

Crystal-fluid interactions in open-framework silicates

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The structural evolution of microporous materials compressed hydrostatically in a fluid is drastically affected by the potential crystal-fluid interaction, with a penetration of new molecular species through the zeolitic voids in response to applied pressure.

On the basis of recent experimental findings and computational modelling studies, it was observed that when no crystal-fluid interaction occurs, the effects of pressure are mainly accommodated by tilting of (quasi-rigid) tetrahedra around the bridging O atoms. Tilting of tetrahedra is the dominant mechanisms at low-mid P -regime, whereas distortion and compression of tetrahedra dominate the mid-high P regime. The deformation mechanisms are governed by the topological configuration of the tetrahedral framework, but the compressibility of the cavities is controlled by the ionic and molecular host content, resulting in different unit-cell volume compressibility in isotypic structures. One of the most common deformation mechanisms in zeolitic framework is the increase of channels ellipticity.

Not all the zeolites experience a P -induced intrusion of new monoatomic species or molecules from the P -transmitting fluids. For example, natural zeolites, with well-stuffed channels at room conditions, tend to hinder the penetration of new species through the zeolitic voids. Several variables govern the sorption phenomena at high pressure: the “free diameters” of the framework cavities, the configuration of the extra-framework population, the partial pressure of the penetrating molecule in the fluid (if mixed with other non-penetrating molecules), the rate of P -increase, the surface/volume ratio of the crystallites under investigations, the temperature at which the experiment is conducted. The most recent findings allow us to provide an overview of the intrusion phenomena of monoatomic species (*e.g.*, He, Ar, Kr), small (*e.g.*, H₂O, CO₂) and complex molecules, along with the P -induced polymerization phenomena, (*e.g.*, C₂H₂, C₂H₄, C₂H₆O, C₂H₆O₂, BNH₆, electrolytic MgCl₂·21H₂O solution), with potential technological and geological implications.

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