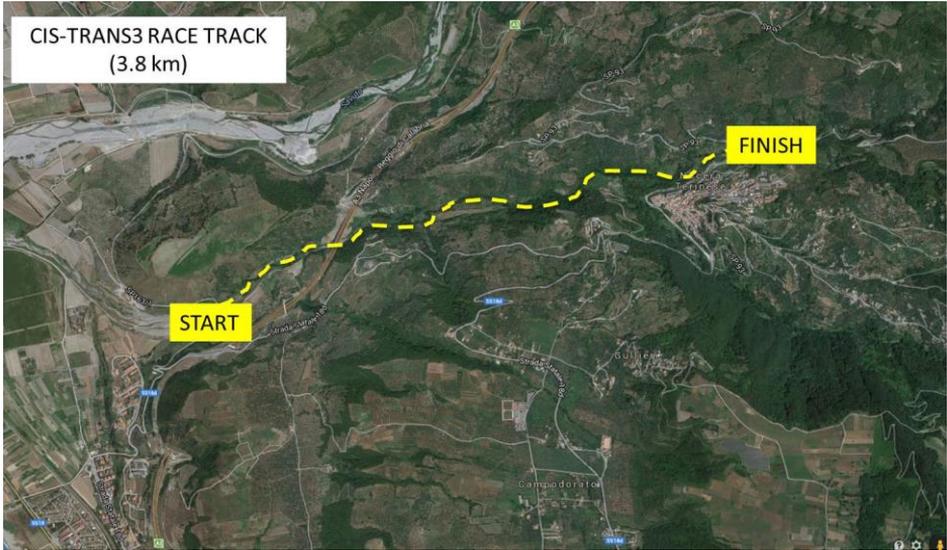
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**Jointly Meeting of the
 Italian Zeolite Association (AIZ)
 Czech-Italian-Spanish (CIS) Conference
 Italian Interdivisional Catalysis Group (GIC)
 11-14th June 2019 - Amantea (CS) - ITALY**

PROGRAM

Tuesday, 11 th June	
14:30-16:00	Registration
16.00-16:30	Opening
16:30-17:15	<i>PL1 – Plenary: Giuseppe Bellussi</i>
17:15-18:15	Session Tu-1 (O1 – O3)
18:15-18:55	Awards Session
18:55-19.30	<i>IL1 – Invited: Carlo Perego</i>
20:00	Welcome Party

Wednesday, 12 th June		
08:30-09:15	<i>PL2 – Plenary: Jiří Čejka</i>	
09:20-10:40	Session We-1a (O4 – O6 / SO1 & SO2)	Session We-1b (O7 – O9 / SO3 & SO4)
10:40-11:00	<i>Coffee Break</i>	
11:00-13:00	Session We-2a (O10 – O14 / SO5 & SO6)	Session We-2b (O15 – O19 / SO7 & SO8)
13:00-15:30	<i>Lunch and Free Time</i>	
15:30 - 17:10	Session We-3 (O20 – O22 / SO9 – SO12)	
17:10-19:00	<i>Poster Session + Refreshments</i>	
19:00:20:00	<i>General Assembly AIZ</i>	<i>General Assembly GIC</i>
20:30	<i>Dinner</i>	



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Thursday, 13 th June	
08:30-09:15	<i>PL3 – Plenary: Avelino Corma</i>
09:20-10:40	Session Th-1 (O23 & O24 / SO13 – SO16)
10:40-11:00	<i>Coffee Break</i>
11:00-11:30	<i>IL2 – Invited: Adriano Zecchina</i>
11:30-13:00	<i>Microsymposium Carlo Lamberti</i>
11:30-11:50	<i>KN1</i>
11:50-13:00	(O25 & O26 / SO17 – SO19)
13:00-15:30	<i>Lunch and Free Time</i>
15:30-16:50	Session Th-2 (O27 & O28 / SO20 – SO23)
16:50-20:00	<i>Social Event - CIS-TRANS3</i>
20:30	<i>Dinner</i>

Friday, 14 th June	
08:30-09:05	<i>IL3 - Invited: Suheil Abdo</i>
09:10-10:50	Session Fr-1 (O29 – O31 / SO24 – SO27)
10:50-11:20	<i>Coffee Break</i>
11:20-12:40	Session Fr-2 (O32 – O34 / SO28 & SO29)
12:40-13:00	<i>Final remarks</i>

TUESDAY, 11TH JUNE

14:30-16:00	Registration
16:00-16:30	Opening
16:30-17:15	PL1 - Giuseppe Bellussi: The energy transition towards a zero emission energy supply system (Chair: Girolamo Giordano)
17:15-18:15	Session Tu-1
17:15-17:35	O1 - PÉREZ-BOTELLA: Influence of zeolite framework topology in the CO ₂ /CH ₄ separation
17:35-17:55	O2 - GARBARINO: On the role of La ₂ O ₃ and SiO ₂ in the formulation of Ni/Al ₂ O ₃ based CO ₂ methanation catalysts
17:55-18:15	O3 - NACHTIGALL: Fast room temperature lability of aluminosilicate zeolites
18:15-18:55	Award's talks (Chairs: Giuseppe Cruciani and Fabrizio Cavani)
18:15-18:35	Premio Gottardi 2019 - CAMPANILE: Facile synthesis of nanostructured cobalt pigments by Co-A zeolite thermal conversion and its application in porcelain manufacture
18:35-18:55	Premio Parmaliana 2019 - FIORENZA: Modified TiO ₂ -based catalysts for energy production and environmental protection
18:55-19:30	IL1 - Carlo Perego: Giuseppe Bellussi and zeolite science: a long history of success
20:00	Welcome Party

WEDNESDAY, 12TH JUNE

8:30-9:15	PL2 - Jiří Čejka: Adorable zeolites and catalysts (Chair: David Serrano)	
9:20-10:40	Session We-1a (Chair: Domenico Caputo)	Session We-1b (Chair: Matteo Guidotti)
09:20-9:40	O4 - PAPANIKOLAOU: Effect of a mild NH ₄ OH treatment on local structure and acidic sites distribution of Fe-MFI	O7 - BENSALD: Aqueous phase reforming of sugar-based biorefinery streams: from the simplicity of model compounds to the complexity of real feeds
9:40-10:00	O5 - MARTÍNEZ ORTIGOSA: Silicalite synthesized by the dual-template technique: a solid state NMR study	O8 - PAONE: Comparing batch and gas-flow conditions in the transfer hydrogenation of alkyl levulinates promoted by ZrO ₂ catalyst
10:00-10:20	O6 - ZANARDI: Crystalline hybrid organic-inorganic gallosilicates: synthesis and crystal structure	O9 - TABANELLI: Glycerol carbonates as an innovative alkylating agents for phenolics
10:20-10:30	SO1 - PATEROVA: Use of Lewis and Brønsted acids as catalysts for β-pinene oxide rearrangement to prepare myrtenol and myrtanal	SO3 - MALARA: Transfer hydrogenolysis of aromatic ethers promoted by Pd/Fe3O4 electrospun nanomaterials
10:30-10:40	SO2 - SAJAD: Catalytic activity of noble metal clusters encapsulated in zeolites	SO4 - PASSALACQUA: Cyclic voltammetric studies of small iridium clusters for energy carrying molecules
10:40-11:00	Coffee Break	
11:00-13:00	Session We-2a (Chair: Giovanna Vezzalini)	Session We-2b (Chair: Michela Signoretto)
11:00-11:20	O10 - ALONSO-DONCEL: Tuning mesoporosity in hierarchical ZSM-5 zeolite by changing the silylation agent functionality	O15 - BONELLI: Reverse micelles sol-gel synthesis allows both bulk doping and heteroatoms surface enrichment in Mo-doped TiO ₂ nanoparticles
11:20-11:40	O11 - FABBIANI: Polymerization of hexadiene and phenylacetylene confined in silica zeolite channels	O16 - GUIDOTTI: Copper-containing microporous molecular sieves and organically modified clays applied in the defence against the olive tree fly pest
11:40-12:00	O12 - CAMETTI: Structural modifications and thermal stability of Cd ²⁺ -exchanged stellerite, a zeolite with STI framework type	O17 - SANTACESARIA: Preparation of nanostructured catalysts by grafting metal alkoxides on the surface of oxides supports
12:00-12:20	O13 - COMBONI: High-pressure cold methanol intrusion in MFI-zeolites	O18 - STUCCHI: Post-synthesis modification of gold-silver nanoparticles: a way to tune catalytic activity and selectivity
12:20-12:40	O14 - KUBŮ: Encapsulation of metal nanoparticles (NPs) within zeolite frameworks via 2D to 3D transformation	O19 - Mino: Photocatalysis on shape-engineered TiO ₂ nanoparticles: a closer look into the surface processes by in situ spectroscopies
12:40-12:50	SO5 - ERIGONI: Synthesis and characterization of organosiliceous hybrid materials containing acid functionalities	SO7 - ARMANDI: Amphoteric surfaces stemming from the partial collapse of hybrid aluminosilicate nanotubes: an IR spectroscopy assessment
12:50-13:00	SO6 - LEO: Direct α-arylation of ketones efficiently catalyzed by Cu-MOF-74	SO8 - CAVUOTO: Synthesis of biosurfactants by solid acid catalysts
13:00-14:00	Lunch	
14:00-15:30	Free Time	
15:30-17:10	Session We-3 (Chair: Joaquín Pérez Pariente)	
15:30-15:40	SO9 - YUE: Multiple phase transformations during the synthesis of germanosilicate UOS	
15:40-15:50	SO10 - BELVISO: Synthetic zeolite and laser effect: preliminary data	
15:50-16:00	SO11 - ARDIT: The ferroelastic phase transition in ZSM-5 zeolites: chemistry vs. thermodynamic	
16:00-16:20	O20 - BONURA: The key role of metal-zeolite interaction for stability of hybrid catalysts during CO ₂ -to-DME hydrogenation	
16:20-16:30	SO12 - PŘECH: Silica metal-oxide pillared zeolites – green selective oxidation catalysts	
16:30-16:50	O21 - VILLAMAINA: Cu-CHA catalysts for NH ₃ -SCR: the roles of SiO ₂ /Al ₂ O ₃ and Cu loading in the Cu-sepation	
16:50-17:10	O22 - CAMPISI: Selective catalytic oxidation of ammonia (NH ₃ -SCO) on iron beta zeolite catalysts prepared by ion exchange and solvated metal atom dispersion	
17:10-19:00	Poster Session + Refreshments	
19:00-20:00	General Assembly AIZ	General Assembly GIC
20:30	Dinner	

THURSDAY, 13TH JUNE

8:30-9:15	PL3 - Avelino Corma: Inspiration from research and technology by ENI and G. Bellussi (Chair: Maksym Opanasenko)
9:20-10:40	Session Th-1
9:20-9:40	O23 - VESELÝ: Zeolites in Pechmann condensation: Impact of framework topology and type of acid site
9:40-10:00	O24 - CASTOLDI: Metal-doped zeolites for low-T NOx adsorption: operando FT-IR spectroscopy and reactivity studies
10:00-10:10	SO13 - LOPEZ-RENAU: Catalytic biomass pyrolysis over KH-ZSM-5 zeolite with acid-base properties
10:10-10:20	SO14 - CHENET: Adsorption of p-hydroxybenzaldehyde onto zeolites for water remediation: evaluation of the competition between contaminant and natural organic substances
10:20-10:30	SO15 - PALOMINO-CABELLO: Sulfonamides photodegradation assisted by $\alpha\text{Fe}_2\text{O}_3\text{-TiO}_2\text{-P/K}_2\text{S}_2\text{O}_8$ system
10:30-10:40	SO16 - CONFALONIERI: Dehydraton of an azeotrope solution at high pressure through a differential penetration of ethanol and water in Si-chabazite
10:40-11:00	Coffee Break
11:00-11:30	IL2 - Adriano Zecchina: Contribution of spectroscopies to zeolites and microporous materials science (Chair: Silvia Bordiga)
11:30-13:05	Microsymposium Carlo Lamberti (Chair: Gloria Berlier)
11:30-11:50	KN1 - BORFECCHIA: Understanding selective redox chemistry in Cu-zeolites: a synchrotron-enhanced multi-technique perspective
11:50-12:10	O25 - VAN BOKHOVEN: In situ characterization of zeolitic catalysts
12:10-12:30	O26 - BUSCA: Cobalt metal catalysts in the hydrogen chemistry: support and preparation effects in CO ₂ methanation and ethanol steam reforming
12:30-12:40	SO17 - GIGLI: New insights on the crystal structure of ZSM-12 with azonia spiro salts
12:40-12:50	SO18 - CROCELLÀ: Advanced spectroscopic characterization of acidic sites in hierarchically structured zeolites as catalysts for hindered substrates
12:50-13:00	SO19 - BELTRAMI: Neutron and <i>in situ</i> synchrotron x-ray powder diffraction analysis to study the thermal activation of NH ₃ omega zeolite
13:00-14:00	Lunch
14:00-15:30	Free Time
15:35-16:50	Session Th-2 (Chair: Francesco Di Renzo)
15:30-15:40	SO20 - POLISI: First hints on pressure-induced amino acids condensation in mordenite
15:40-15:50	SO21 - BRUNDU: Thermal transformation of (NH ₄ , Ba)-clinoptilolite to monocelsian, mullite, and cristobalite
15:50-16:00	SO22 - MANCINELLI: One-step deposition method for the synthesis of a nanocomposite membrane based on reduced graphene oxide/zeolite-A for adsorption of metal ions with enhanced antibacterial properties
16:00-16:20	O27 - GÓMEZ-HORTIGÜELA: Conformational sieving effect of ephedrine derivatives during the synthesis of zeolite materials
16:20-16:40	O28 - PIRONE: Nitrous oxide decomposition over copper-containing ZSM-5: unravelling the isothermal oscillatory behavior
16:40-16:50	SO23 - ATZORI: Mesoporous NiO-CeO ₂ mixed oxides for CO and CO ₂ co-methanation
16:50-20:00	Social Event
20:30	Dinner

FRYDAY, 14TH JUNE

8:30-9:05	IL3 - Suheil Abdo: Key role of zeolitic technologies in meeting current and future societal needs (Chair: Petr Nachtigall)
09:10-10:50	Session Fr-1
9:10-9:20:	SO24 - VYSKOČILOVÁ: Solid acid catalysts for the direct hydration of dihydromyrcene
9:20-9:30	SO25 - ESPOSITO: Study of the effect of preparation procedure on the formation of active and stable ceria-zirconia supported molybdenum oxide catalysts for cyclooctene epoxidation
9:30-9:50	O29 - BELTRAMI: Mesoporous ZSM-5 loaded with amino acids: does secondary mesoporosity affect sorption capacity and thermal regeneration?
9:50-10:10	O30 - MAZUR: A kinetics study into the hydrolysis and intercalation processes within the ADOR mechanism
10:10-10:30	O31 - DIAZ: Ti-SBA-15 with tailor made pore size and particle morphology for epoxidation of vernonia oil
10:30-10:40	SO26 - CUMPLIDO: Synthesis of Al-rich ZSM-12 zeolite using a dabco derivative as a structure-directing agent
10:40-10:50	SO27 - PAPANIKOLAOU: Ni zeo-type catalysts for algal oil upgrading: role of acidity and active-site accessibility
10:50-11:20	Coffee Break
11:20-12:50	Session Fr-2 (Chair: Siglinda Peratoner)
11:20-11:40	O32 - GUTIÉRREZ-RUBIO: Guaiacol hydrodeoxygenation over Ni ₂ P supported on 2D-zeolites
11:40-11:50	SO28 - BOCCIA: Alkali metals promoted Ru/Al ₂ O ₃ catalysts for CO ₂ methanation
11:50-12:10	O33 - PIZZOLITTO: Effect of grafting solvent in the optimisation of SBA-15 acidity for levulinic acid production
12:10-12:30	O34 - LEO: Different activity and stability of Fe-containing MOF materials for fenton oxidation processes
12:30-12:40	SO29 - LÓPEZ-HERNÁNDEZ: CO catalytic oxidation reaction as a tool to evaluate the nature of Ag-catalysts
12:40-13:00	Final remarks



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Plenary Lectures



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**PL1. THE ENERGY TRANSITION TOWARDS A ZERO EMISSION
ENERGY SUPPLY SYSTEM**

Giuseppe Bellussi

The temperature of the Earth has increased dramatically over the last century. However, even more worrying than this is the increased concentration of CO₂ in the atmosphere that has recently exceeded 400 ppm. This signal indicates the need for a reduction of the anthropic GHG emissions. This problem does not have a simple solution, given the fact that even today over 1 billion people do not have access to electricity and over two and a half billion do not have the means to cook healthily and safely. A great effort is underway worldwide to develop renewable energy sources, but the projections of some of the major public agencies indicate that until 2050 fossil fuels will still make a significant contribution to satisfy energy demand. It will therefore be necessary to increase the effort on renewables and at the same time reduce the carbon footprint of fossils. The presentation is aimed to review the contributions that the new technologies can make in this context.

