Engineered zeolites for ethylene management in active packaging

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saes group

making innovation happen, together

Outline

- SAES Group
- SAES Functional Polymers
- Zeolites Technological Platform
- SAES Engineered Zeolites
- Conclusion

Core Business and Vision

SAES® is an **advanced functional materials** Group, focusing its business on the **development and production of proprietary and specifically engineered solution (components and systems)** for many industrial and scientific applications.

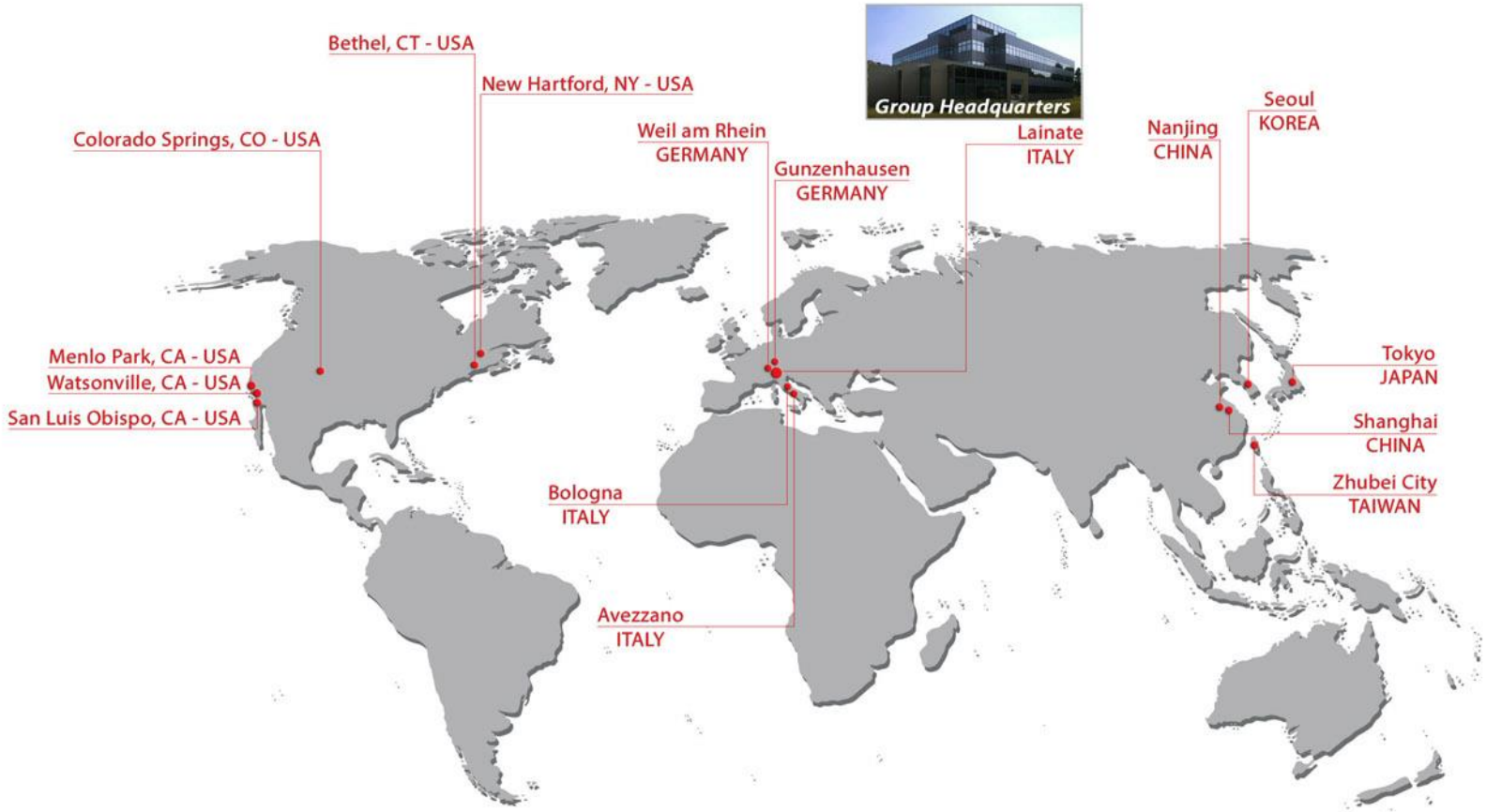
For more than **70 years**, our **technology** has been supporting **innovation** in the:

- Information and Displays industry,
- Lamp industry,
- Vacuum and Ultra-high Vacuum applications,
- Vacuum tubes and electronic devices industry,
- Ultra-high gas purification,
- Renewable Energies area.

