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BOOK OF FULL ABSTRACTS

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Italian Zeolite Association (AIZ)
Czech-Italian-Spanish (CIS) Conference
Italian Interdivisional Catalysis Group (GIC)





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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INSIGHTS ON Ga-FERRIERITE CATALYST: X-RAY POWDER DIFFRACTION CHARACTERIZATION AT AMBIENT CONDITIONS

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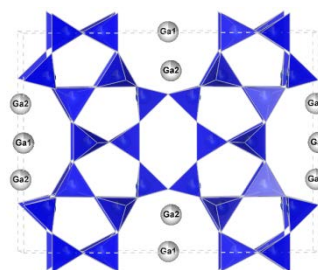
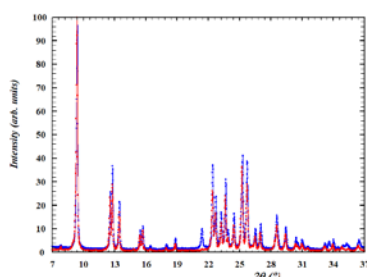
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Due to their unique catalytic performances in light hydrocarbon aromatization, gallium-containing zeolites have been extensively investigated. Newest applications concern the conversion of biomass into biofuels and bio-based chemicals.¹⁻² Ga-zeolite catalysts can be obtained through hydrothermal crystallization in presence of the suitable template agent or postsynthesis treatments, such as galliation, recrystallization, impregnation, chemical vapor deposition (CVD) and ion exchange.^{1 (and ref. in)} Although all the listed treatments are suitable to introduce gallium into both tetrahedrally coordinated framework and interstitial non-framework positions, the most used are impregnation or ion-exchange process. Incorporation of Ga⁺³ cations into framework positions is the main source of lattice charge defects, which give rise to Brønsted acidic Si-OH-Ga bridging hydroxyl group and, consequently, to the ion exchange properties. On the contrary, extraframework Ga³⁺ determines the presence of Lewis acid sites, which also are originated from oxo cations GaO⁺ in exchanged framework positions. Due to its size, gallium in framework positions is metastable; hence, the thermal treatment can cause the migration of Ga³⁺ to extraframework positions and its progressive aggregation in form of isolated, dimeric and polymeric species up to oxide nanoparticles.³⁻⁵ According to this, gallium migration upon heating leads to the appearance of a different type of Lewis acid sites.⁶ As a consequence, after this treatment Ga-zeolites can possess both Brønsted and Lewis acid sites, which can work separately or in a synergistic way in acid catalyzed reactions.⁷⁻⁸ In spite of the growing interest on Ga-catalysts, it has been decided to characterize, from a structural point of view, a Ga-ferrierite zeolite by using X-ray powder diffraction analysis. The aim of the project was the characterization of the zeolite structure at ambient conditions, detection and 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. The FER sample used in this work is a synthetic commercial siliceous ferrierite, purchased in its ammonium form from Zeolyst International (code CP914C, namely NH₄-FER in this work). The SAR is equal to 20. The Na₂O content is <0.05 wt. % and the surface area is 400 m² g⁻¹. Ga-substituted zeolite was obtained by using the batch method (*i.e.*, solution containing Ga(NO₃)₃ 10 mM and NaOH 1 M, in contact with zeolites at 40 °C for 24 h). The Ga-catalyst was then analysed through X-ray powder diffraction at Room Temperature (*i.e.*, data collection on D8 ADVANCE DaVinci diffractometer of the University of Ferrara). A comparison of NH₄-FER and



Ga-FER X-ray diffraction patterns (Fig.1) clearly highlighted that peak intensities are markedly different in the entire 2θ region investigated. At the same time, diffraction peak positions are different, and consequently, unit-cell parameters are modified (Ga-FER: $a=18.8389(7)$ Å, $b=14.0882(4)$ Å, $c=7.4493(2)$ Å, $V=1977.1(1)$ Å³; NH₄-FER: $a=18.8477(8)$ Å, $b=14.1049(5)$ Å, $c=7.4425(2)$ Å, $V=1978.6(1)$ Å³). Moreover, the absence of *I*-centering forbidden peaks indicates that the space group does not change after Ga-exchange. Consequently, the *Immm* space group was also adopted in Ga-FER structure refinement, which was performed starting from the framework atomic coordinates reported by Martucci et al.⁹ for the same NH₄-sample used in this work.



Rietveld refinement revealed the incorporation of about 1.0 Ga ions per unit cell spread over two partially occupied sites (Ga1 and Ga2 sites, respectively), not detected in the precursor. At the same time, variations on both framework bond distances and angle suggested the incorporation of gallium in the tetrahedral sites. X-ray absorption spectroscopy with EXAFS (*i.e.*, extended X-ray absorption fine structure spectroscopy) was used to investigate the local environment of Ga. Correlation between the Ga contents (molecules per unit cell), as determined by chemical and Rietveld analysis, and coordination numbers as well as bond distances to neighbouring atoms will be derived.

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