Tu.11
16:30

Chair Girolamo GIORDANO

PL2. ADORABLE ZEOLITES AND CATALYSTS

Jiří Cejka

Zeolites are currently the most important heterogeneous catalysts in industrial applications and number of the processes catalyzed by them continuously increases. This presentation addresses key issues and challenges of the synthesis of zeolites using ADOR protocol, which represents a unique synthetic tool for the preparation of new zeolites starting from existing germanosilicate zeolites. Manipulation of individual zeolite layers towards new materials is described followed by examples of adsorption and particularly catalytic behavior of ADORable zeolites.

We.12
08:30

Chair David SERRANO



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**PL3. INSPIRATION FROM RESEARCH AND TECHNOLOGY BY ENI
 AND G. BELLUSSI**

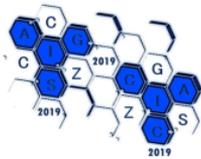
Avelino Corma

Zeolites play a key role in the field of catalysis with well defined single isolated active sites. An important discovery in zeolites was when ENI Technology showed that it was possible to introduce isolated and tetrahedrally coordinated Ti in the framework of silicalite. This opened a new line of research in zeolite catalysis. I will present how the combination of fundamental and technical knowledge developed at ENI TECHNOLOGY end up with a very relevant catalytic process that uses hydrogen peroxide for catalytic oxidations with zeolites and how that work inspired to many of us. We will present our own development with other Ti-molecular sieves, using organic peroxides as oxidant, that also end up with another olefin epoxidation process. We will present how the introduction of other metals opened new possibilities for zeolites as oxidation catalysts.

ENI TECHNOLOGY and the team led by Giuseppe Bellussi, came out with the synthesis and modifications of different zeolites and their use for catalysis. We will present some of that work and its implications in academic and industrial research and technology.

Th.13
08:30

Chair Maksym OPANASENKO



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Invited Lectures



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IL1. GIUSEPPE BELLUSSI AND ZEOLITE SCIENCE: A LONG HISTORY OF SUCCESS

Carlo Perego, Roberto Millini and Paolo Pollesel

Since the beginning of his scientific career in Eni in 1980's, Giuseppe Bellussi soon recognized the technological importance of zeolites, devoting his interest, efforts and passion on zeolites and catalysis. Along with the years he contributed to intensive research in the field achieving important results, including the demonstration of the concept of isomorphous substitution in zeolites (that led to the synthesis and industrial applications of TS-1), the development of new industrial processes of alkylation of aromatics (e.g. cumene and ethylbenzene) and several others. For his achievements in zeolite science and technology, Giuseppe has been recognized with several awards:

- 1992 Don Breck Award from IZA (Montreal),
- Johnson-Matthey EFCATS International Award (Innsbruck),
- 2008 Piero Pino Gold Medal from Industrial Chemistry Division of Italian Chemical Society (Genova),
- 2008 International Zeolite Association Award (Beijing),
- 2013 Eugene Houdry Award from North American Catalysis Society (Louisville, Kentucky),
- 2013 Giacomo Fauser Lecture from Italian Interdivisional Group of Catalysis (Riccione),
- 2014 Emanuele Paternò Gold Medal from Italian Chemical Society (Rende).

The presentation will briefly review the main achievements and results of the huge contribution of Giuseppe on this exciting subject.

Tu.11
18:55

Chairs Giuseppe CRUCIANI & Fabrizio CAVANI



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**IL2. CONTRIBUTION OF SPECTROSCOPIES TO ZEOLITES AND
MICROPOROUS MATERIALS SCIENCE**

Adriano Zecchina

This talk is intending to briefly summarize the contributions of the Turin Group in the study of surface interactions by means of a variety of spectroscopic methods including infrared, diffuse reflectance in the UV - Vis NIR, resonant Raman and XAS. As the Turin group is operative in this field since the second half of the XX century, also the contributions and innovations of other research groups active in the field will be mentioned and discussed. The great impulse given to XAS by Carlo Lamberti will be also emphasized.

Th.13
11:00

Chair Silvia BORDIGA

**IL3. KEY ROLE OF ZEOLITIC TECHNOLOGIES IN MEETING
CURRENT AND FUTURE SOCIETAL NEEDS**

Suheil F. Abdo

Zeolite-based catalytic and separation technologies play a critical role in meeting today's consumer demands and the evolving needs of society to develop new approaches to fulfill these needs in the future in an environmentally friendly and responsible manner. The great versatility of zeolites and other microporous materials form the underlying basis for the many of today's key conversion technologies. An overview of key zeolite-based processes in refining and petrochemical applications will be presented from a perspective that demonstrates the great value derived from applying improved knowledge of their fundamental properties in enabling critical and successful process developments. This presentation will identify the leading technology offerings in the field and highlight some major applications of zeolitic technologies to illustrate their versatility and strong potential in helping the refining and petrochemical industry to meet evolving societal and regulatory needs. Finally, some thoughts on how well-designed academic-industrial collaboration programs could be the most effective paths to help meet these needs.

Fr.14
08:30

Chair Petr Nachtigall



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Awards

June 11th 2019
18:15 – 18:55

Chairs

*Giuseppe CRUCIANI
Fabrizio CAVANI*



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Premio
Gottardi
2019

**FACILE SYNTHESIS OF NANOSTRUCTURED COBALT
PIGMENTS BY CO-A ZEOLITE THERMAL CONVERSION
AND ITS APPLICATION IN PORCELAIN MANUFACTURE**

Assunta Campanile

An innovative and facile synthesis of Co-pigment was carried out by means of thermal conversion of a cobalt-exchanged zeolite. The Na-A [LTA] zeolite was used, since it is a low cost and easily available raw material. The ion exchange mechanism allowed to control, at microscopic level, the composition of the zeolitic precursor. Several chromatic effects could be obtained by varying the treatment temperature and/or the cobalt concentration in the contact solution. The reliability of these new zeolite-based pigments was tested in porcelain manufacture. The developed cobalt pigments were firstly tested in the porcelain mixture to obtain a coloured product. Then the efficacy, in term of colour and aesthetic effect, was proved in some of the most common decoration methods such as ingobbio, colored glazes and “third fire decoration”.

Premio
Parmaliana
2019

**MODIFIED TiO₂-BASED CATALYSTS FOR ENERGY
PRODUCTION AND ENVIRONMENTAL PROTECTION**

Roberto Fiorenza

In this work three different approaches were used to modify the chemico-physical properties of TiO₂ investigating the effects of these changes on the photocatalytic performance both in the photo-oxidation and photo reduction reactions either under UV than solar light irradiation. The first strategy was to add at the commercial TiO₂ another oxide as CeO₂ and/or noble metals as gold or silver to exploit their surface Plasmon resonance effect. The second approach was a structural modification of TiO₂ with the introduction of Ti³⁺ and oxygen vacancies through laser irradiation. The combination (third approach) of a TiO₂ structural modification as the synthesis of inverse opal materials, and chemical modifications as the addition of a host component or doping agent can be a promising strategy to enhance the titania photoactivity under solar light irradiation.



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Session Tu-1

June 11th 2019
17:15 – 18:15

Chair

Girolamo GIORDANO



01. INFLUENCE OF ZEOLITE FRAMEWORK TOPOLOGY IN THE CO₂/CH₄ SEPARATION

*Eduardo Pérez Botella, Miguel Palomino Roca, Susana Valencia
 Valencia, Fernando Rey García*

The separation of CO₂ from methane can be done by using zeolites as adsorbents. The effect of zeolite polarity Si/Al ratio on this separation has been previously studied, however, the isolated effect of structure and topology can only be observed if pure silica materials are used. In this work, different small pore zeolites of purely siliceous composition (CHA, DDR, IHW, ITW and LTA) have been studied in order to establish which pore sizes and topologies favour high selectivities in this separation. Confinement and molecular sieve effects are discussed, as they seem to be the key to achieving the most favourable selectivities. These effects can be exploited by closely fitting adsorbate and adsorbent pore sizes.

02. ON THE ROLE OF La₂O₃ AND SiO₂ IN THE FORMULATION OF Ni/Al₂O₃ BASED CO₂ METHANATION CATALYSTS

Gabriella Garbarino, Tullio Cavattoni, Paola Riani, Maria Flytzani-Stephanopoulos and Guido Busca

The present work attempts to develop, characterize and extensively test 13.6 wt.% Ni/Al₂O₃ based catalysts for CO₂ methanation by adding to the formulation both SiO₂ and La₂O₃ as promoters. Both promoters are reported to stabilize alumina with respect to sintering and loss of surface area, but, on the other hand, they strongly modify the acido/basic properties of the support. For both Ni/Al₂O₃ and Ni/SiO₂-Al₂O₃ catalyst, lanthanum act as a promoter of catalytic activity, while SiO₂ reduces CO₂ methanation activity, probably for its lower dispersing ability. However the best performing catalysts are Ni₁₄La-Al₂O₃ with 14 wt. % La₂O₃ in the formulation and Ni₃₇/La-SiO₂-Al₂O₃ that achieves the highest methane yield (86%) at low temperature (573 K) not far from Ru/Al₂O₃ performances.



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O3. **FAST ROOM TEMPERATURE LABILITY OF
ALUMINOSILICATE ZEOLITES**

*Petr Nachtigall, Christopher J. Heard, Lukas Grajciar, Cameron M. Rice,
Suzi M. Pugh, Sharon E. Ashbrook, Russell E. Morris*

A particularly valued feature of aluminosilicate zeolites is their perceived stability under mild conditions. The presence of relatively strong Si-O and Al-O bonds in the materials lead to the perception that zeolites are static compounds. Here we demonstrate that even at room temperature zeolites show significant, fast lability of their bonds when in contact with liquid water. We present computational studies that suggest potential chemical pathways by which the lability might occur with low barriers and we demonstrate experimentally that isotopic substitution of ^{17}O in the zeolitic framework rapidly occurs at room temperature. The observation that zeolites are dynamic entities will be of great importance to our understanding of their behavior under wet or steam conditions, which is important for many catalytic processes or in synthetic manipulations that rely on hydrolysis, such as the ADOR process.



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09:20 – 10:40

Chair:

Domenico CAPUTO



04. EFFECT OF A MILD NH₄OH TREATMENT ON LOCAL STRUCTURE AND ACIDIC SITES DISTRIBUTION OF Fe-MFI

Georgia Papanikolaou, Paola Lanzafame, Siglinda Perathoner, Gabriele Centi, Massimo Migliori, Enrico Catizzone, Alfredo Aloise, Girolamo Giordano

In this work demonstrated that the treatment with NH₄OH creates mesopores in Fe-MFI with a different mechanism with respect to the conventional desilication treatment. In fact, the mesoporosity in Fe-MFI appears as result of the dissolution and reprecipitation of the thin amorphous layer, which lead to the assembling of Fe-MFI nanocrystals, and creates isolated defects on the surface of these nanocrystals. The reassembling process induces also changes in the acidity and hydrophobic character, leading to an enhanced activity in the etherification of HMF (5-hydroxymethylfurfural) to 5-(ethoxymethyl)furan-2-carbaldehyde (EMF). Moreover, for treatment times with NH₄OH longer than 6 h, there is an effective, although minimal, desilication with worsening of the catalytic performances. This proper desilication, differently from the reassembling mechanism, leads to a loss of microporous surface area, mesoporosity and acidity characteristics.

05. SILICALITE SYNTHESIZED BY THE DUAL-TEMPLATE TECHNIQUE: A SOLID STATE NMR STUDY

Joaquín Martínez-Ortigosa, Jorge Simancas, J. Alejandro Vidal-Moya, Bruno Alonso, Fernando Rey, Teresa Blasco

Pure silica MFI zeolites have been synthesized using tetraethylammonium (TEA), tetraethylphosphonium (TEP) and a mixture of both as SDAs, and characterized by a series of techniques and more specially by NMR. The results indicate smaller MFI crystals with higher amount of connectivity defects for samples synthesised with TEP, and that TEA and TEP are present in the same crystals in the sample synthesized by the co-template route. 19F NMR signal changes with the amount of TEP indicating variations in the local environment of fluoride. 2D NMR experiments (1H-1H NOESY and 1H-13C HETCOR) ensures the close proximity of the two SDAs and of the zeolite defects with the SDAs inside the MFI-type zeolites.



O6. **CRYSTALLINE HYBRID ORGANIC-INORGANIC
 GALLOSILICATES: SYNTHESIS AND CRYSTAL STRUCTURE**

*Stefano Zanardi, Giuseppe Bellussi, Erica Montanari, Michela Bellettato,
 Wallace O. Parker Jr., Angela Carati, Caterina Rizzo, Giuseppe Cruciani,
 Roberto Millini*

Eni Carbon Silicate (ECS) materials form a family of crystalline hybrid organic-inorganic metallo-silicates discovered in the Eni's laboratories. Determination of crystal structure revealed a common feature i.e. the stacking of inorganic layers covalently bound by the organic component. The aluminosilicate layers are made of $[AlO_4]$ tetrahedrons bound to four $[CSiO_3]$ tetrahedrons. The first act as a spacer among silsesquioxane units. In order to evaluate other trivalent elements as spacers, it was considered the replacement of Al by B and Ga. The former increased the crystallization rate, the later drove to the obtainment of both previously reported aluminosilicate ECS materials and new crystalline phases. A deep chemico-physical characterization allowed the crystal structure elucidation of the new Ga-ECS phases.

SO1. **USE OF LEWIS AND BRØNSTED ACIDS AS CATALYSTS FOR
 β -PINENE OXIDE REARRANGEMENT TO PREPARE
 MYRTENOL AND MYRTANAL**

*Iva Paterova, Barbora Fidlerova, Michal Vavra, Eliska Vyskocilova,
 Libor Cerveny*

β -Pinene oxide rearrangement is an important reaction producing fine chemicals, such as myrtenol, myrtanal and perillyl alcohol. The first two products are formed by opening the epoxy ring of the molecule and perillyl alcohol by both epoxy and carbon ring opening. This work is aimed at products obtained by epoxy ring opening only. The type of solvent has an effect on the course of α - or β -pinene oxide rearrangement in the presence of acid catalysts. Therefore, several solvents such as acetonitrile, tetrahydrofuran, toluene and 1,4-dioxane were tested in combination with different Lewis acids, namely $FeCl_3$, $AlCl_3$, $SnCl_2$, $ZnBr_2$ a $ZrCl_4$. The highest selectivity (90 %) to the desired products at the total conversion was achieved using $SnCl_2$ (5 mol% to the substrate) and 1,4-dioxane as the solvent after 5 minutes of reaction.



SO2. **CATALYTIC ACTIVITY OF NOBLE METAL CLUSTERS
ENCAPSULATED IN ZEOLITES**

Mehran Sajad, Roman Bulanek, Martin Kubů, Yuyan Zhang

Unique behavior of noble metal clusters is not similar to single atoms or nanoparticles. Recently, transformation of 2D zeolites to 3D form have been found as an efficient method for generation of stable Pt subnanometric clusters which can protect such species against aggregation and sintering.¹ In this contribution, reactivity of noble metal clusters encapsulated in different zeolite has been reported. Noble metals (Pt, Pd) were encapsulated within zeolites by transformation of 2D zeolite into 3D form (MWW) or by the ADOR process (IPC-2, IPC-4). Catalyst were characterized by powder XRD, SEM/TEM imaging, N₂ adsorption/desorption isotherms, IR spectroscopy and H₂-TPD. To test the catalytic properties of the encapsulated nanoparticles, we have chosen hydrogenation of propene and (O)DH of ethanol.