Since 2004 our **NiTi smart materials solutions** have been innovating:

- the Medical devices industry,
- the Consumer electronics industry,
- the Automotive industry,
- the White Goods and Domotic industries.

Global Presence



- Saes Group has a worldwide presence thanks to its subsidiaries located in Europe, USA and Asia
- The company is headquartered in Lainate (Milan), Italy
- The Group has 10 manufacturing facilities: six in the USA, two in Italy and two in Germany
- In Asia the Group can count on subsidiaries located in Japan, China, South Korea and Taiwan
- The worldwide presence of the Group is also ensured by a number of authorized distributors

Our Research and Innovation

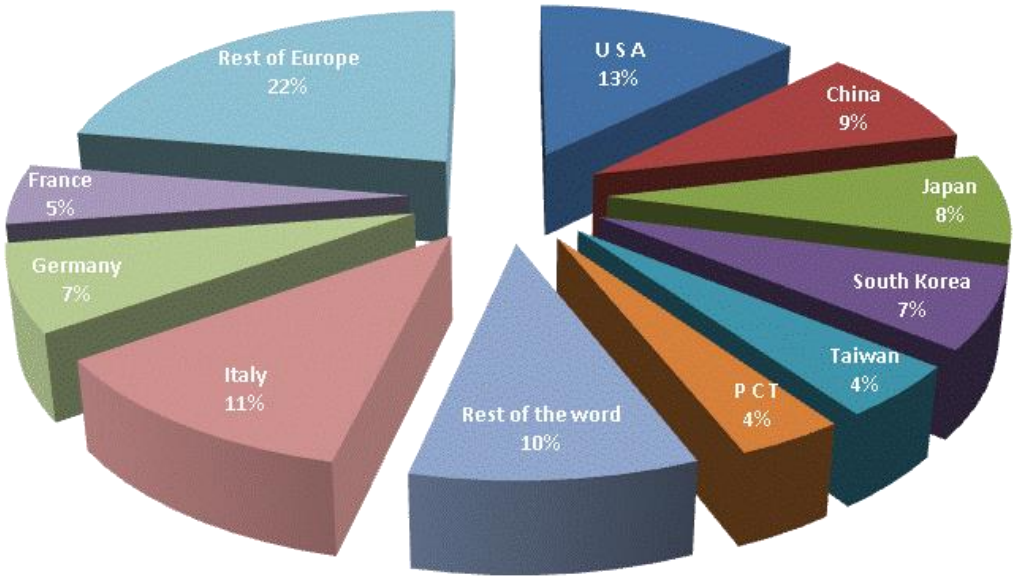
Key Figures

- About **10%** of net sales allocated to R&D every year
- State-of-the-art corporate laboratories covering a surface of over 3,300 sq. m.
- More than 150 highly skilled people engaged in RDI activities world-wide. Almost 17% of the total workforce of the Group:
  - about 50% are graduated (mainly in Physics, Chemistry, Engineering and Material Science)
  - 20% of graduated are PhD
- 233 Scientific Papers and Conference Proceeding published in the last 20 years
- Strong cooperation with Universities and R&D centers

SAES IP Portfolio

- About 8-10 new inventions per year are protected by patent application filings
- Over 300 inventions (SAES case/Patent Families) in 70 years

Patents & Applications by Geographic Area



- At present about 1300 "live" elements (Granted Patents and Patent Applications)
- About 70 Trademarks protected in SAES history, 38 still "alive".
- About 1-2 requests of registration for new trademark(s) per year.

