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BOOK OF FULL ABSTRACTS

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

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In analogy to ferromagnetism and ferroelectricity, ferroelasticity can be defined by large elastic nonlinearities that lead to elastic hysteresis behavior. Ferroelasticity produces interfacial twin walls where localized effects (e.g. superconducting twin boundaries and ferroelectricity) cannot be observed at the bulk scale (i.e. different forces act on the atoms at the local and bulk scales).¹ We thus have an intermediate structural length scale - the mesostructure. Actually, microstructural features modify the ideal crystal structure of a crystalline material and often lead to phase transitions that change its crystallographic symmetry. These ferroelastic phase transitions can be described through Landau-type theories at both the crystal structure and mesostructure levels.²

Zeolite Socony Mobil-5 (ZSM-5), with MFI framework topology, belongs to the pentasil zeolite family and is characterized by a three-dimensional pore system formed by two intersecting sets of tubular channels delimited by 10-membered rings of tetrahedra: the so-called straight channel parallel to the [010] direction and the sinusoidal channel parallel to the [100] direction. Its unique microporous structure coupled with high surface area, mechanical, thermal, biological, and chemical stability has promoted ZSM-5 as one of the most employed synthetic zeolites in catalysis and adsorption processes.^{e.g.3} The as-synthesized template-containing form of ZSM-5 exhibits the orthorhombic topological symmetry (s.g. *Pnma*). After thermal treatment the crystal symmetry is lowered to the monoclinic *P2₁/n*. Upon heating ZSM-5 is known to experience a displacive $m \leftrightarrow o$ phase transition (i.e., from the monoclinic *P2₁/n* to the orthorhombic *Pnma*) at different transition temperatures (T_c) depending on framework composition (i.e. the Si/Al ratio), lattice defect density, as well as amount and physical-chemical properties of guest molecules. Reported for the first time by Wu et al.,⁴ it has been shown that aggregates of twin domains of the monoclinic framework reversibly displace into an orthorhombic single crystal upon heating, suggesting that the ZSM-5 monoclinic polymorph has the features of a ferroelastic material.⁵

According to the Landau theory, the temperature evolution of a ZSM-5 (Si/Al = 140) unloaded and has been characterized through the analysis of the spontaneous strain variation before and after the adsorption of organic contaminants (i.e. toluene, 1,2-dichloroethane, methyl-tert-butyl-ether, and binary mixtures of them).^{6,7} The first main result is that all the investigated samples undergo a $m \leftrightarrow o$ phase transition with a tricritical character (i.e. between second order and first order). This fact is of relevance because the strain fluctuations within the domain structure of materials showing tricritical phase transitions are generally less relevant than those associated to truly second order transitions.⁸ Secondly, the adsorption of different organic contaminants strongly affect the T_c and the thermodynamic features related with the phase transition.



Indeed, the excess enthalpy part of the free-energy expansion (which derives from the coefficients of the Landau potential) is strictly related with the enthalpy of guest molecules adsorption (ΔH_{ad}).

Although the dependence among T_c , Si/Al ratio, and the enthalpy change ΔH related to the ferroelastic $m \leftrightarrow o$ phase transition in ZSM-5 compounds has been already outlined,⁹ the thermodynamic processes that govern these relationships at both the crystal structure and mesostructure levels have to be still disclosed.

For this reason, in this contribution the ferroelastic $m \leftrightarrow o$ phase transition in a ZSM-5 (with Si/Al ratio of 250) and a silicalite (Si/Al ratio $\rightarrow \infty$) synthesized by a common procedure has been monitored through the combination of *in-situ* X-ray powder diffraction at high-temperature and calorimetric experimental techniques. The definition of new trends among the chemical and thermodynamic parameters of above is provided.

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