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Chair:

Matteo GUIDOTTI

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07. **AQUEOUS PHASE REFORMING OF SUGAR-BASED
BIOREFINERY STREAMS: FROM THE SIMPLICITY OF
MODEL COMPOUNDS TO THE COMPLEXITY OF REAL FEEDS**

*Giulia Zoppi, Giuseppe Pipitone, Alessandra Frattini, Samir Bensaid,
Raffaele Pirone*

The hemicellulose fraction in lignocellulosic biomass is not effectively fermented and can be valorized in alternative ways (drop-in fuel production, biohydrogen etc.). In this work we explored the valorization of the pentoses through aqueous phase reforming (APR) in the 230-270 °C and at different carbon concentration (0.3-1.8 C wt.%). Glucose, xylose and relevant sugar alcohols (sorbitol and xylitol) were chosen as model compounds, with xylose being subjected to APR for the first time. Test of synthetic mixtures did not show the presence of competitive adsorption issues. Moreover, a real stream coming from a bioethanol plant (hydrolysate) was tested. The higher hydrogen yield obtained from sugar alcohols prompted to evaluate a dual configuration hydrogenation-APR that led to a net positive production of hydrogen.

08. **COMPARING BATCH AND GAS-FLOW CONDITIONS IN THE
TRANSFER HYDROGENATION OF ALKYL LEVULINATES
PROMOTED BY ZrO₂ CATALYST**

*Tommaso Tabanelli, Emilia Paone, Paola Blair Vásquez, Rosario
Pietropaolo, Fabrizio Cavani, Francesco Mauriello*

The catalytic conversion of methyl and ethyl levulinate into γ -valerolactone (GVL) by using MeOH, EtOH and 2-PrOH as H-donor/solvent, promoted by the ZrO₂ catalyst, under both batch and gas-flow conditions is investigated. Under batch conditions, 2-propanol was found to be the best H-donor molecule with ethyl levulinate affording the highest yield in GVL. Reactions carried out under continuous gas-flow conditions were found to be by far more efficient showing excellent yields in GVL also when EtOH was used as reducing agent. The experiments clearly show that the ability to release hydrogen of alcoholic H-donor/solvent is the main factor driving CTH processes while their tendency to attack the ester group is the key step in the formation of transesterification products.



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09. GLYCEROL CARBONATES AS AN INNOVATIVE ALKYLATING AGENTS FOR PHENOLICS

*Tommaso Tabanelli, Carlo Giliberti, Rita Mazzoni, Raffaele Cucciniello,
Fabrizio Cavani*

Glycerol carbonate (GlyC) has been tested as an innovative alkylating agents for phenolics. In particular, the presence of both the carbonate and the free hydroxyl groups allows to obtain a peculiar reactivity which is different from the one observed with the more investigated organic carbonates (namely ethylene and propylene carbonate). In this way, a completely innovative and greener synthesis pathway to hydroxymethyl benzodioxanes was achieved by the reaction of GlyC with catechol in the presence of a basic catalyst (NaOCH₃, MgO and Na-Mordenite), in solventless conditions obtaining only water and CO₂ as safe co-products. Similarly, the alkylation with phenol allow to obtain not only the mono but also the di-phenylglyceryl ether, the latter being elusive with the traditional synthesis using other organic carbonates, glycidol or epichlorohydrin.

SO3. TRANSFER HYDROGENOLYSIS OF AROMATIC ETHERS PROMOTED BY Pd/Fe₃O₄ ELECTROSPUN NANOMATERIALS

*Angela Malara, Emilia Paone, Lucio Bonaccorsi, Francesco Mauriello,
Patrizia Frontera*

The catalytic conversion of benzyl phenyl ether (BPE) promoted by Pd/Fe catalysts, under batch conditions and in the presence of 2-PrOH as H-donor/solvent, is investigated. Samples, prepared in the form of nanofibers materials by using the electrospinning technique, named Pd/Fe₃O₄-s and Pd/Fe₃O₄-cos, differed just for the Pd addition method, wet impregnation in the first case and co-electrospinning in the latter. By using Pd/Fe₃O₄-s as catalyst, an appreciable BPE (0.1 M) conversion into phenol and toluene was achieved after 90 minutes at 240 °C. Pd/Fe₃O₄-cos showed a lower BPE conversion but, despite this, a high selectivity in the aromatics productions was maintained. The high activity of Pd/Fe₃O₄-s could be explained considering the better exposure of the catalytic centres of palladium compared to Pd/Fe₃O₄-cos catalyst.



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SO4. **CYCLIC VOLTAMMETRIC STUDIES OF SMALL IRIIDIUM
CLUSTERS FOR ENERGY CARRYING MOLECULES**

*Rosalba Passalacqua, Siglinda Parathoner, Gabriele Centi, Avik Halder,
Stefan Vajda*

The non-delayable quest of sustainable energy infrastructure based on converting solar energy onto energy carrying molecules has renewed interest in tailored catalysts for water splitting and CO₂ reduction reactions (CO₂RR). In this context iridium, has emerged as one of the most interesting materials. In the attempt to identify a direct correlation between particular atom arrangements with a precise electrochemical activity, the survey of several few-atom iridium clusters was started. Herein, we report preliminary results on a small Ir₉ cluster deposited by a new size-selective method developed at the Argonne National Laboratory. The cluster-coated electrode was cycled in 0.1 M NH₄Cl and KOH under N₂ and CO₂. Finally, the CV and SWV curves were compared in order to gain insights on its potential behavior as catalyst for the CO₂RR.



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11:00 – 13:00**

Chair:

Giovanna VEZZALINI



O10. **TUNING MESOPOROSITY IN HIERARCHICAL ZSM-5
ZEOLITE BY CHANGING THE SILANIZATION AGENT
FUNCTIONALITY**

Maria del mar Alonso-Doncel, Ángel Peral, Ruy Sanz, David P. Serrano

The selection of an adequate organosilane have been demonstrated as a crucial factor for preparing hierarchical ZSM-5 zeolites with a controlled mesopore sizes when synthesized by crystallization of silanized protozeolitic units. The role of amine and phenyl groups of organosilanes has been studied in this work, as well as the length of the organosilane chain and the number of effective anchoring points of these molecules. Catalysts prepared have been tested in low-density polyethylene (LDPE) cracking reactions, and it has been found that a more uniform mesopore size distribution of the hierarchical zeolites induces changes in the catalytic activity during reaction, the LDPE degradation occurs in a narrower temperature range.

O11. **POLYMERIZATION OF HEXADIENE AND
PHENYLACETYLENE CONFINED IN SILICA ZEOLITE
CHANNELS**

Rossella Arletti, Giorgia Confalonieri, Francesco Di Renzo, Marco Fabbiani, Ettore Fois, Julien Haines, Gianmario Martra, Simona Quartieri, Mario Santoro, Gloria Tabacchi, Giovanna Vezzalini

Conductive polymers obtained by the polymerization of hydrocarbons are of great interest for many technological applications. Their protection inside a confining matrix is necessary to protect their properties. We tuned a procedure to promote the penetration and the polymerization of phenylacetylene and hexadiene into a pure silica mordenite, exploiting the nano-confinement effect in the porous material. The resulting material was characterized by many techniques (XRPD, TGA, IR, DFT calculations) to unravel its structure and the host-guest relationships. Hints of polymerization were found in both systems which can be used as starting point for the formation of carbon nanowires. The new hybrid material can be exploited for environmental purposes, for example in gas sensors, sensitive to air pollutants.



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**O12. STRUCTURAL MODIFICATIONS AND THERMAL STABILITY
 OF Cd²⁺-EXCHANGED STELLERITE, A ZEOLITE WITH STI
 FRAMEWORK TYPE**

Georgia Cametti, Sergey V. Churakov

Stellerite is a natural Ca-zeolite with **STI** framework type. In this study we investigated the crystal structure and the thermal stability of the completely Cd²⁺-exchanged form of stellerite by means of *in situ* Single Crystal X-ray Diffraction (SCXRD) and *ab initio* Molecular Dynamics (MD) simulations. The structure at room temperature (RT) is found to be monoclinic, space group *F2/m*. Cd²⁺ ions are surrounded by H₂O at average bonding-distance of 2.35 Å. In the investigated temperature range (25-375°C) the unit-cell volume contraction is 22% of that measured at RT. The main structural transformations are described by the rupture of two T-O-T connections. This process leads, at 225°C, to the formation of a different structural topology compared to the one observed for Ca-stellerite.

**O13. HIGH-PRESSURE COLD METHANOL INTRUSION
 IN MFI- ZEOLITES**

*Davide Comboni, Paolo Lotti, G. Diego Gatta, Francesco Pagliaro,
 Enrico Catizzone, Massimo Migliori, Girolamo Giordano, Marco Merlini,
 Michael Hanfland*

In the last decades several efforts were devoted to explore the *P*-mediated intrusion of molecules in zeolites. MFI-zeolites are commonly used as catalysts to produce olefins, representing an appealing alternative to the high-energy demanding Steam Cracking process. At ambient conditions, only the surfaces of the zeolite crystallites are believed to be active in the methanol-to-olefins process. However, thanks to pressure, the methanol can penetrate and diffuse through the zeolitic channels potentially enhancing the methanol-to-olefins (MTO) conversion process. In this regard, we investigated, via *in situ* X-ray powder synchrotron diffraction experiments the high pressure behavior of six MFI-zeolites with different chemistry composition. The main aim is to obtain information on the optimal chemistry composition of a potential MFI-catalyst in MTO conversion process.



O14. **ENCAPSULATION OF METAL NANOPARTICLES (NPS)
 WITHIN ZEOLITE FRAMEWORKS VIA 2D TO 3D
 TRANSFORMATION**

Martin Kubů, Yuyan Zhang, Michal Mazur

We introduced Pt/Pd nanoparticles within the MWW framework during the swelling process of lamellar zeolitic precursor (MCM-22P) and its subsequent 2D to 3D transformation. Surfactants with different carbon chain lengths (C₁₂, C₁₄, C₁₆, C₁₈) were used as swelling agents. Moreover, we extended this method to other zeolite precursors like IPC-1P via the ADOR (Assembly-Disassembly-Organization-Reassembly) process and encapsulated Pt/Pd nanoparticles into IPC-2 and IPC-4 materials. Different loading of metal NPs was used. All synthesized materials were investigated by PXRD, sorption, ICP-OES, SEM, and TEM methods. Structural and textural analysis proved no significant changes after the metal NPs encapsulation. Synthesized materials were investigated in the shape-selectivity hydrogenation of nitroarenes to anilines.

SO5. **SYNTHESIS AND CHARACTERIZATION OF
 ORGANOSILICEOUS HYBRID MATERIALS CONTAINING
 ACID FUNCTIONALITIES**

*Andrea Erigoni, Candela Segarra, Ivana Miletto, Geo Paul, Fernando Rey
 García Enrica Gianotti, Leonardo Marchese, Urbano Diaz*

Sulfonic acid moieties have been reported to be valid candidates for incorporating super-acid functionalities into mono- and eventually multifunctional inorganic materials. In this work we report a multi-step synthesis of silica supported aryl-sulfonic acids, in which the aromatic ring is either protonated or fluorinated. A detailed spectroscopic characterization by coupling FTIR and ss NMR with the adsorption of probe molecules was used to study the acidity of the sulfonic groups and their interaction with the surface silanols of the inorganic supports. Typical textural properties of mesoporous materials were observed by N₂ physisorption analysis at 77 K. The adsorption of probe molecules with different basic strength such as CO and ammonia has been useful not only to assess the acidity of the sulfonic groups but also to evidence the interaction of the acid sites with the hydrophilic silica surface that can modify the relative acidity of sulfonic acids.

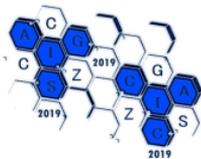


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SO6. **DIRECT α -ARYLATION OF KETONES EFFICIENTLY
 CATALYZED BY Cu-MOF-74**

Pedro Leo, Gisela Orcajo, David Briones, Fernando Martínez, Guillermo Calleja

The activity and reusability of Cu-MOF-74 as heterogeneous catalyst were studied in the Cu-catalyzed C-C cross-coupling reaction of 4-iodotoluene (4-IT) with acetylacetone (AcAc) to direct synthesis of α -aryl-ketones. Cu-MOF-74 is characterized by having unsaturated copper sites into its highly porous metal-organic framework that can efficiently interact with the substrates. The influence of critical reaction variables were evaluated and optimized for achieving almost complete conversion of substrates. The C-arylation between 4-IT and AcAc proceeded only in the presence of Cu-MOF-74 material. It also displayed a remarkable structural stability, regarding its XRD patterns and solid recovery degree after several reaction cycles. This catalyst showed promising results in comparison to other homogeneous and heterogeneous Cu-based catalysts.



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**June 12th 2019
11:00 – 13:00**

Chair

Michela SIGNORETTO



O15. REVERSE MICELLES SOL-GEL SYNTHESIS ALLOWS BOTH BULK DOPING AND HETEROATOMS SURFACE ENRICHMENT IN Mo-DOPED TiO₂ NANOPARTICLES

*Roberto Nasi, Serena Esposito, Francesca S. Freyria, Marco Armandi,
 Tanveer A. Gadhi, Simelys Hernandez, Paola Rivolo, Nicoletta Ditaranto,
Barbara Bonelli*

TiO₂ nanoparticles containing 0.0, 1.0, 5.0, and 10. wt.% Mo were prepared by a reverse micelle template assisted sol-gel method allowing the dispersion of Mo atoms in the TiO₂ matrix. Their textural and surface properties were characterized by means of X-ray powder diffraction; micro-Raman spectroscopy; N₂ adsorption/desorption isotherms at -196°C; Energy Dispersive X-ray analysis coupled to Field Emission Scanning Electron Microscopy; X-ray Photoelectron Spectroscopy; Diffuse Reflectance UV-Vis spectroscopy and ζ-potential measurement. The photocatalytic degradation of Rhodamine B (under visible light and low irradiance) in water was used as a test reaction, as well. The ensemble of the obtained experimental results was analyzed in order to figure out the actual state of Mo in the final materials, showing the occurrence of both bulk doping and Mo surface species, with progressive segregation of MoOx species occurring only at higher Mo content.

O16. COPPER-CONTAINING MICROPOROUS MOLECULAR SIEVES AND ORGANICALLY MODIFIED CLAYS APPLIED IN THE DEFENCE AGAINST THE OLIVE TREE FLY PEST, BACTROCERA OLEAE

*Matteo Guidotti, Rinaldo Psaro, Roberto Consolo, Alessandro Caselli,
 Roberto Rappuoli, Chiara Bisio, Giacinto S. Germinara, Elisabetta
 Gargani*

Bactrocera oleae, the olive tree fly, is the most significant phytophagous insect associated with olive tree cultivations in the Mediterranean area. To mitigate such threat, two series of solids aiming at causing a negative impact on the life cycle of *B. oleae* were prepared: 1) Cu(II)-exchanged clinoptilolite zeolites, from mineral origin, and 2) organically modified montmorillonite clays, over which aliphatic aldehydes have been deposited. Thanks to the immobilisation within the solids, lower concentrations of bioactive species may be applied onto the olive tree, reducing the undesired dispersal of it into the environment and leading to a



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controlled release of the repellent agent during the treatment. Extremely promising results were obtained for the trees treated with Cu(II)-clinoptilolite and with aldehyde-containing montmorillonite clays, in terms of reduction of both fly infestation (reduced by 97%) and damages on the olive fruit.