SAES Core

Key Core Competences

- Surface Science
- Advanced Metallurgy
- Gas-Solid Interaction
- Macro-molecular Chemistry

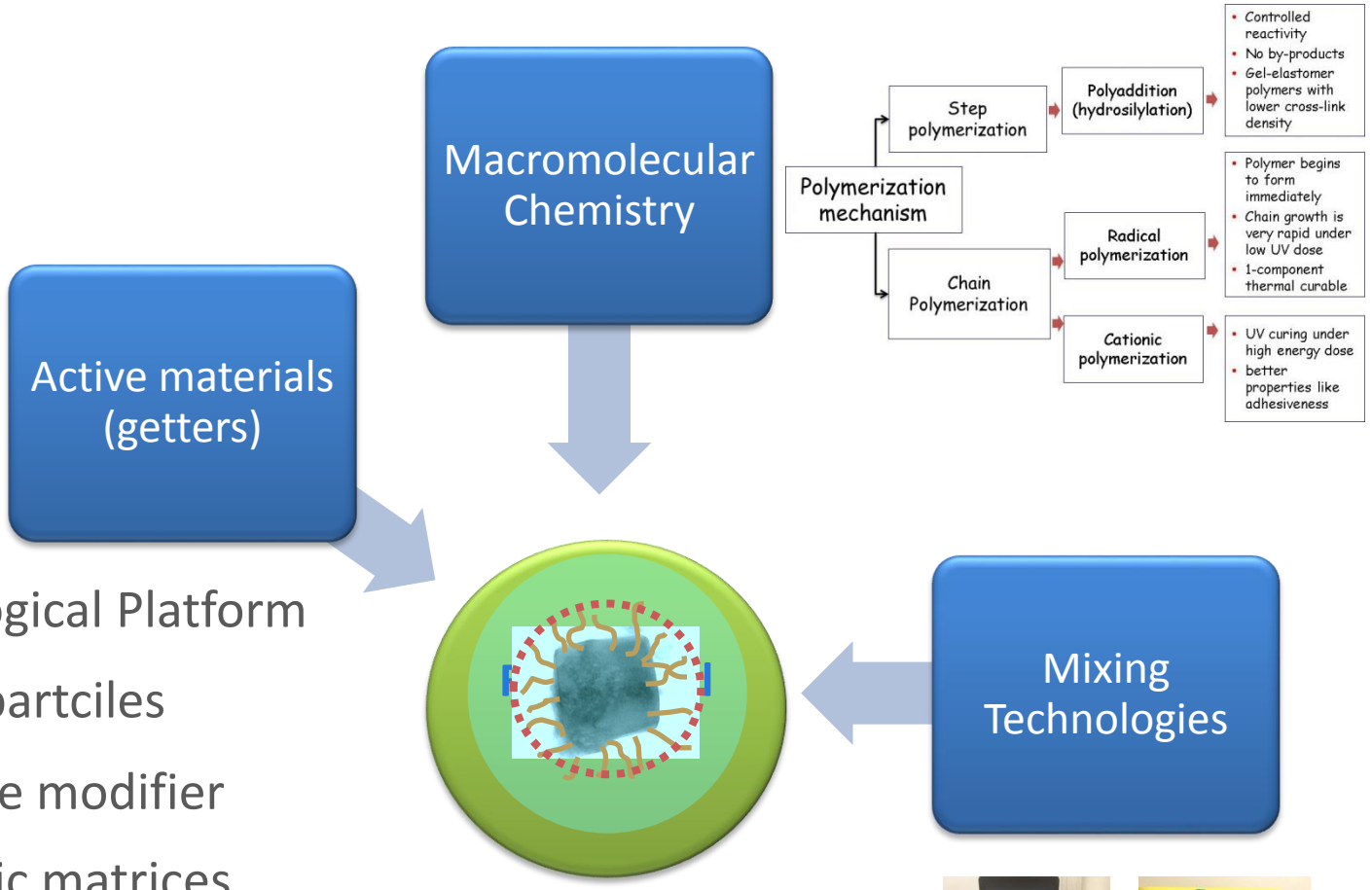
ADVANCED FUNCTIONAL MATERIALS

Core Technological Platforms

- GETTERING & DISPENSING
- SHAPE MEMORY ALLOYS
- PURE GAS HANDLING
- FUNCTIONAL POLYMER

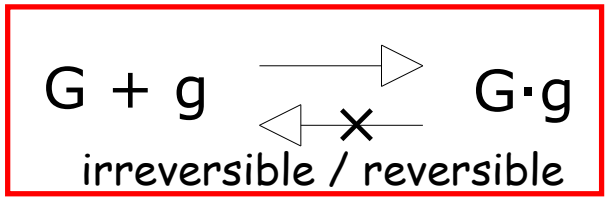
SAES Functional Polymers

- Technological Platform
  - Nanopartciles
  - Surface modifier
  - Organic matrices



