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# BOOK OF FULL ABSTRACTS

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







## XVI National Congress of Zeolites Science and Technology



## 8<sup>th</sup> Czech-Italian Spanish Conference on Molecular Sieves and Catalysis



## XXI National Congress of Catalysis

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## NEUTRON AND *IN SITU* SYNCHROTRON X-RAY POWDER DIFFRACTION ANALYSIS TO STUDY THE THERMAL ACTIVATION OF NH<sub>4</sub> OMEGA ZEOLITE.

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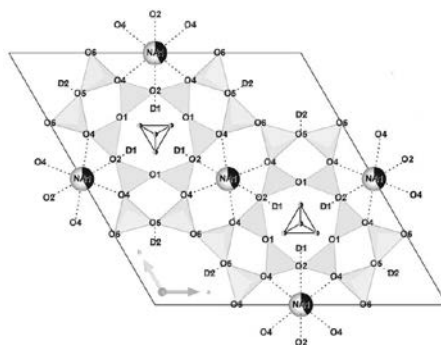
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Acidic zeolites are usually used by petroleum industries as high-performing catalysts for isomerization of xylenes, paraffin hydroisomerization, catalytic cracking, and heavy oil hydrocracking.<sup>1-4</sup> Catalytic properties arise from the presence of protons bonded to framework oxygen atoms, which act as Brønsted acid sites. Hence, the determination of their nature, position, density and strength is mandatory to predict acid catalyst efficiency and function. Despite the large number of experimental techniques that can be used to investigate zeolites acidity (e.g., TPD,<sup>5,6</sup> X-ray photoelectron spectroscopy,<sup>7-8</sup> solid state NMR<sup>9-11</sup>, and quantum chemical calculations<sup>12-15</sup>) neutron and *in situ* Synchrotron X-ray powder diffraction is considered fundamental to understand the environment within the zeolite framework. Neutron diffraction is used to probe Brønsted acid sitting; synchrotron X-ray diffraction offers the possibility to obtain a picture of the zeolite thermal behaviour, allowing the continuous monitoring of bond distances and angles upon dehydration as well as desorption processes of extraframework molecules. To form bridging OH groups in zeolites, charge-compensating cations are exchanged with ammonium ions and then expelled through thermal treatment, which guarantees the Si-OH-Al groups formation<sup>16</sup>. The study of ammonium-exchanged zeolites upon thermal treatment offers the advantage to obtain the acidic form in *real-time* conditions. Based on this, it has been decided to study the progressive activation of NH<sub>4</sub> precursor of omega zeolite (*i.e.*, synthetic counterpart of natural mazzite). This purpose was achieved studying the evolution of structural features, continuously monitoring kinetics and the material dynamic behaviour induced by ammonium ions calcination. All the information gained were combined with the calcined and deuterated omega structural characterization via powder neutron diffraction, which gave informations about the number and the position of hydroxyl groups in the calcined D-omega. The sample of zeolite omega (Na<sub>6.6</sub>TMA<sub>1.8</sub>(H<sub>2</sub>O)<sub>22.2</sub>[Al<sub>8.4</sub>Si<sub>27.6</sub>O<sub>72</sub>]-MAZ) used was synthesized at the Laboratoire de Matériaux Catalytiques et Catalyse en Chimie Organique, (CNRS, Montpellier, France) and then NH<sub>4</sub>-ion exchanged three times at room temperature and other three times at 90°C (Na<sub>2.4</sub>TMA<sub>0.9</sub>(H<sub>2</sub>O)<sub>4.2</sub>(NH<sub>4</sub>)<sub>20.0</sub>[Al<sub>8.4</sub>Si<sub>27.6</sub>O<sub>72</sub>]). *In situ* synchrotron X-ray powder analysis were performed at ESRF (Grenoble) from room temperature to 900 °C, with a heating rate of 5°C/min. Neutron powder data of D-omega were collected at the D2B beamline of ILL (Grenoble) at 4 K of temperature. Data collected upon heating highlighted the occurrence of structural distortions driven by the thermal treatment,



which also determined TMA template degradation and ammonium ions calcination. Although the symmetry remained unchanged within all the temperature range investigated, non-reversible and transient structural distortions of 6MR, 8MR and gmelinite cage were evidenced. The most noticeable deformation occurs on the gmelinite cage, due to the progressive O2 framework oxygen atom shift towards the centre of cavity (*i.e.*, as proved by the decrease of O1-O2 distance). O2 framework oxygen shift suggests the formation of a O2-H Brønsted acid site, whose location was highlighted by neutron structure refinement of D-mega sample. Neutron refinements highlighted also the presence of a second acid site, detected on the O5 framework oxygen (Fig.1), thus confirming what suggested by the progressive lightening of T-O5 distance at increasing temperature. All the informations gained through this multitechnical approach provided a basis for the interpretation of the omega shape selectivity in reactions of growing importance in the oil and petrochemical industries.



**Figure 1.** proton sites distribution within D-omega zeolite

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