O17. PREPARATION OF NANOSTRUCTURED CATALYSTS BY GRAFTING METAL ALKOXIDES ON THE SURFACE OF OXIDES SUPPORTS

Elio Santacesaria

Metal alkoxide grafting technique can be used for changing the acid-base and/or the redox properties of the surface of an oxide rich in hydroxyls. The preparation of catalysts by grafting different commercial available alkoxides, such as: Si, Ti, Zr, and V on the surface of oxides, such as: SiO₂, Al₂O₃ and TiO₂, is described. The performances of the acid catalysts were evaluated by adequate test reactions such as: methanol dehydration, skeletal isomerization of 1-butene and alkane isomerization and cracking. The redox properties of vanadium based catalysts, obtained by grafting vanadyl alkoxide on SiO₂ and TiO₂/SiO₂ supports, have been tested in reactions, such as: the SCR of NO with NH₃, the Oxidative Dehydrogenation (ODH) of ethanol and methanol to formaldehyde and acetaldehyde, the ODH of propane, isobutane and n-butane.

O18. POST-SYNTHESIS MODIFICATION OF GOLD-SILVER NANOPARTICLES: A WAY TO TUNE CATALYTIC ACTIVITY AND SELECTIVITY

Marta Stucchi, Andrea Jouve, Stefano Cattaneo, Sofia Capelli, Alberto Villa, Laura Prati

Carbon supported gold catalysts are highly active in the liquid phase oxidation of glycerol. In particular, bimetallic particles show enhanced activity, diverse selectivity and higher stability. Au–Ag catalysts supported on TiO₂ by sequential deposition–precipitation method showed higher conversion than monometallic Au/TiO₂ in CO oxidation, confirming the synergistic effect between Au and Ag. Moreover, the catalyst activation temperature influenced both the catalytic activity and nanoparticles composition. Theoretical studies investigating the segregation of Ag in Au-Ag NPs, reporting that segregation behaviors are



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composition, size and temperature dependent. Based on these facts and considering the already proven efficiency of Au-Ag bimetallic catalysts in glycerol oxidation, here we compared the catalytic activity and selectivity of differently synthesized and post-treated Au-Ag/TiO₂ catalysts for glycerol oxidation. The same post-treatment had a different outcome on the nanoparticles features, and this reflected on the catalytic activity and selectivity.

O19. PHOTOCATALYSIS ON SHAPE-ENGINEERED TiO₂ NANOPARTICLES: A CLOSER LOOK INTO THE SURFACE PROCESSES BY *IN SITU* SPECTROSCOPIES

Lorenzo Mino, Francesco Pellegrino, Francesco Moriggi, Michele Ceotto, Giuseppe Spoto, Valter Maurino, Gianmario Martra

TiO₂ nanoparticles (NPs) are widely employed to face environmental and energy issues. In particular, shape-engineered TiO₂ anatase nano-sheets with dominant {001} facets are investigated to exploit different functional behaviors with respect to usual bipyramidal TiO₂ anatase NPs, mainly exposing {101} facets. We studied the surface hydrophilicity and Lewis acidity of different shape-engineered TiO₂ NPs to clarify the surface physico-chemical features which influence their photocatalytic activity. Moreover, using a new *in situ* IR setup, we monitored the evolution of the intermediates and products during the photocatalytic reactions, directly looking at the catalyst surface. This approach clarifies the precise role of the different surfaces in determining the NPs photoactivity providing design rules for the preparation of NPs optimized for specific applications.

S07. AMPHOTERIC SURFACES STEMMING FROM THE PARTIAL COLLAPSE OF HYBRID ALUMINOSILICATE NANOTUBES: AN IR SPECTROSCOPY ASSESSMENT

Marco Armandi, Roberto Nasi, Francesca S. Freyria, Serena Esposito, Barbara Bonelli

The aluminosilicate Methyl-Imogolite (Me-IMO), with formula (OH)₃Al₂O₃SiCH₃, can be synthesized by one-pot template-free procedure. Its structure consists of bundles of nanotubes (NTs), with an inner diameter of *ca.* 2 nm. The outer surface consists of a curved gibbsite-like, whereas the inner one is lined with Si-CH₃ groups. Although its structure is unstable above *ca.* 570 K, the thermal collapse of the NTs yields to a microporous buckled structure that still shows a considerable surface area



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($557 \text{ m}^2\text{g}^{-1}$) and porous volume ($0.31 \text{ cm}^3\text{g}^{-1}$), with new surface functionalities. The present work attempts to provide insight into the surface properties of collapsed Me-IMO (Me-IMO-c). To this aim, IR spectroscopy of adsorbed probe molecules (*i.e.* Acetone, NH_3 , CO and CO_2) was mainly adopted.

SO8. SYNTHESIS OF BIOSURFACTANTS BY SOLID ACID CATALYSTS

*Valeria Pappalardo, Denise Cavuoto, Federica Zaccheria,
Nicoletta Ravasio*

The synthesis of α -d-glucose-palmitic acid esters was reached in acetylacetone at different temperatures by using several montmorillonite clays: the commercial KSF, K10 and K30, and cation-exchanged K10/Fe. The best results was obtained in presence of K10/Fe clay catalyst (43% conversion at $100 \text{ }^\circ\text{C}$). After flash chromatography purification, the esters were characterized by NMR and mass spectrometry analyses. The HLB values were calculate and the interfacial tension and critical micelle concentration (CMC) evaluated. The catalyst activity was correlated to the amount of acidic sites and the total surface area.



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11-14th June 2019 - Amantea (CS) - ITALY

Session We-3

June 12th 2019
15:30 – 17:10

Chair

Joaquin PÈREZ PARIENTE



SO9. MULTIPLE PHASE TRANSFORMATIONS DURING THE SYNTHESIS OF GERMANOSILICATE UOS

Qiudi Yue, Maksym Opanasenko

The synthesis of germanosilicates with structures depending on the crystallization time was applied for a fixed chemical composition with SiO_2 : GeO_2 : OSDA: HF: H_2O = 0.5: 0.5: 0.9: 1: 8 at 170 °C. 3-Ethyl-1-methyl-3H-imidazol-1-ium was used as structure-directing agent. Optimization of crystallization time allowed to separate two pure phases (**STW** and **Phase 1**) before the crystallization of final phase of IM-16 (**UOS**). The **STW** is formed in a short time and possesses a hexagonal bipyramid shape of the crystals. The pure **STW** can be obtained in 12 hours. With the prolonging time, a new **Phase 1** was generated inside the **STW** crystal. The pure **Phase 1** can be separated in 7 days. It has a spindle-shaped crystals formed by aggregation of small rods. The nanosized rod-shape **Phase 1** grows to laminar crystals with the increasing of time. Finally, a pure **UOS** phase was formed in 14 days.

SO10. SYNTHETIC ZEOLITE AND LASER EFFECT: PRELIMINARY DATA

Claudia Belviso, Ambra Guarnaccio, Stefano Orlando, Antonio Lettino, Francesco Cavalcante

This paper documents preliminary laboratory tests performed to investigate the effects of laser technique on zeolite crystalline structure and morphology. In the last few years, nanosized zeolites have been attracting great attention due to the numerous applications of these minerals and many literature data have documented the use of various techniques for zeolite nanocrystals formation. However, besides the conventional methods, alternative approaches such as laser-induced fragmentation have been used to control the size of zeolite. The use of laser for the fragmentation of materials is a well known method for the colloidal metal particles reduction but recently this approach has also been tested in the rapid preparation of zeolite nanocrystals. Starting from the few aforementioned literature data, we show the preliminary results about the effect of laser on particle size of LTA zeolite. Laser-irradiated samples were studied by scanning electron microscopy (SEM) and X-ray diffraction analysis (XRD). Morphological results indicated that amorphization and changes in particle zeolite size took place after the laser irradiation.



SO11. **THE FERROELASTIC PHASE TRANSITION IN ZSM-5 ZEOLITES: CHEMISTRY VS. THERMODYNAMIC**

Matteo Ardit, Giuseppe Cruciani

One ZSM-5 and one silicalite zeolite samples characterized by different Si/Al ratio (i.e. Si/Al = 250 and $\rightarrow \infty$, respectively) have been investigated through the combination of *in-situ* X-ray powder diffraction at high-temperature and calorimetric experimental techniques. A more in-depth understanding of the relationship between chemical (i.e. Si/Al ratio) and thermodynamic (i.e. transition temperature, T_c and enthalpy change, ΔH) properties related to the ferroelastic monoclinic-orthorhombic phase transition has been provided through a Landau-type theory approach.

O20. **THE KEY ROLE OF METAL-ZEOLITE INTERACTION FOR STABILITY OF HYBRID CATALYSTS DURING CO₂-TO-DME HYDROGENATION**

*Giuseppe Bonura, Massimo Migliori, Catia Cannilla, Aldo Mezzapica,
 Leone Frusteri, Serena Todaro, Alfredo Aloise, Girolamo Giordano,
 Francesco Frusteri*

Hybrid catalysts were recently proposed as efficient systems for one-pot hydrogenation of CO₂-to-DME, although a rapid decay of activity pushes the need for more stable multifunctional systems. In this work, the influence of home-made zeolite samples, integrated in a weight ratio of 1:1 with a CuO-ZnO-ZrO₂ metal-oxide(s) phase, was investigated under long-term stability tests, in a fixed bed reactor to assess the activity-selectivity pattern of the hybrid catalyst as well as their deactivation trend during operation time. A linear dependence of the deactivation rate both on the temperature of onset reduction and strong acidity highlighted how the extent of interaction between the metal-oxides phase with the zeolite surface as well as the strength of the acid sites significantly control the catalyst stability.



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**SO12. SILICA METAL-OXIDE PILLARED ZEOLITES – GREEN
 SELECTIVE OXIDATION CATALYSTS**

Jan Přeč, Jiří Čejka

Selective oxidation is one of the important reactions in organic synthesis. Oxidation reaction using hydrogen peroxide can be catalysed efficiently by titanosilicate and tin-silicate zeolites. We present a silica-metal oxide pillaring concept, which is a simple and efficient tool to prepare catalysts with enhanced active site accessibility starting from layered zeolite precursors. Silica-titania pillared **MFI** and **UTL**-based lamellar catalysts catalyse epoxidation of bulky cyclic olefins and terpenes while tin-silica pillared catalysts are active in Baeyer-Villiger oxidation of polycyclic ketones and Meerwein-Ponndorf-Verley reduction of furfural with 2-propanol. The latter reaction can be catalysed also using silica-zirconia pillared catalyst.

**O21. CU-CHA CATALYSTS FOR NH₃-SCR: THE ROLES OF
 SiO₂/Al₂O₃ AND Cu LOADING IN THE Cu-SPECIATION**

*Roberta Villamaina, Isabella Nova, Enrico Tronconi, Maria Pia Ruggeri,
 Jillian Collier, Andrew York, Dave Thompsett*

We investigated the role of two characteristic parameters, the Cu content and the SiO₂/Al₂O₃ ratio (SAR), of Cu-CHA catalysts dedicated to the NO_x abatement through the NH₃ Selective Catalytic Reduction (NH₃-SCR). These two parameters, indeed, are important indices to determine the location, mobility and nature of Cu active sites present in the zeolite catalysts (ZCu^{II}OH and Z₂Cu^{II}), which in turn might have an impact on the SCR activity. Four characterization tests, namely H₂-TPR, NH₃ and NO₂ adsorption + TPD and NO+NH₃-TPR, were carried out in order to evaluate how these two parameters affect the interaction between NH₃ and nitrates with the catalyst surface and the reducibility of the active sites. Moreover, these transient tests allowed to probe the speciation of Cu sites in Cu-CHA with simple and well-established techniques.



O22. **SELECTIVE CATALYTIC OXIDATION OF AMMONIA
(NH₃-SCO) ON IRON BETA ZEOLITE CATALYSTS PREPARED
BY ION EXCHANGE AND SOLVATED METAL ATOM
DISPERSION**

*Sebastiano Campisi, Melissa G. Galloni, Antonella Gervasini, Filippo
Bossola, Claudio Evangelisti*

Beta zeolite has been functionalized with ca. 2 wt.% Fe to obtain catalysts for the NH₃-SCO reaction. Fe deposition was performed by solvated metal atom dispersion (SMAD) and ionic-exchange (IE) procedures. ZSM-5 was selected as reference structure known to assure high dispersion of isolated centers when functionalized by IE. Transmission electron microscopy with element maps enlightened on the Fe-species distribution and dimension on the two zeolites. SCO activity on Fe/zeolites started at ca. 300°C, without no clear effect of the size of Fe on the reaction activity/selectivity. The experimental results indicated that not only isolated well-dispersed iron species, but also SMAD-derived Fe nanoparticles worked with excellent performances in the ammonia oxidation reaction with high activity in terms of conversion, selectivity to dinitrogen, and stability.



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Session Th-1

June 13th 2019
09:20 – 10:40

Chair:

Maksym OPANESENKO

O23. **ZEOLITES IN PECHMANN CONDENSATION: IMPACT OF FRAMEWORK TOPOLOGY AND TYPE OF ACID SITE**

Ondřej Veselý, Mariya Shamzhy, Pavla Eliášová

Pechmann condensation is a reaction for preparing coumarins, which are important intermediates in fine chemical synthesis. Unlike previously used homogenous catalysts, zeolites possess many advantages, such as tuneable acidity and shape selectivity. However, narrow size of zeolite micropores limit the mass transfer and thereby leaves a portion of the active sites inside the crystal unused. This drawback can be overcome by using the hierarchical zeolites. In this contribution, zeolites with different channel systems (MTW, *BEA, MFI) were prepared in both bulk and hierarchical “nanosponge” form and different compositions (aluminosilicate, gallosilicate). Their performance was investigated in the Pechmann condensation of phenols.

O24. **METAL-DOPED ZEOLITES FOR LOW-T NO_x ADSORPTION: OPERANDO FT-IR SPECTROSCOPY AND REACTIVITY STUDIES**

Lidia Castoldi, Roberto Matarrese, Irene Dubini, Luca Lietti, Sara Morandi

Cold-start can contribute up to 80–90% of the total drive cycle emissions, so the NO_x removal at low temperature is a significant challenge. Low-temperature NO_x adsorbers (LTNA) catalysts based on zeolites are here investigated to this end. Metal-promoted zeolites (Y, ZSM-5, FER and SSZ-13) have been prepared, characterized and tested by means of NO_x adsorption/TPD. The nature of the adsorbed NO_x species has been analyzed by operando FT-IR spectroscopy. The obtained results indicate that: i) the framework structure of the zeolite significantly affects the adsorption capacity; ii) the high temperature thermal treatment increases the adsorption capacity of the sample; iii) the presence of water in the feed depresses the NO_x storage. Moreover, a reducing pretreatment in H₂ or CO tends to agglomerate the metal (i.e. Pd) decreasing the storage capacity, but it seems reversible.

SO13. **CATALYTIC BIOMASS PYROLYSIS OVER KH-ZSM-5
ZEOLITE WITH ACID-BASE PROPERTIES**

Luis M. López-Renau, Laura García, Héctor Hernando, Gema Gómez-Pozuelo, Juan A. Botas, David P. Serrano

Biomass fast pyrolysis is a route to produce bio-oils with potential applications as liquid fuels or source of bio-based chemicals, but their complex composition and poor properties, derived from its high oxygen content, difficult these uses. This work reports the results achieved in fast pyrolysis of wheat straw over nanocrystalline KH-ZSM-5 zeolite as catalyst in terms of bio-oil upgrading. The removal of a great part of the strong acid sites by ion-exchange with K^+ results in a more favorable deoxygenation route in terms of both mass and energy yields, minimizing the occurrence of overcracking and coke formation reactions. Moreover, the basicity generated in the zeolite can promote ketonization and aldol condensation reactions between the components of bio-oil, having an important role in the deoxygenation selectivity.