SAES Active Materials

- Key properties of getter materials are:
  - kinetics of the capture process (adsorption, absorption, chemical reaction)
  - capacity (weight of specific chemical species captured by unit weight of getter)
  - partial pressure of a specific chemical species in equilibrium with getter



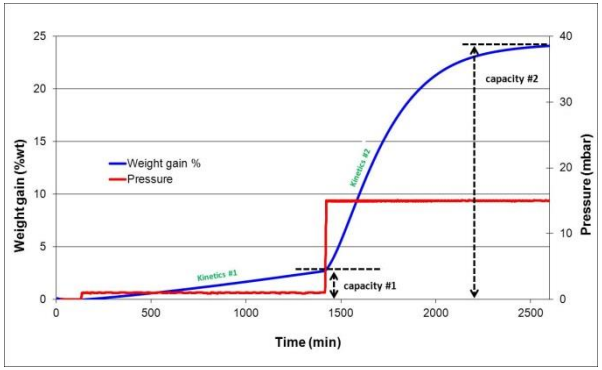
- Conventional getters:
  - pure metals (Ba, Ca, Ti)
  - metal alloys (ZrVFe, ZrCo, TiNi, etc.)
  - inorganic, non metal
  - Oxide systems

- New getters for Functional Polymers:
  - nanoxides
  - Inorganic salts (solid solution)
  - Micro and nano zeolites

SAES Nanotechnology

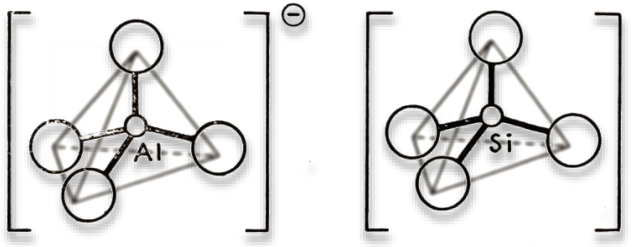
- Typical approaches to obtain nanosized materials
  - top-down
  - bottom-up

- SAES LABs have developed different approaches dealing with the preparation, modification, dispersion, manipulation, observation and control of matter on dimensional scales from few microns down to tens nanometers able to show innovative reactive, mechanical, optical and superficial properties
  - Synthetic routes:
    - Sol-gel hydrothermal synthesis
    - Colloidal synthesis
    - Microsizing and nanosizing
    - In situ polymer synthesis



Zeolites Structure

- Microporous solids, accordingly to IUPAC definition
- Crystalline alumino-silicates, with regular open tridimensional nanosized porous framework
- Pores with defined nanosized dimensions
- Zeolite framework: made of SiO_4 and AlO_4 tetrahedral units, sharing oxygen between every two consecutive units
- So far there are **231** zeolite framework types