SO14. **ADSORPTION OF P-HYDROXYBENZALDEHYDE ONTO
ZEOLITES FOR WATER REMEDIATION: EVALUATION OF
THE COMPETITION BETWEEN CONTAMINANT AND
NATURAL ORGANIC SUBSTANCES**

Tatiana Chenet, Elena Sarti, Luisa Pasti, Elisa Rodeghero, Annalisa Martucci

Toluene is a hydrocarbon belonging to the BTEX class (Benzene, Toluene, Ethylbenzene, Xylene) which is frequently detected in all environmental compartments due to its wide use as solvent, antiknock agent in gasoline, and for the production of benzene. In this study we tested the efficiency of zeolites as eco-compatible adsorbent material for the removal of the organic contaminant toluene from aqueous matrices containing the natural component p-hydroxybenzaldehyde (p-HBA). p-HBA is one of the monomers of humic acids derived from the biodegradation of lignin, these substances are commonly found in surface and ground waters and, due to their dimensions similar to the zeolites pore size, could interfere in the adsorption of organic pollutants.

SO15. **SULFONAMIDES PHOTODEGRADATION ASSISTED BY $\alpha\text{Fe}_2\text{O}_3\text{-TiO}_2\text{-P/ K}_2\text{S}_2\text{O}_8$ SYSTEM**

Sandra Y. Mendiola, Carlos Palomino Cabello, Aracely Hernández, Gemma Turnes, Jorge L. Guzmán, Laura Hinojosa

In this communication, the photocatalytic degradation of the mixture of sulfadiazine, sulfamerazine, and sulfamethazine was carried out with $\alpha\text{Fe}_2\text{O}_3\text{-TiO}_2\text{-P}$ under visible light. The $\alpha\text{Fe}_2\text{O}_3\text{-TiO}_2\text{-P}$ was synthesized by the microwave-assisted sol-gel method and their morphology and physicochemical properties were determined. The optimal photocatalytic performance was found to be using 0.75 g/L of 0.5 $\alpha\text{Fe}_2\text{O}_3\text{-TiO}_2\text{-P}$ catalyst at solution pH 10 showing low mineralization percentage (27 %) resulted from the rapid recombination of photogenerated e^-/h^+ pairs. This may be suppressed through the introduction of an external e^- acceptor ($\text{K}_2\text{S}_2\text{O}_8$) to the catalytic process, obtaining a mineralization of SNs nearly 69 % within 300 min.

SO16. **DEHYDRATION OF AN AZEOTROPE SOLUTION AT HIGH PRESSURE THROUGH A DIFFERENTIAL PENETRATION OF ETHANOL AND WATER IN SI-CHABAZITE**

Giorgia Confalonieri, Simona Quartieri, Giovanna Vezzalini, Gloria Tabacchi, Ettore Fois, T. Jean Daou, Rossella Arletti

In this work we tested a silica chabazite (Si-CHA) in the absorption of water/ethanol molecules from an azeotropic solution. Synchrotron X-ray powder diffraction data show that both water and ethanol penetrate Si-CHA at both ambient and HP conditions. However, while at P_{amb} the water:ethanol ratio absorbed inside Si-CHA is similar to that of the azeotropic mixture, upon compression we observed a dehydration effect. In fact, at 1.84 GPa, Si-CHA extraframework content corresponds to a composition much richer in water than the azeotropic one. At 2.44 GPa the external solution crystallizes (to be compared to 4.8 GPa, the crystallization pressure of the azeotrope). Since pure ethanol crystallizes at about 1.9 GPa, this confirms the azeotrope dehydration. Results obtained by XRPD at 1.84 GPa were also compared to those obtained by DFT calculations.



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Microsymposium Carlo Lamberti

June 13th 2019

09:20 – 13:00

Chair

Gloria BERLIER

Session Th-1, June 13th



KN1. **UNDERSTANDING SELECTIVE REDOX CHEMISTRY
IN Cu-ZEOLITES: A SYNCHROTRON-ENHANCED
MULTI-TECHNIQUE PERSPECTIVE**

Elisa Borfecchia

Cu-exchanged zeolites are attracting increasing attention as platforms for high-impact selective redox chemistry, including NH_3 -mediated selective catalytic reduction of harmful nitrogen oxides (NH_3 -SCR) and direct selective oxidation of methane to methanol (DMTM). Quantitative determination of Cu-speciation in the zeolite framework under realistic reaction conditions is essential to keep advancing the field. This contribution will focus on recent research about NH_3 -SCR and DMTM over Cu-zeolites, to underpin general principles and challenges about the characterization of structural/chemical dynamics in these systems. The role of *in situ/operando* synchrotron X-ray spectroscopy, integrated with laboratory-based multi-technique characterization, computational modelling and systematic performance evaluation, will be emphasized.

O25. **IN SITU CHARACTERIZATION OF ZEOLITIC CATALYSTS**

Jeroen A. van Bokhoven

Synchrotron-based *in situ* XRD and Al K edge XAS were performed to determine the processes that occur during steam activation of zeolite Y. Zeolite Y is the most-used catalyst in the upgrading of the heavy fraction of oil in the FCC process, which is the major source of gasoline and olefins. Diffraction provides details about the crystallinity, the crystal structure, and the location of extra-framework species, provided they occupy crystallographic positions. X-ray spectroscopy yields the local aluminum coordination, irrespective of crystallinity of the species. XAS and XRD are therefore perfectly complementary and both provide the ability to measure under *in situ* conditions. Fundamental insight into the structural changes that occur will be described as well as the method development that was needed to record and analyze the data.



O26. **COBALT METAL CATALYSTS IN THE HYDROGEN
 CHEMISTRY: SUPPORT AND PREPARATION EFFECTS IN CO₂
 METHANATION AND ETHANOL STEAM REFORMING**

Gabriella Garbarino, Paola Riani, Guido Busca

Unsupported and SiO₂-supported cobalt nanoparticles (NPs) were prepared starting from different precursors and with different procedures, and were tested in both CO₂ methanation (CME) and Ethanol Steam Reforming (ESR). NPs prepared by reduction of Co salts by NaBH₄ are contaminated by boron. They are not active in CME but are very active in ESR, with very low methane coproduction. Boron-free unsupported nanoparticles are active in CME but deactivate rapidly due to the formation of encapsulating carbon. They are also active in ESR but a little less selective than unsupported B-contaminated Co. SiO₂-supported cobalt is active in both CME and ESR. However, catalyst prepared from acetate is more stable than that prepared from nitrate. Slow deactivation is due to particle sintering and embedding in silica.

SO17. **NEW INSIGHTS ON THE CRYSTAL STRUCTURE OF ZSM-12
 WITH AZONIA SPIRO SALTS**

*Lara Gigli, Roberto Millini, Elisa Rodeghero, Giuseppe S. Nunziante,
 Annalisa Martucci, Jasper R. Plaisier*

The role of organic additive in zeolites crystallization is still a debated question. In this work, the amount, conformation, position and orientation of the SDA 6-azonia-spiro-[5,5]-undecane hydroxide, used for the synthesis of high silica ZSM-12 zeolite, was explored in detail through synchrotron X-ray powder diffraction and thermal analysis. The XRPD pattern shows several peaks not belonging to the well-known space group C2/c, highlighting that the presence of the template cause a lowering of the space group symmetry (Cc) and a three times enlargement of the unit-cell along the b-axis. The Rietveld refinement combined with the geometry optimization tool of the software EXPO allowed us to localized and understand the arrangement of the SDA molecules in the 12MR of the zeolite at the base of the space group symmetry lowering.



SO18. **ADVANCED SPECTROSCOPIC CHARACTERIZATION OF
 ACIDIC SITES IN HIERARCHICALLY STRUCTURED
 ZEOLITES AS CATALYSTS FOR HINDERED SUBSTRATES**

*Valentina Crocellà, Matteo Signorile, Alessia Airi, Tommaso Tabanelli,
 Francesca Bonino, Fabrizio Cavani, S. Bordiga*

We employed a non-commercial two-in-one template, with dual structure-directing abilities in different length scales, for the synthesis of a series of hierarchically structured ZSM-5 zeolites, i.e. possessing multiple levels of porosity (interconnected micro and mesopores). An advanced characterization step by means of IR spectroscopy with different probe molecules allowed us to fully assess the speciation and the distribution of the acidic sites of these materials, evaluating their accessibility and their actual location. Then, by comparing the information obtained by IR spectroscopy with catalytic tests, we will evaluate if possible positive effects on activity of the materials are connected just to the presence of mesoporous cavities or if other features (such as the location of the active sites and/or the presence of defects) play a key role.

SO19. **NEUTRON AND *IN SITU* SYNCHROTRON X-RAY POWDER
 DIFFRACTION ANALYSIS TO STUDY THE THERMAL
 ACTIVATION OF NH₄ OMEGA ZEOLITE**

*Giada Beltrami, Francesco di Renzo, Ilaria Parodi, Maria de Lourdes
 Guzman-Castillo, Francois Fajula, Annalisa Martucci*

Acidic zeolites are important catalysts that are exploited by the petroleum industry in different fields, such as isomerization of xylenes, catalytic cracking and heavy oil hydrocracking. Different routes can be used to investigate zeolites acidity. Among all the techniques, neutron and Synchrotron powder diffraction analysis have a key-role to obtain information about functions and performances of zeolites catalysts under operating conditions. Neutron diffraction is used to probe Brønsted acid sitting, while *in situ* powder diffraction allows to constantly monitor the evolution of zeolites structural features upon heating. In this work, for the first time, detailed information on the thermal activation of the omega zeolite in its NH₄ form by combining neutron and *in situ* synchrotron powder diffraction techniques are provided.



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Session Th-2

**June 13th 2019
15:35 – 16:50**

Chair

Francesco DI RENZO



SO20. **FIRST HINTS ON PRESSURE-INDUCED AMINO ACIDS
CONDENSATION IN MORDENITE**

Michelangelo Polisi, Marco Fabbiani, Rossella Arletti, Giovanna Vezzalini, Gianmario Martra, Francesco Di Renzo, Simona Quartieri

In this synchrotron XRPD study we have investigated the possible condensation, under high pressure, of amino acids confined inside 1D mordenite (MOR) channels. Glycine (GLY) and Alanine (ALA) were adsorbed in a synthetic Na-MOR and compressed using penetrating and non-penetrating pressure transmitting media. The results of the structural refinement of MOR loaded with GLY show that molecules are arranged in a configuration compatible with the formation of the peptide bond. However, as confirmed by the elemental analysis, the amount of adsorbed GLY is too low to allow the condensation reaction. The composite materials obtained loading MOR with α -ALA and β -ALA are more promising, containing higher amounts of amino acids. IR and Raman spectra of these samples show some features compatible with the formation of the peptide bond.

SO21. **THERMAL TRANSFORMATION OF (NH₄, Ba)-
CLINOPTILOLITE TO MONOCELSIAN, MULLITE, AND
CRISTOBALITE**

Guido Cerri, Antonio Brundu, Eleonora Sale

Three samples of (NH₄, Ba)-clinoptilolite, having different Ba²⁺/NH₄⁺ ratios, were heated for 2 h up to 1200 °C, and up to 32 h at 1100 and 1200 °C. The zeolite progressively underwent to dehydration, deammoniation, dehydroxylation, amorphization (between 700-900 °C), and crystallization of new phases. Amorphization temperature increased with Ba²⁺ content. Monocelsian, mullite and cristobalite/tridymite were obtained from all samples heated 32 h at 1100 °C, besides a residual glass \leq 9%. Type, quantity and order of nucleation of the phases were affected by the Ba²⁺/NH₄⁺ ratio, but also by temperature and duration of heating. Hexacelsian, the metastable polymorph of Ba-feldspar, was never recorded among crystallization products.



SO22. ONE-STEP DEPOSITION METHOD FOR THE SYNTHESIS OF A NANOCOMPOSITE MEMBRANE BASED ON REDUCED GRAPHENE OXIDE/ZEOLITE-A FOR ADSORPTION OF METAL IONS WITH ENHANCED ANTIBACTERIAL PROPERTIES

Maura Mancinelli, Arianna Di Pompilio, Eduarda I. de Castro, Luisa Pasti, Gianluigi Rosatelli, Giovanni Di Bonaventura, Jairo J. Pedrotti, Annalisa Martucci

In this work, we present the development of a nanocomposite membrane based on reduced graphene oxide (r-GO) and zeolite 3A. This innovative nanotechnology embraces the concepts of water reuse and water efficiency, with an environmentally friendly, energy-efficient and rapid development, for wastewater and industrial wastewater treatment. The synthesis involves with a one-step deposition by vacuum filtration on a nylon substrate, of a homogeneous mixture of graphene oxide and zeolite 3A powder, then reduced to r-GO with a hydrazine treatment. The bactericidal properties of the membrane were tested in liquid medium, against four multi-drug resistant clinical isolates species (Gram-positive: Staphylococcus aureus Sa2 and Gram-negative: Escherichia coli APN1, Pseudomonas aeruginosa PaPh32 and AC12a).

O27. CONFORMATIONAL SIEVING EFFECT OF EPHEDRINE DERIVATIVES DURING THE SYNTHESIS OF ZEOLITE MATERIALS

David Nieto, Joaquín Pérez-Pariente, E. Toran, Fernando López-Arbeloa, Luis Gómez-Hortigüela

A novel effect found during the synthesis of zeolitic materials, which we designate as “conformational sieving effect”, is reported. We study a new structure-directing agent, (1S,2S)-benzyl-pseudoephedrine, which has a prochiral N atom that becomes a new stereogenic centre upon protonation. Through a combination of NMR and DFT, we are able to monitor the occurrence of the different isomers. In aqueous solution, a higher concentration of the S isomer is observed. Unexpectedly, the opposite is found for the occluded molecules within the AFI zeolitic aluminophosphates, where a preferential incorporation of the other isomer (with N in R configuration) is observed. This is explained because of the different conformations adopted by each isomer, with the latter displaying



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an elongated shape that can better fit within the AFI nanochannels.

O28. NITROUS OXIDE DECOMPOSITION OVER COPPER-CONTAINING ZSM-5: UNRAVELLING THE ISOTHERMAL OSCILLATORY BEHAVIOR

*Marco Piumetti, Tahrizi Andana, Samir Bensaid, Marco Armandi,
Barbara Bonelli, Raffaele Pirone*

The catalytic decomposition of N₂O appears a promising solution, as it makes the N₂O abatement possible at the emission source and at lower temperatures than the conventional thermal abatement technology. In particular, Cu-containing ZSM-5 catalysts can be good candidates for potential applications. In the present work, the preparation method, the nature of the active species, the morphological features and the redox properties of copper sites were studied by complementary techniques to determine the role of Cu species involved in the decomposition of N₂O. The findings suggest that the N₂O decomposition activity depends on the exchanged Cu species and may take place over both Cu²⁺ and Cu⁺ species. In particular, the co-presence of Cu²⁺/Cu⁺ (able to undergo redox cycles) seems responsible for isothermal oscillations.

SO23. MESOPOROUS NiO CeO₂ MIXED OXIDES FOR CO AND CO₂ CO-METHANATION

*Luciano Atzori, Maria G. Cutrufello, Daniela Meloni, Barbara Onida,
Delia Gazzoli, Andrea Ardu, Roberto Monaci, Maria F. Sini, Elisabetta
Rombi*

Mesoporous NiO-CeO₂ mixed oxides were prepared by means of the soft-template method with nominal Ni/Ce molar ratios between 0.3 and 4.0. All samples were characterized by different techniques as to their chemical composition, structure, morphology, texture, basic properties, and specific metal surface area. The catalytic performance was investigated in the CO and CO₂ co-methanation, under different reaction conditions. Catalytic tests were performed under atmospheric pressure and 300 °C, using CO/CO₂/H₂ molar compositions equal to 1/1/7 and 1/1/5, and space velocities of 72000 and 450000 cm³h⁻¹g_{cat}⁻¹. In addition, on a selected sample, the influence of reaction temperature, of a wider range of space velocities (48000-450000 cm³h⁻¹g_{cat}⁻¹), and thermal stability were also investigated.