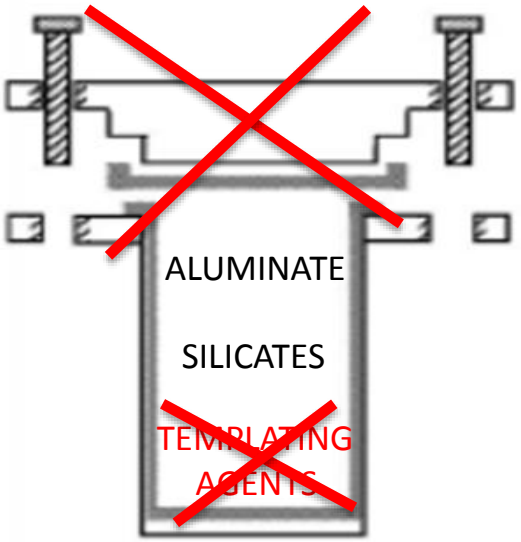


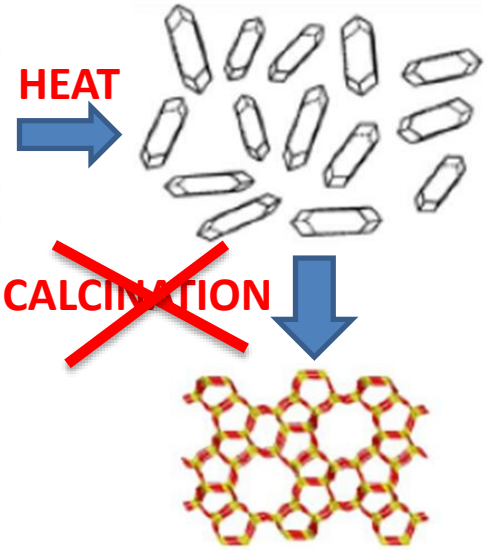
negatively charged AlO_4 tetrahedral unit

Zeolite – state of the art approach

SOL-GEL HYDROTHERMAL SYNTHESIS FOR NANOZEOLITES

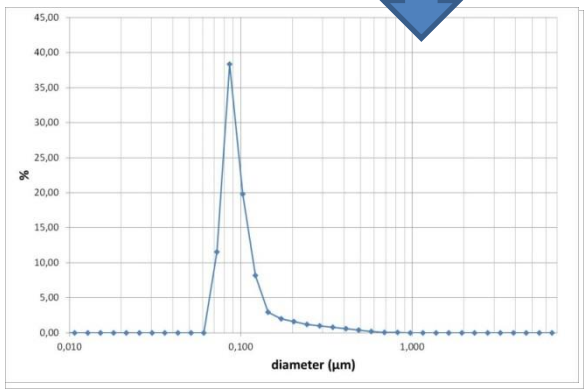
- **low T and atmospheric pressure**
  - no need of high-T autoclave
- **no need of templating agent**
  - No calcination
  - process step reduction
- **purification**
  - effective filtration
  - agglomerate-free drying





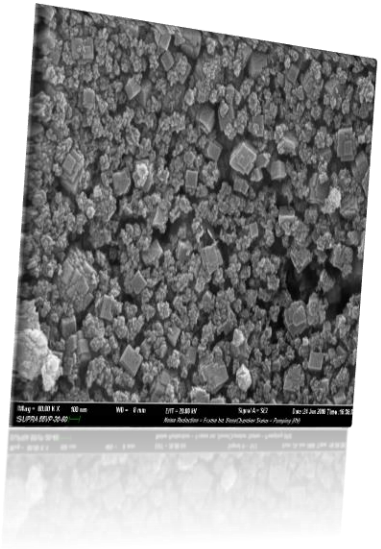
PURIFICATION

narrow distribution of sub-micrometer-sized primary particles

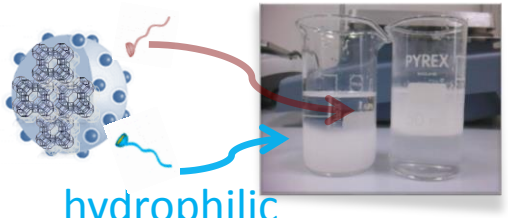


From a versatile Technology to a unique Platform

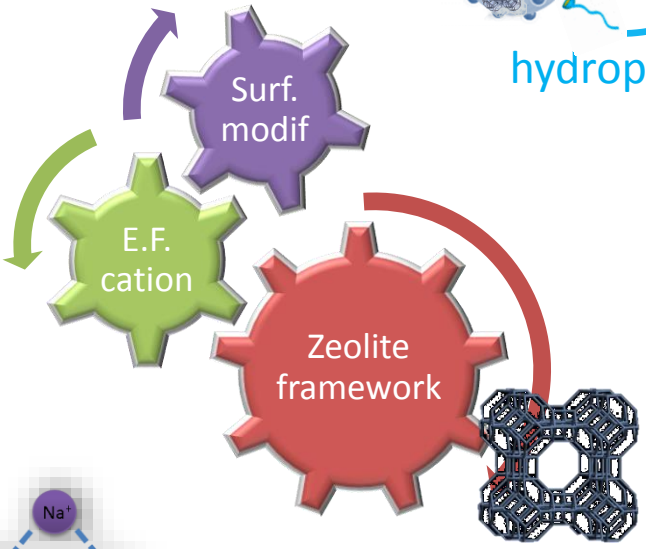
- SAES ZeoTec:

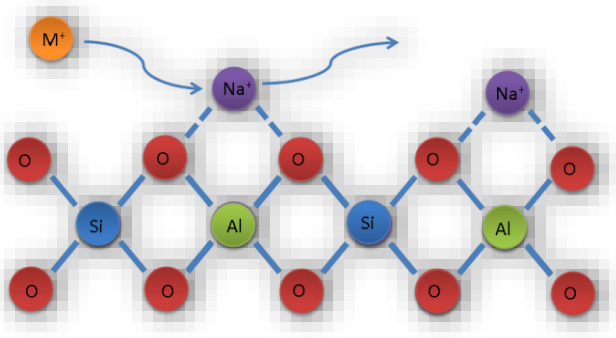


hydrophobic

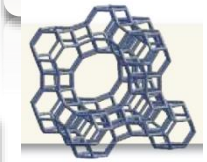


hydrophilic



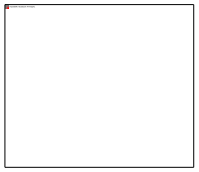


FAU



LTA

LTL



ZSM-5

MOR

SAES Active Package

- Zeolites adsorption capacities and sorption kinetics for different gases
  - H_2O, CO_2, O_2…

Ethylene

- is the natural ripening hormone of plants

Applicant: SAES Getters S.p.A.
Inventors: A. Colombo, P. Vacca, M. Riva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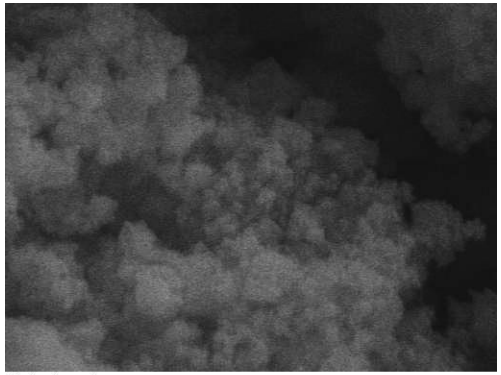
(10) International Publication Number
WO 2016/125050 A1

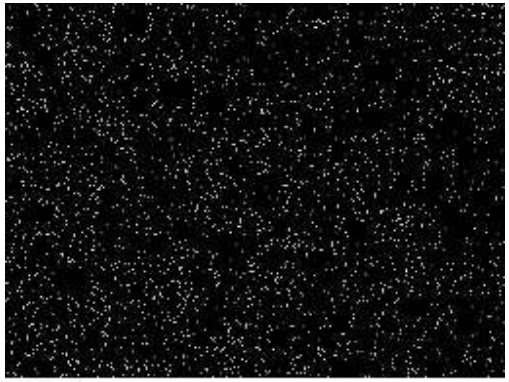
- SAES R&D has developed an active package, comprising zeolites having LTA framework, able to improve the quality of gaseous atmosphere within package itself, with particular reference to the presence of ethylene

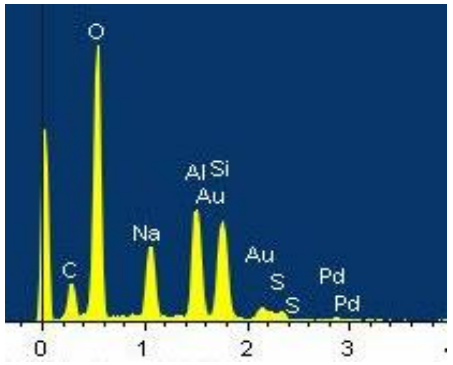
- SAES solution is capable to maintain fruit and vegetables property in the presence of varying environmental conditions:
  - Temperature
  - Humidity
  - Other gasses (typical VOC under fruit transport)

SAES Approach

- SAES approach:
  - Zeolites as active materials: mainly based on LTA framework with pore size of 4.2Å
  - Zeolites exchanged with Pd to coordinate C_2H_4





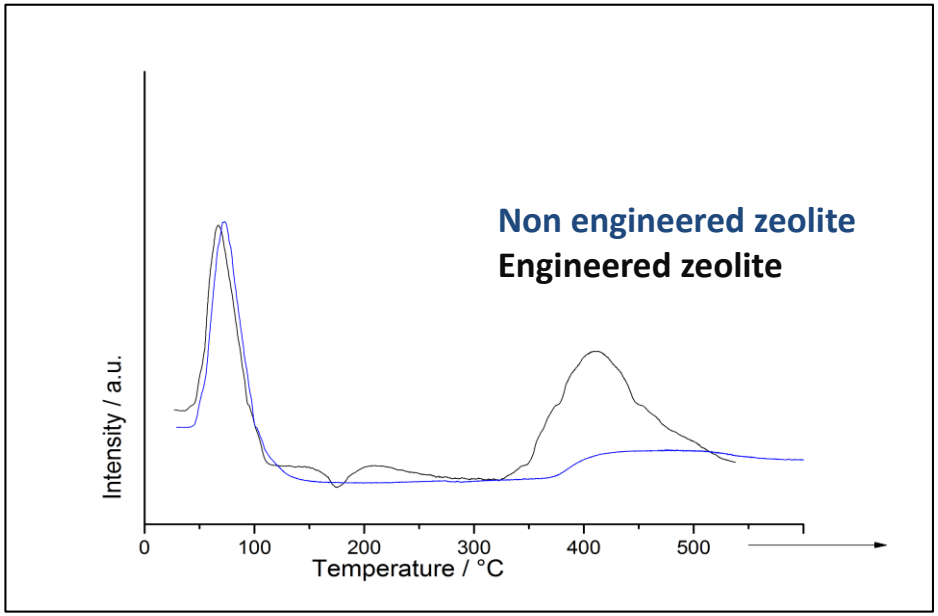


  - Particle size <10 µm
  - LTA-Na, with Na^+, are suitable materials for water interaction
  - Modified zeolites to reduce water interaction

Sample	H_2O sorption capacity (15mbar)	ICP Na amount
Hydrophilic LTA	18,0% wt	14,0% wt
Modified LTA	4,4% Wt	5,2% wt