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Session Fr-1

**June 14th 2019
09:10 – 10:50**

Chair

Petr NACHTGALL



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SO24. SOLID ACID CATALYSTS FOR THE DIRECT HYDRATION OF DIHYDROMYRCENE

Eliška Vyskočilová, Denisa Šimáčková, Lada Sekerová, Libor Červený

Hydration of dihydromyrcene (3,7-dimethylocta-1,6-diene) to dihydromyrcenol (citronellene, 2,6-dimethyloct-7-en-2-ol) is an important reaction in fragrance industry. Direct hydration is preferred comparing indirect due to the more simple arrangement and lower amount of used reactants. Wide spectrum of solid acids (e.g. montomorillonite K 10, Siral type materials, zeolites beta and Y with different ratio Si/Al) was tested in this reaction and compared with homogeneous catalysts (e.g. *p*-toluenesulfonic acid). The highest selectivity (80 %) to dihydromyrcenol using heterogeneous catalyst at 45 % conversion was achieved when zeolite beta (37) was used. Achieving of higher conversion (more than 45 %) was a complex problem, but the desired product could be simply separated from the reaction mixture.

SO25. STUDY OF THE EFFECT OF PREPARATION PROCEDURE ON THE FORMATION OF ACTIVE AND STABLE CERIA-ZIRCONIA SUPPORTED MOLYBDENUM OXIDE CATALYSTS FOR CYCLOOCTENE EPOXIDATION

Rosa Turco, Marco Armandi, Luca Spiridigliozzi, Gianfranco Dell'Agli, Barbara Bonelli, Serena Esposito, Martino Di Serio

Molybdenum oxide was dispersed onto the ceria-zirconia support by co-precipitation or wet impregnation, using ammonium eptamolybdate tetrahydrate as precursor. The benefits of the precipitating agent on the MoO_x dispersion and activity were evaluated by means of a detailed structural and surface characterization. The activity and reusability of MoO_x/CeO₂-ZrO₂ catalysts are assessed in cyclooctene epoxidation with *cumene hydroperoxide* to investigate the differences that arise from the preparation route and from specific Mo-support interactions. A detailed evaluation of molybdenum (Mo) leaching from the ceria-zirconia supported catalyst was carried out by analysis of reaction solution and blank test.



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O29. MESOPOROUS ZSM-5 LOADED WITH AMINO ACIDS: DOES SECONDARY MESOPOROSITY AFFECT SORPTION CAPACITY AND THERMAL REGENERATION?

Giada Beltrami, Luisa Pasti, Tatiana Chenet, Lara Gigli, Jasper Plasier, Girolamo Giordano, Massimo Migliori, Alfredo Aloise, Enrico Catizzone, Annalisa Martucci

Hierarchically Organized ZSM-5 is built on a multilevel pore network, which makes it a promising adsorbent for biochemical molecules, such as amino acids. Despite their primary role in the enhancement of catalyst effectiveness, no structural investigation about amino acids adsorption/desorption processes on mesoporous ZSM-5 have ever been performed. In this work, the *in situ* structural characterization of mesoporous ZSM-5 after adsorption of L-lysine ($C_6H_{14}N_2O_2$) and leucine ($C_6H_{13}NO_2$), as single compounds from aqueous solution is presented for the first time. All the results obtained through *in situ* Synchrotron X-ray powder diffraction (MCX Beamline, Elettra) allowed to determine mesoporous ZSM-5 sorption capacity as well as thermal regenerability, which are fundamental information for the development of superior zeolite biocatalysts.

O30. A KINETICS STUDY INTO THE HYDROLYSIS AND INTERCALATION PROCESSES WITHIN THE ADOR MECHANISM

Michal Mazur, Susan E. Henkelis, Russell E. Morris, Jiří Čejka

The hydrolysis (disassembly, D) and rearrangement (organization, O) steps of the assembly–disassembly–organization–reassembly (ADOR) process for the synthesis of zeolites have been studied. Germanium-rich UTL was subjected to hydrolysis conditions in water to understand the effects of temperature (100, 92, 85, 81, 77, and 70 °C). Samples were taken periodically over a 30 h period, and each sample was analyzed by powder X-ray diffraction. The results show that the hydrolysis step is solely dependent on the presence of liquid water, whereas the rearrangement is dependent on the temperature of the system. The kinetics has been investigated using the Avrami–Erofeev model. With increasing temperature, an increase in the rate of reaction for the rearrangement step was observed, and the Arrhenius equation was used to ascertain apparent activation energy for the rearrangement from the kinetic product of the disassembly (IPC-1P) to the thermodynamic product of the rearrangement (IPC-2P). From this information, a mechanism for this transformation can



be postulated.

O31. **Ti-SBA-15 WITH TAILOR MADE PORE SIZE AND PARTICLE MORPHOLOGY FOR EPOXIDATION OF VERNONIA OIL**

Yaregal Awoke, Yonas Chebude, Carlos Márquez-Álvarez, Isabel Díaz

Vernonia galamensis is a native weed of East Africa, including Ethiopia, that contains high concentration of naturally epoxidized oil in its seed, which could be used as a potential substitute for currently used epoxy oils. Apart from an epoxy group, vernonia oil contains a double bond that could be further epoxidized yielding a low viscosity high oxirane vegetable oil that does not compete with food crops. Our study deals with a solvent free epoxidation of vernonia oil using Ti-SBA-15. The long fibers commonly observed in SBA-15 could be avoided obtaining small crystals with plate morphology having the channels running along the short axis of the crystal. Ti was incorporated by co-condensation as well as grafting methods. Ti-grafted large pore SBA-15 gives the highest double bond conversion (71 %) with more than 80 % of epoxide selectivity.

SO26. **SYNTHESIS OF Al-RICH ZSM-12 ZEOLITE USING A DABCO DERIVATIVE AS A STRUCTURE-DIRECTING AGENT**

María P. Cumplido, María J. Díaz-Cabañas

The synthesis of zeolites using different DABCO derivatives structure-directing agents (SDAs) by high-throughput synthesis techniques was studied. It allows to analysis how the size, shape and charge of the SDAs affects to the zeolitic structure using different molar composition of B, Al, Na and/or K in the synthesis gel and working at different crystallization temperatures and times. Making use of a SDA with a high charge density was possible to obtain the zeolite ZSM-12 with a low Si/Al rate, what has a great interest in its use as an acid catalytic in chemical processes with industrial relevance. The synthesis of ZSM-12 with the same SDA and lower Si/Al ratios in the synthesis gel are being studied.



SO26. **Ni ZEO-TYPE CATALYSTS FOR ALGAL OIL UPGRADING:
ROLE OF ACIDITY AND ACTIVE-SITE ACCESSIBILITY**

*Georgia Papanikolaou, Gianfranco Giorgianni, Paola Lanzafame,
Salvatore Abate, Siglinda Perathoner, Gabriele Centi*

The role of the acidity and active site accessibility of micro-mesoporous zeo-type catalysts containing Ni, was investigated in the hydroconversion reaction of methyl palmitate, selected as a model molecule of microalgal oil. The textural and acidic properties of the catalysts, as well as the size and dispersion of the Ni NPs were analyzed by different techniques (porosimetry, NH₃-TPD, CO chemisorption), and correlated to the results of the catalytic testing, evidencing that the key factors, governing the activity of these systems are the metal surface area and the accessibility of the acid sites. The best performances are obtained by depositing Ni NPs on desilicated/dealluminated Beta zeolite, due to the highest accessibility to the acid sites conferred by the Al extraframework removal following the deallumination treatments.



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Session Fr-2

June 14th 2019
11:20 – 12:40

Chair

Siglinda PERATONER



O32. **GUAIACOL HYDRODEOXYGENATION OVER Ni₂P
SUPPORTED ON 2D-ZEOLITES**

Santiago Gutiérrez-Rubio, Inés Moreno, Antonio Berenguer, Jan Přeck, Maksym Opanasenko, Cristina Ochoa-Hernández, Patricia Pizarro, Jiří Čejka, Juan M. Coronado, David P. Serrano

Different 2D zeolites, including lamellar ZSM-5 (L-ZSM-5), the corresponding silica pillared ZSM-5 (PI-ZSM-5) and an MCM-22 sample, were investigated as nickel phosphide supports and evaluated as catalysts for guaiacol hydrodeoxygenation (HDO). Loaded materials preserved a high crystallinity, reduced adsorption capacity and modified acidic properties. HDO experiments shown higher conversions and HDO efficiencies for ZSM-5 type zeolites than MCM-22, which denotes that MFI zeolitic structure favors the deoxygenation of phenolic compounds, and attributed to the combination of high surface area and optimal acidic properties. Thus, the best HDO performance was obtained over Ni₂P supported on the pillared ZSM-5 (conversion = 78 %, HDO selectivity = 95 %).

SO28. **ALKALI METALS PROMOTED Ru/Al₂O₃ CATALYSTS FOR CO₂
METHANATION**

Stefano Cimino, Francesca Boccia, Luciana Lisi

Alkali metals (Na, K and Li) promoted 1% Ru/Al₂O₃ catalysts were developed for the reaction of CO₂ methanation with H₂. Catalysts were prepared by introducing the alkali metal before or after ruthenium dispersion on alumina while also changing the Ru/alkali metal ratio. The Li-promoted catalyst is the best performing material showing a CO₂ conversion significantly higher than that of the parent 1% Ru/Al₂O₃ catalyst with a high selectivity to methane. Quite good performance is also achieved using the catalyst with a relatively low NaCO₃ load. On the contrary, high amounts (10% wt.) of NaCO₃ or K₂CO₃ depress CO₂ conversion mostly activating the reverse water gas shift reaction. The activity and selectivity to CH₄ have been correlated with results of materials characterization highlighting the role of CO₂ adsorption and carbonate decomposition.



O33. **EFFECT OF GRAFTING SOLVENT IN THE OPTIMISATION OF SBA-15 ACIDITY FOR LEVULINIC ACID PRODUCTION**

Cristina Pizzolitto, Elena Ghedini, Federica Menegazzo, Michela Signoretto, Alessia Giordana, Giuseppina Cerrato, Giuseppe Cruciani

In this work, the attention has been focused on the valorization of lignocellulosic biomass for the productions of levulinic acid (LA). It has been chosen as target products due to its potential as intermediate to produce a crowd of other chemicals. The attention has been concentrated on the formulation of an acid active catalyst for the hydrolysis of glucose to LA. Therefore, a deeper modification of SBA-15 with sulfonic groups using post-synthesis grafting method was performed. In particular, this work focuses on the role of different grafting solvents. The traditional one is toluene, which is flammable and toxic. For this reason, investigation on a safer and environmentally more friendly solvent has been carried out, focusing on hexane, toluene and a mixture of water and NaCl. It was found that solvent highly affects morphological and chemical features of the materials; the best catalytic results were obtained with the catalyst prepared in water and NaCl, as this solvent mixture allows to guarantee the best distribution of sulfonic groups over the surface leading to the best acid catalyst.

O34. **DIFFERENT ACTIVITY AND STABILITY OF Fe-CONTAINING MOF MATERIALS FOR FENTON OXIDATION PROCESSES**

Pedro Leo, Gisella Orcajo, Guillermo Calleja, Fernando Martínez

Metal-organic frameworks (MOFs) have attracted great interest as a promising candidate for sustainable energy and environmental remediation. Fe-based MOF materials have been explored as catalyst for advanced Fenton oxidation processes. These materials were tested for the degradation of methylene blue as model pollutant through Fenton oxidation. The Fe-based MOF materials were selected based on their constituents such as the oxidation state of the metal ($\text{Fe}^{2+}/\text{Fe}^{3+}$), the type of inorganic cluster and the carboxylic organic linking ligand. The results evidenced the viability of using Fe-carboxylic-MOF materials as heterogeneous Fenton catalysts and the effect of the iron metal-ligand coordination on the overall catalytic performance and chemical stability.



SO29. **CO CATALYTIC OXIDATION REACTION AS A TOOL TO
EVALUATE THE NATURE OF Ag-CATALYSTS**

*Irene López-Hernández, Clara García, Vera Truttmann, Stephan Pollitt,
Noelia Barrabés, Günter Rupprechter, Fernando Rey Gracia,
Antonio E. Palomares*

Due to the particular properties of zeolites, they have been used in different fields, being the catalysis one of the most important. Although in many processes zeolites can be used without any modification, in many others, it is necessary to introduce metals as the active phase. Depending on the methods used for the metal introduction, different metal species are obtained, resulting in different catalytic properties. In this work, some catalysts based on silver supported on zeolite have been prepared using different methods. The nature of these species has been studied by the CO catalytic oxidation reaction. The results show that the catalysts prepared by the ion exchange method and with Ag-nanoclusters stabilize the cationic silver or form cationic nanoclusters that cannot be stabilized when the impregnation method is used and silver is auto-reduced.



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POSTER Session

**June 12th 2019
17:30 – 19:00**



P.1 PREPARATION OF MESOPOROUS Al-MCM-41 FROM ALGERIAN BENTONITE

Tewfik Ali-Dahmane, Lamia Brahmi, Rachida Hamacha, Frédéric Villieras, Abdelkader Bengueddach

The mesoporous material Al-MCM-41 is usually synthesized by using laboratory reagents as silicate sources and aluminium source. The main aim of this work is to replace these expensive laboratory reagents by more cost effective ones. The Algerian bentonite low-cost mass clay materials are used as silicate and aluminate sources separately by adopting an alkaline fusion process to extract both silicon and aluminium. The results revealed that the properties of Al-MCM-41 synthesized from bentonite depend on both elemental composition and mineral phase contents of the used bentonite. Pure and highly ordered hexagonal mesoporous Al-MCM-41 with uniform pore sizes and a high specific surface area have been successfully synthesized without any phases which exist in natural bentonite.

P.2 INVESTIGATION OF CATALYTIC ACTIVITY OF ZSM-5 BASED MICRO MESOPOROUS ALUMINOSILICATES IN PRINS CYCLISATION OF (-)-ISOPULEGOL WITH BENZALDEHYDE

Roman Barakov, Ekaterina Kholkina, Päivi Mäki-Arvela, Chloe Lozachmeuer, Nataliya Shcherban, Dmitry Yu. Murzin

Micro-mesoporous aluminosilicate containing ZSM-5 nanoparticles with the size of 36 nm demonstrated a higher catalytic activity in Prins cyclisation of (-)-isopulegol with benzaldehyde than other investigated mesoporous zeolite and mesoporous molecular sieves. Thus a complete conversion was achieved after 2 h and selectivity towards the desired product with the tetrahydropyran structure is 68 %. The results can be explained by the developed mesoporosity ($V_{\text{meso}} = 0.51 \text{ cm}^3/\text{g}$, $D_{\text{meso}} = 11 \text{ nm}$) in ZSM-5 with morphology of nanoparticles and the presence of catalytically active strong acid sites on the mesopore surface of the sample (concentration $25 \mu\text{mol/g}$). The highest selectivity to the desired product at 80 % conversion of (-) isopulegol is achieved using material with the ratio of Brønsted and Lewis acid sites of 2.7.



P.3 **ENTRAPPING OF IBUPROFEN AND ATENOLOL WITHIN Y ZEOLITE: A NEUTRON POWDER CHARACTERIZATION AFTER DRUGS ADSORPTION**

Giada Beltrami, Luisa Pasti, Tatiana Chenet, Annalisa Martucci

Pharmaceuticals products are considered to be among the most common organic wastewater contaminants due to their widespread use and slow natural degradation, which still makes their complete removal from water a challenging task. Due to their unique properties, zeolites have already proved their efficiency as sorbent materials in wastewater treatments. Based on the excellent results obtained, it has been decided to study the removal of two pharmaceutical products (ibuprofen and atenolol) from aqueous solution by organophilic zeolite Y (Si/Al ratio=200). The aim was to determine the zeolite efficiency in adsorption processes of pharmaceutical compounds characterized by high molecular dimensions. Results gained suggest that Y zeolite could be successfully used as sorbent material in water remediation processes from drugs.