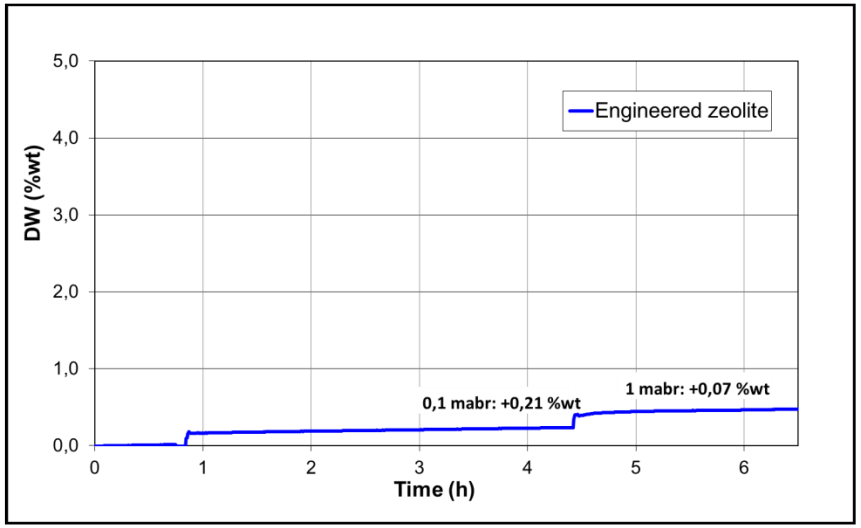
Engineered Zeolites Characterization

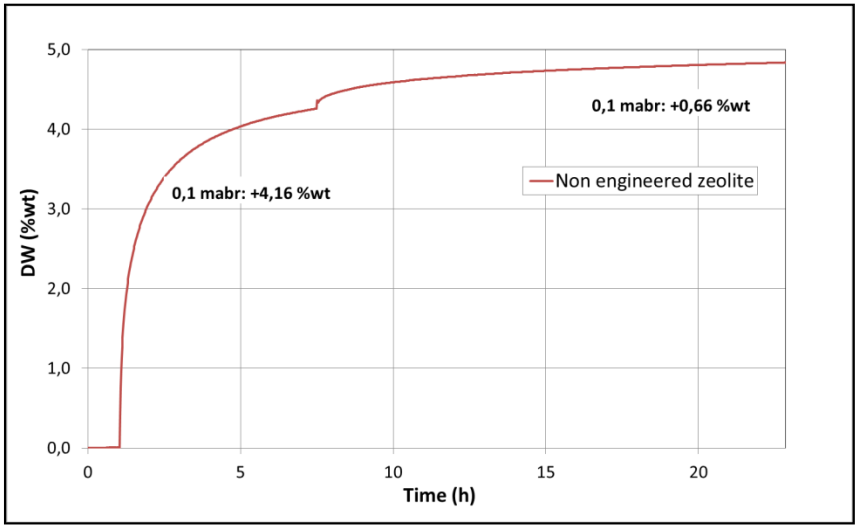
- SAES-Pd zeolites have been characterize by Temperature Programmed Desorption (TPD)
  - Steps of analysis:
    - Thermal activation
    - Saturation by injection of gaseous ethylene in static condition
    - Sample heating in He
    - Gas outflowing → analyzed by a thermal conductivity detector (TCD)



Engineered Zeolites Selectivity

- Ethylene is often present with other typical VOC released by transportation fuels
- Cyclohexane has been adopted as a tester molecule to evaluate the selectivity of zeolites
- Gravimetric analysis have been performed by Microbalance:
  - Zeolites activated at 180°C under vacuum overnight
  - Zeolites equilibrated under N_2 atm

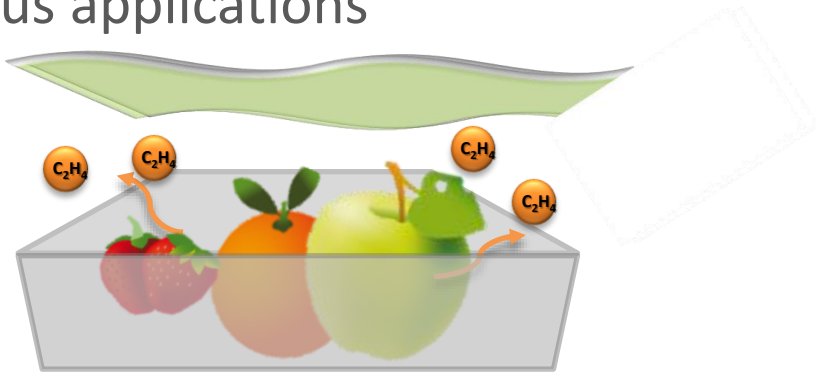




Sample	C_6H_{12} Sorption capacity (0.1 mbar)	C_6H_{12} Sorption capacity (1.0 mbar)
Engineered zeolite	0,21	0,07
Non Engineered zeolite	4,16	0,66

Outlook

- SAES R&D technologies allow the integration of engineered materials into polymeric matrixes obtaining Functional Polymers suitable for various applications



*Ethylene production from different fresh produce types			
Low (<1,0ml kg $^{-1}$ h^{-1})	Moderate (1-10 ml kg $^{-1}$ h^{-1})	High (1-100 ml kg $^{-1}$ h^{-1})	Very high (>100 ml kg $^{-1}$ h^{-1})
Strawberry, orange, lemon, onion	Banana, mango, tomato	Apricot, peach, pear	Apple, avocado, passion fruit

*Platinum Metals Rev. 2009, 53, (3)

- The capacity of engineered zeolites is enough to guarantee the atmosphere control into a typical package

Conclusion

- SAES Functional Polymers Technology allows the development of innovative systems for advanced packaging
- SAES engineered zeolites represent an active material for ethylene management in packaging applications
- SAES products are able to ensure high selectivity and efficient adsorption for different gases
- SAES nanotechnology enables the integration of new functionalities through conventional manufacturing process (slot die, blading, lacquering)

Acknowledgments

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  - Paolo Vacca, PhD, Head of Materials Chemistry Lab
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Thank you for your attention

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