P.4 **INSIGHTS ON GA-FERRIERITE CATALYST: X-RAY POWDER DIFFRACTION CHARACTERIZATION AT AMBIENT CONDITIONS**

Giada Beltrami, Luisa Pasti, Tatiana Chenet, Lara Gigli, Giuliana Aquilanti, Annalisa Martucci

Due to their unique catalytic performances in light hydrocarbon aromatization, gallium-containing zeolites have been extensively investigated. Newest applications concern the conversion of biomass into biofuels and bio-based chemicals. In spite of the growing interest on Ga-catalysts, it has been decided to study a Ga-ferrierite zeolite by using X-ray powder diffraction analysis. The aim of the project was to characterize the zeolite structure at ambient conditions, through the detection and the quantification of Ga(⁺³) cations in framework and non-framework positions as well as the determination of water complex presence and their role in the completion of extraframework Ga(⁺³) coordination. Indeed, all these informations are of primary importance to determine the efficiency of Ga-ferrierite as catalyst.



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P.5 EVIDENCE OF MIXED-LIGAND COMPLEXES IN CU-CHA BY REACTION OF CU NITRATES WITH NO/NH₃ AT LOW TEMPERATURE

*Chiara Negri, Elisa Borfecchia, Michele Cutini, Kirill A. Lomachenko,
 Ton V.W. Janssens, Silvia Bordiga, Gloria Berlier*

The reactivity with a NO/NH₃ mixture of Cu-nitrate complexes formed on the surface of a Cu-CHA catalyst active in the Selective Catalytic Reduction of NO_x with NH₃ was followed at 50 °C by *in situ* FTIR, XAS and Diffuse Reflectance UV-Vis spectroscopies, supported by DFT calculations. In presence of NO/NH₃ (or NH₃ alone), chelating bidentate framework interacting Cu^{II}-nitrates formed mixed-ligand mobile [Cu^{II}(NH₃)₃(NO₃)]⁺ complexes, with infrared bands at 1624 (δNH₃), 1430 and 1325 cm⁻¹ (monodentate νNO₂asym and νNO₂sym, respectively) and peculiar UV-Vis fingerprints. XAS showed that during this transformation the Cu^{II}/Cu^I reduction observed in similar conditions at 200 °C hardly occurred.

P.6 QUANTIFICATION OF BRØNSTED ACIDITY OF H-[GA]-ZSM-5

*Ana Canaleta Safont, Carlos Palomino Cabello, Carlos Otero Areán,
 Gemma Turnes Palomino*

Aiming at studying their acidity, protonic gallosilicates [Ga]-ZSM-5 were synthesized following a hydrothermal procedure from gels having Si/Ga ratios of 25, 50 and 75. Likewise, for comparison, protonic zeolites [Al]-ZSM-5 having Si/Al ratios of 25 and 50 were also prepared. Brønsted acidity of the structural Si(OH)Ga groups in the gallosilicates ZSM-5 type, were quantified by means of IR spectroscopy at a variable temperature, (VTIR) using CO and N₂ as probe molecules; this instrumental technique enables simultaneous measurement of the bathochromic shift of the stretching O–H mode (Δν_{OH}) of the Brønsted acid group interacting (through hydrogen bonding) with the probe molecule and the corresponding ΔH⁰ value of the CO and N₂ adsorption process. The results clearly showed that the gallosilicates are significantly less acidic than the aluminosilicates, whichever acidity indicator is used; Δν_{OH} or ΔH⁰.



P.7 ROLE OF H₂O AND O₂ DURING THE REACTIVE ADSORPTION OF H₂S ON MgO/AC AT LOW TEMPERATURE

Stefano Cimino, Elisabetta M. Cepollaro, Nicola Gargiulo, Domenico Caputo, Luciana Lisi

H₂S reactive adsorption on MgO, CuO, ZnO dispersed onto activated carbon is investigated in different gas streams, containing either N₂, or O₂/H₂O, at room temperature and in a lab-scale fixed-bed reactor. Sorbents performances are analyzed in terms of H₂S adsorption capacity and adsorption rate and data are correlated with the sulphur species formed upon adsorption and in the different experimental conditions. Temperature Programmed Desorption (TPD), porosimetric and XPS analyses are performed in order to support the adsorption dynamic tests. The presence of O₂ and H₂O determines a remarkable increase in H₂S adsorption capacity, favouring the formation of different sulphur species such as sulphides, sulphates and, above all, elemental sulphur.

P.8 STUDIES ON THE ABSORPTION AND DESORPTION OF ACETONITRILE ON MFI SAMPLES FOR THE QUANTIFICATION OF THE MOLAR CONCENTRATION OF ZEOLITE ACID SITES BY FT-IR SPECTROSCOPY

Francesco Dalena, Alfredo Aloise, Massimo Migliori, Girolamo Giordano

This research work shows the possibility to quantitatively measure (through measurements acquired by FT-IR spectrophotometer) the acid sites present in some types of MFI zeolites at different Si/Al ratios, after a classic hierarchization treatment. These zeolites samples (at different Si/Al ratios) were desilicated with a solution of NaOH 0.1 M, at a temperature of 338 K and at different desilication times (15, 30, 60 min). The hierarchical zeolites samples were studied by FT-IR spectroscopy with consequent acetonitrile absorption experiments. The purpose of the analysis is to evaluate the acid strength of the Si-OH-Al groups in function of the increase of the volume of the pores of the mesoporous crystal and how the Bronsted acid sites vary according to the change from microporous to mesoporous zeolites.



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**P.9 OBSERVATIONS OF SILVER CLUSTERS IN MOF MIL-100(Fe)
 INCORPORATED USING DIFFERENT METHODS**

Rubén Mahugo, Alvaro Mayora2, Manuel Sánchez-Sánchez, Isabel Díaz

MOF MIL-100(Fe) prepared at room temperature and under sustainable conditions has been impregnated with Ag by different techniques: i) solid state reaction, ii) wetness impregnation and iii) ion exchange. The objective of this work is to identify which of these impregnation methods leads to a more efficient Ag distribution within the pores, more homogeneous and smaller in Ag@MIL-100(Fe) materials. Transmission electron microscopy is an ideal technique for locating/identifying metal nanoparticles on the surface or inside the pores of the MOF. In this case, it has shown the benefit of incorporation methods by wetness impregnation or ion exchange to the detriment of the solid state reaction in the case of MIL-100(Fe), a MOF with neutral network, but not in the Sod-ZMOF whose network has a negative charge.

**P.10 SYNTHESIS AND CHARACTERIZATION OF HIERARCHICAL
 ZEOLITES FOR ENVIRONMENTAL APPLICATIONS**

Melodj Dosa, Marco Piumetti, Samir Bensaid, Nunzio Russo, Debora Fino

Zeolites are interesting materials that can be used as sieve, catalysts, supports and adsorbents in several chemistry engineering field. These materials have a defined structure with a fixed pores dimension. However, this characteristic could be a limitation because the zeolite can absorb only the species that can go through and react in its structure. For this reason, new type of zeolite with new cavities and pores were studied: the hierarchical zeolite. To obtain these materials, in this work, a desilication and after a dealumination process were followed. The obtained hierarchical ZSM-5 was characterized by XRD, N₂ physisorption and FESEM microscopy. The final purpose is to study this new material as support for catalytic oxidation reaction, such as CO and soot oxidation.



P.11 **NANOSTRUCTURED TiO₂ MIXED PHASES: SYNTHESIS, PROPERTIES AND PHOTOCATALYTIC DEGRADATION OF SOME NITROGEN CONTAINING EMERGING POLLUTANTS**

Francesca S. Freyria, Nicola Blangetti, Serena Esposito, Roberto Nasi, Marco Armandi, Barbara Bonelli

The goal of this work is the preparation and study of nanostructured mesoporous titanium dioxide (TiO₂) both containing mixed crystalline phases and doped with heteroatoms (e.g. Fe) with the aim of improving their photocatalytic activity for the degradation of emerging water pollutants (Eps). In aquatic environment, it is possible to find a significant number of Eps, which are molecules that are difficult to remove by common wastewater treatments. Among these, N-containing Eps are very dangerous either for the aquatic life or human health. In this study, the degradation of two N-containing Eps (simazine and n-phenylurea) was used as a test reaction, both under UV light and simulated solar light. To vary the polymorph TiO₂ percentages, we applied three types of synthesis by changing the kind of template. Different reaction mechanisms have been found: brookite phase positively affects the photocatalytic activity of pure-TiO₂ whereas Fe-doping has a positive impact under the solar light.

P.12 **TEMPLATE-REMOVAL-ASSOCIATED STRUCTURAL MODIFICATION OF ZSM-5 ZEOLITE WITH DIFFERENT Si/Al RATIO BY IN SITU SYNCHROTRON POWDER DIFFRACTION**

Lara Gigli, Giada Beltrami, Matteo Ardit, Jasper R. Plaisier, Massimo Migliori, Girolamo Giordano, Annalisa Martucci

The template burning (or calcination) of the as-synthesized zeolite material is a key step in their activation for its application as a catalyst. The thermal behaviour of a zeolite is influenced by several intrinsic chemical and structural factors (i.e. framework topology, Si/Al ratio, charge-compensating cations, coordination of bare cations, crystal size, heating rate, etc.). In this work the evolution of cell parameters, the framework modification, together with the degradation of the TPA⁺ and the release of water have been studied upon heating, in the range between 25 and 800 ° C, on four ZSM-5 zeolites with different Si/Al ratio (11, 15, 26, 42), in situ synchrotron radiation powder diffraction.



P.13 **PST-29: A MISSING MEMBER OF THE RHO FAMILY OF
 EMBEDDED ISORETICULAR ZEOLITES**

H. Lee, Jiho Shin, W. Choi, Hyun June Choi, T. Yang, X. Zou, S. B. Hong

We report the synthesis and structure of PST-29, the second generation of the RHO family of embedded isorecticular zeolites, the structure of which was proposed about 50 years ago but has remained undiscovered until now. We were able to synthesize this cage-based small-pore zeolite using N,N'-dimethyl-diazabicyclo[2.2.2]octane dications as an organic structure-directing agent (SDA) in the presence of both Na⁺ and K⁺ ions. When adding a small amount of seed crystals to the synthesis mixture, we were also able to synthesize PST-29 with a higher Si/Al ratio (4.5 vs 3.5), and thus with a higher stability, in the same mixed-SDA system. The Na⁺ form of this PST-29 has a comparable CO₂ uptake to the Na⁺ form of zeolite rho, but is characterized by much faster adsorption kinetics, suggesting its high potential as a CO₂ adsorbent.

P.14 **FACILE SYNTHESIS OF NANOSTRUCTURED COBALT
 PIGMENTS BY CO-A ZEOLITE THERMAL CONVERSION AND
 ITS APPLICATION IN PORCELAIN MANUFACTURE**

*Barbara Liguori, Assunta Campanile, Gennaro Cavaliere, Valter L. De
 Bartolomeis, Domenico Caputo*

An innovative and facile synthesis of Co-pigment was carried out by means of thermal conversion of a cobalt-exchanged zeolite. The Na-A [LTA] zeolite was used, since it is a low cost and easily available raw material. The ion exchange mechanism allowed to control, at microscopic level, the composition of the zeolitic precursor. Several chromatic effects could be obtained by varying the treatment temperature and/or the cobalt concentration in the contact solution. The reliability of these new zeolite-based pigments was tested in porcelain manufacture. The developed cobalt pigments were firstly tested in the porcelain mixture to obtain a coloured product. Then the efficacy, in term of colour and aesthetic effect, was proved in some of the most common decoration methods such as *ingobbio*, colored glazes and “third fire decoration”.



P.15 **THEORETICAL INVESTIGATION OF THE MQMAS NMR CHARACTERISTICS FROM THE AB INITIO MOLECULAR DYNAMICS FOR CHA ZEOLITE**

Song Lu, Federico Brivio, Petr Nachtigall

NMR parameters such as isotropic chemical shift (δ_{iso}), quadrupolar coupling constant (C_q), and asymmetry parameter (η) are very sensitive to the Al distributions, which can be accurately determined. Reliable theoretical investigation requires time-averaging of calculated NMR signals. To include dynamical aspects we calculate the ^{27}Al MAS NMR spectra of a large set of structures obtained from the ab initio molecular dynamics trajectories. In this way it is possible to build a statistically significant ensemble that takes into account the dynamics of the system under particular realistic environment (e.g. water content, pH and temperature). We believe that the relationship between aluminium distribution and NMR spectra can give a detailed understanding of structure/activity relationship in an important class of zeolite-based catalysts.

P.16 **BASICITY OF MWW ZEOLITES AND KNOEVENAGEL CONDENSATION**

*Anna Wojtaszek-Gurdak, Vanesa Calvino-Casilda, Aneta Grzesinska,
Rosa Martín-Aranda, Maria Ziolk*

MWW zeolites have different possible structural, textural and compositional modifications. Pillaring of MCM-22 precursor towards MCM-36 allowed the formation of catalyst effective in Knoevenagel condensation. The solids were totally characterized by different technics; ICP-OES, N_2 adsorption, XRD, XPS, TG/DTA, FTIR combined with pyridine adsorption, 2-propanol decomposition, for evaluation of chemical, structural and surface properties. All materials were used in Knoevenagel condensation of benzaldehyde with ethyl cyanoacetate and ethyl acetoacetate.



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P.17 **MESOPOROUS ZINC OXIDE FOR THE DELIVERY OF
CLOTRIMAZOLE**

*Sara S.Y. Mohamed, Mauro Banchero, Luigi Manna, Silvia M. Ronchetti,
Barbara Onida*

Mesoporous zinc oxide (Meso-ZnO) was prepared, characterized and loaded with clotrimazole (CTZ), a poorly water-soluble antifungal drug, in order to enhance CTZ water solubility and bio-availability. The Meso-ZnO was synthesized by precipitation method. The adsorption of CTZ was performed using supercritical CO₂ as a solvent. The material was characterized before and after CTZ adsorption by X-ray diffraction, nitrogen adsorption analysis, IR spectroscopy and Field Emission Scanning Electron Microscopy. Meso-ZnO appeared as aggregates of interconnected nanoparticles having crystalline wurzite structure, with a specific surface area of about 56 m²/g and pore size of 10 nm. CTZ adsorbed onto Meso-ZnO was amorphous and its amount was about 8.45 % w/w. In vitro release test showed that the Meso-ZnO was able to deliver efficiently CTZ.

P.18 **OXIDATION OF GLUCOSE TO GLUCARIC ACID USING
SUPPORTED GOLD CATALYSTS**

*Eleonora Monti, Stefania Solmi, Calogero Morreale, Tommaso Tabanelli,
Nikolaos Dimitratos, Fabrizio Cavani*

Glucaric acid (GA) is one of the building blocks derived from biomass with higher added value; the study of a more sustainable process to produce GA is of great scientific and practical interest. This work is dealing with the synthesis of GA from oxidation of D-Glucose in aqueous solvent with molecular oxygen, using solid catalysts based on supported tailored Au nanoparticles (NPs). At first it has been studied how the nanoparticles size can affect the reaction behavior, preparing Au NPs with different methods. Then we prepared mono metallic NPs supported on a range of supports (nominal metal loading 1 % wt) to study the influence of metal-support interaction. The catalytic tests suggest that metal-support interaction, particle size, metal dispersion, porosity and nature of ligand have a strong influence in the yield to the desired product.



P.19 **NEW INSIGHTS INTO THE MONOCLINIC-TO-
 ORTHORHOMBIC PHASE TRANSITION IN MFI- ZEOLITES**

*Francesco Pagliaro, Paolo Lotti, Davide Comboni, G. Diego Gatta,
 Enrico Catizzone, Massimo Migliori, Girolamo Giordano, Marco Merlini,
 Michael Hanfland*

Zeolites with a MFI framework topology are currently used as catalyst in several industrial processes, for instance in the methanol-to-olefins (MTO) and methanol-to-gasoline (MTG) synthesis. The success of this kind of zeolites is due to their channels selectivity, relatively low cost and easiness of synthesis. A monoclinic ($P2_1/n11$)-to-orthorhombic ($Pnma$) phase transition (hereafter MOPT) has been reported to occur below 1.1 GPa in ZSM-5 zeolites. In this light, the aim of this study is to investigate the pressure-induced MOPT varying the zeolite composition. For this reason, six MFI zeolites with different chemical composition were synthesized and studied at high pressure by *in-situ* synchrotron X-ray powder diffraction with a diamond anvil cell. The MOPT has been found to occur at lower pressure with respect to what previously reported, and a control of the chemical composition on the high-pressure behavior has been observed.

P.20 **USE OF SURFACTANT MODIFIED NATURAL ZEOLITES
 (SMNZ) FOR POLLUTANT ANIONS REMOVAL**

*Antonio Peluso, Barbara Galzerano, Paolo Aprea, Domenico Caputo,
 Bruno de Gennaro*

In the present research we verified a possible use of a phillipsite-rich tuff (NYT), superficially modified by sorption of HDTMA-Br and HDTMA-Cl, as an alternative adsorbent for removing arsenate and chromate from wastewater. The surface modified natural zeolite (SMNZ) samples were prepared by contacting HDTMA-Br and HDTMA-Cl with a tuff bed in a dynamic column exchange system. Moreover, kinetic and thermodynamic experiments were carried out using ordinary batch equilibrium techniques. Equilibrium isotherms data showed a higher anion uptake for the PHI-SMNZ modified with HDTMA-Br when compared with the HDTMA-Cl modified sample. Kinetic studies demonstrated As(V) and Cr(VI) removal is very fast: it reaches 80% in 1 hour and 100% in 2 hours for both anions.



P.21 **HEXAVALENT CHROMIUM REMOVAL FROM AQUEOUS SOLUTIONS BY AMINO FUNCTIONALIZED MIL-101(CR) MOF**

*Haniyeh Jalayeri, Paolo Aprea, Domenico Caputo, Antonio Peluso,
 Francesco Pepe*

Amino-functionalized MIL-101(Cr), or AFMIL, was tested for the adsorption of Cr(VI) from aqueous solutions. Batch kinetic data for $K_2Cr_2O_7$ removal from water using AFMIL indicated that the adsorption process is rather fast, and can be described by assuming that the limiting step is intraparticle diffusion, with a weak dependence of diffusivity on temperature. Adsorption isotherms, evaluated at three different temperatures in the range of 25°–60°C, showed an adsorbent–adsorbate interaction energy in the order of 21 kJ·mol⁻¹, thus suggesting a markedly chemical phenomenon. The highest observed adsorption capacity of AFMIL toward Cr(VI) was 44 mg·g⁻¹ for a liquid phase concentration of 140 mg·L⁻¹ at T=60°C. Overall, the experimental results indicate that AFMIL is very interesting for Cr(VI) removal from water.

P.22 **CATALYTIC ACTIVITY OF GOLD NANOCUSTERS IMMOBILIZED ON MESOPOROUS SBA-15 FUNCTIONALIZED WITH AMINE GROUPS**

A.Mato, Javier Agúndez, Alvaro Mayoral, Joaquín Pérez-Pariente

Au nanoclusters (AuNCs, d < 1 nm) have been prepared by a two-liquid phases system that involves a solution of gold in aqua regia and rosemary oil as organic phase, and they have been immobilized on NH₂-functionalized mesoporous SBA-15 material, rendering Au contents in the range 0.067 - 0.7 wt%. The activity of these materials in the catalytic oxidation of cyclohexene at atmospheric pressure by using O₂ as oxidant is higher than that of analogous Au catalysts immobilized on SH- and SO₃-bearing SBA-15, the order of activity being Au/-NH₂ > Au/-SO₃ » Au/-SH. The AuNCs do not aggregate to form Au nanoparticles during reaction. The catalysts are very selective to the allylic oxidation of cyclohexene, with cyclohexenyl hydroperoxide as intermediate unstable product and cyclohexenone and cyclohexenol (one/ol=1.6) as stable products.



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P.23 **UNUSUAL REACTIVITY OF BENZALDEHYDE AND DIOXANE
IN PRESENCE OF CLAY MATERIALS**

Daniel Cvejn, Iveta Martausová, Alexandr Martaus, Jan Přečh, Ondřej Veselý, Zdenek Lacný, Jan Nedoma, Radek Martínek

In this contribution we describe products of clay-catalyzed reaction of benzaldehyde with 1,4-dioxane over six types of cationically exchanged vermiculites (Ni^{2+} VMT, Mg^{2+} VMT, Fe^{3+} VMT, Al^{3+} VMT, Sn^{4+} VMT, Zr^{4+} VMT) and on a wild-type vermiculite. The main product of the reaction has consistently been observed as 2-phenyl-1,3-dioxolane, the benzoic acid has been often present in presence of the air as the main impurity. The individual catalysts differed in the composition of other products and byproducts as well as in the selectivity and yield of dioxolane product.

P.24 **CHLOROACETANILIDE COMPOUNDS: EVIDENCE OF
ADSORPTION OF S-METOLACHLOR USING DIFFERENT
ZEOLITES TOPOLOGY**

Elisa Rodeghero, Matteo Pecorari, Luisa Pasti, Tatiana Chenet, Annalisa Martucci

Volatile Organic Compounds (VOCs) and Persistent Organic Pollutants (POPs) are the main pollutants macro-categories which affect each environmental matrix and in particular aquatic ecosystem is seriously compromised by both these pollutant classes. In light of this, adsorption from water solution of herbicides pertain to the chloroacetanilide family (POPs class) has been investigated. Specifically, the removal of (s)-Metolachlor by means MTW, MFI, FAU and BEA zeolites has been explored. Based on chromatographic results, sample that showed the best adsorption performances has been characterized through both XRPD and thermal analysis. The last one highlighted a total weight loss close to 20wt% according to chromatographic results whereas XRPD has permitted to achieved structural evidences of herbicide adsorption.



P.25 SYNTHESIS AND CHARACTERIZATION OF PURE SILICA AND ALUMINOSILICATE STW ZEOLITES

Andrés Sala, Susana Valencia, Fernando Rey

STW is a medium pore size zeolite containing helical channels of 10 MR having a chiral structure what makes it a material of great interest. It was firstly obtained as silicogermanate constituted by the mixture of the two enantiomorphs and recently, it has been described using organic structure directing agents designed to selectively obtain one enantiomer or the other. Moreover, it is also possible to synthesize this structure as purely siliceous as well as aluminosilicate allowing its use as adsorbent and catalyst. However, the aluminosilicate STW zeolites described contain low amount of Al or this is not fully incorporated in the framework. In this work we have synthesized and characterized STW zeolites with variable aluminum content and in pure silica composition for further use in catalytic and adsorption processes.

P.26 MO-EXCHANGED FERRIERITE FOR PHOTOCATALYTIC SELECTIVE OXIDATION OF CYCLOHEXANE

Diana Sannino, Vincenzo Vaiano

Heterogeneous photocatalysis has been widely investigated as a novel technique for environmental detoxification either in water and air. However, photocatalysis can be applied also to organic syntheses in mild conditions. Zeolites have been reported to be active photocatalysts under UV irradiation. In this study, we investigated the photooxidation of cyclohexane on ferrierite and ferrierite-supported MoO_x in a gas-solid continuous flow reactor. Under UV irradiation ferrierite-supported MoO_x showed the presence of benzene and cyclohexene indicating the occurrence of photocatalysed cyclohexane oxydehydrogenation. By contrast, ammonium exchanged ferrierite exhibited high activity for total oxidation to carbon dioxide. The influence of Mo loading on cyclohexane conversion and benzene production was also evaluated.



P.27 **THE TRANSFORMATION OF DIISOPROPYL BENZENE AS A MODEL REACTION FOR THE STUDY OF THE CATALYTIC ACTIVITY OF ZEOLITE BETA**

Marisol Grande-Casas, A. Landaeta-Pérez, Joaquín Pérez-Pariente, Enrique Sastre

Beta zeolites with crystal size in the range between 0.07 - 3.50 μm have been synthesized, with similar Si/Al ratio 11.5 - 20. The samples show different mesoporous area in the range between 83 - 289 m^2/g , and there is an inversely proportional correlation, between mesopore area and crystal size. These samples were tested in the transformation of 1,3 diisopropylbenzene, in a fixed bed reactor at 200°C. Samples with higher mesoporous area and smaller crystal size have higher selectivity to the products of disproportionation (1,3,5 triisopropylbenzene and 1,2,4 triisopropylbenzene), i.e., lower isomerization/disproportionation ratio.

P.28 **ZSM-5 ZEOLITES MODIFIED WITH ZINC AND THEIR EFFECT ON THE CRYSTAL SIZE IN THE CONVERSION OF METHANOL TO LIGHT AROMATICS AND OLEFINS**

Misael García-Ruiz, Diana Sanjurjo-Tárralo, Raquel Sáenz-Vaque, Marisol Grande-Casas, Carlos Márquez-Álvarez, Dora A. Solís-Casados, Julia Aguilar-Pliego, Enrique Sastre

Several Zn/ZSM-5 catalysts have been synthesized in order to analyze the influence of some of their physical-chemical properties, specifically the zeolite crystal size and the way to incorporate the Zn, in their behavior in the methanol reaction, especially in terms of selectivity, stability and resistance to deactivation. All the catalysts are quite stable at 400 °C, however, an increase in the reaction temperature drastically reduces their lifetime. The incorporation of Zn increases the selectivity to BTX aromatics, because of the flavoring power of the metal. On the other hand, it has been observed for all the catalysts that an increase in the reaction temperature causes an increase in the selectivity towards the aromatic products (BTX and higher).



P.29 **AN IN-SITU RAMAN AND REACTIVITY STUDY OF THE
 TRANSFORMATION OCCURRING IN Nb-DOPED VANADYL
 PYROPHOSPHATE CATALYST**

*Laura Setti, Aurora Caldarelli, Fabrizio Cavani, Tommaso Tabanelli,
 Francesco Puzzo, Nikolaos Dimitratos, Carlo Lucarelli, Carlotta Cortelli,
 Silvia Luciani*

The industrial production of maleic anhydride is achieved by the selective oxidation of *n*-butane using vanadyl pyrophosphate (VPP) as catalyst. It has recently been reported that the key factor to obtain a moderately active but highly selective catalyst is the *in-situ* generation, under reaction conditions, of a discrete amount of δ -VOPO₄ on the catalyst surface. In order to improve the catalytic performance, the industrial catalyst has been doped with controlled amounts of a Nb⁵⁺ compound. The role and the amount of Nb was investigated by means of both reactivity experiments and in-situ Raman spectroscopy. It was found that the promoting effect shown by Nb occurred already for a very low amount of it, favouring the generation of a discrete amount of the desired δ -VOPO₄ compound, and its performance was improved over that of the undoped VPP.

P.30 **DEVELOPMENT OF MESOPOROUS CATALYSTS FOR
 VALUABLE CHEMICAL PRODUCTION FROM GLUCOSE**

*Gea Bortolomiol, Somayeh Taghavi, Elena Ghedini, Cristina Pizzolitto,
 Giuseppe Cruciani, Federica Menegazzo, Michela Signoretto*

This work focuses on the hydrolysis of glucose, the main constituent of lignocellulosic biomasses, in order to obtain 5-HMF, one of the most prominent bio-based chemicals. Various mesostructured silica titania SBA-15 type supports with different molar amounts of Ti were synthesized using two different methods. The effect of Ti inside the silica network was taken into account. Hydrothermal and mechanical properties of the materials were investigated; all the samples were characterized by different techniques and they were tested for the hydrolysis of glucose. Thus, a great improvement of the SBA-15 stability properties was achieved by the introduction of Ti in the silica material. Ti modified catalyst presented in glucose hydrolysis a slightly higher carbon balance indicating a lower production of undesired products such as humins.



P.31 MATERIALS DERIVED FROM TITANIUM METAL-ORGANIC FRAMEWORKS: APPLICATION FOR THE DEGRADATION OF ORGANIC POLLUTANTS

Neus C. Sánchez, Gemma T. Palomino, Carlos P. Cabello

In this communication, we report on the preparation of titanium metal-organic frameworks and their use as precursors to obtain derived carbons and oxides by a simple calcination step. Their structure, morphology, porosity and band gap energy were studied using powder X-ray diffraction, electron microscopy, nitrogen adsorption-desorption isotherms measured at 77 K and UV-vis diffuse reflectance spectroscopy. The prepared materials were evaluated for the batch photocatalytic degradation of organic dyes from aqueous solution under visible light irradiation.

P.32 STRENGTH OF ZEOLITIC BRØNSTED ACID SITES: RATE OF H/D ISOTOPIAL EXCHANGE VS. ETHANOL DEHYDRATION ACTIVITY

Jan Vaculík, Roman Bulánek, Jiří Kotera, Martin Kubů

Zeolites are very important group of solid acidic heterogeneous catalysts. Their catalytic properties depend on the nature, number and strength of their Brønsted acid sites (BAS). In this contribution, the acidity of selected high-silica zeolites like MFI, FER, MWW and MOR were investigated. Properties and strength of Brønsted acid sites was studied by measurement of (i) the rate of H/D isotopical exchange between ethane and OD groups on zeolite and (ii) frequency shifts of the IR band related to Al(O-H)Si vibrations and its intensity changes under various temperatures. Obtained kinetic parameters of isotopical exchange reaction, dissociation enthalpies of BAS and rates of ethanol dehydration reaction over investigated zeolites were compared and discussed in broader context.

P.33 IMPROVING APPLICATION POTENTIAL OF GERMANOSILICATE ZEOLITES: POST-SYNTHESIS TAILORING THE ACTIVE SITES COUPLED WITH GE RECYCLING

Jin Zhang, Qiudi Yue, Yong Zhou, Maksym Opanasenko, Mariya V. Shamzhy

Germanosilicate zeolites characterized by low framework densities and multipore systems are of renewed interest as prospective shape-selective



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catalysts. However, the low hydrothermal stability and high price of Ge limiting the practical use of Ge-containing zeolites necessitates a development of approaches for cost efficient production of germanosilicate zeolite-based catalysts. Herein, a sequential 2 step post-synthesis approach: 1) leaching and subsequent recycling of Ge, 2) incorporation of three- and tetravalent elements generating catalytically active Bronsted and/or Lewis acid sites into de-germanated zeolite is proposed and optimized. Our results indicate that tailoring the active sites by post-synthesis of germanosilicate zeolites can be used to design new effective catalysts.

P.34 FROM WASTE TO VALUE: AQUEOUS PHASE REFORMING OF LIGNIN-HTL BY-PRODUCTS

*Giulia Zoppi, Giuseppe Pipitone, Sergio Bocchini, Andrea Maria Rizzo,
Samir Bensaid, Raffaele Pirone*

The NH_3BH_3 hydrolysis over Ru catalysts supported on MFI zeolites was investigated, focusing on the role of the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio and comparing the performance of this system with those of Ru on other supports. The results showed that Ru/H-MFI30 was the most active system. It was proposed that the activity is affected from the accessibility of Ru on the zeolite pores more than acidity and size of Ru particles.

P.35 ASSESSING CATALYTIC PYROLYSIS OVER NANOCRYSTALLINE ZSM-5 ZEOLITE FOR THE THERMOCHEMICAL VALORIZATION OF WASTE ELECTRICAL AND ELECTRONIC EQUIPMENT (WEEE)

*Alessia Marino, Alfredo Aloise, Javier Feroso, Patricia Pizarro,
Massimo Migliori, Girolamo Giordano, David P. Serrano*

Catalytic pyrolysis technology is a promising alternative route for the valorization of the growing amounts of plastic wastes. In this work, the catalytic pyrolysis of real WEEE over a nanocrystalline ZSM-5 zeolite is approached. The influence of the main reaction variables (temperature, catalyst/feed ratio) and the role of the zeolite properties on the products distribution has been studied. The catalytic pyrolysis over n-ZSM-5 zeolite allows to attain an oil fraction rich in monocyclic non-oxygenated aromatics and aliphatics, as well as gases, char ($\approx 1\%$) and coke on the catalyst, in proportions dependent on the reaction conditions. The products distribution dramatically changed compared to thermal pyrolysis, in which only waxes and partially decomposed solid were obtained.

