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The role of hydrogen multicenter bond in transport properties of materials

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Abstract – The transport barrier for hydrogen atoms through the hexagonal channels of a novel nanoporous ZnO polymorph, analogue of the zeolite sodalite, has been found to be influenced by the formation of a multicenter bond involving hydrogen itself and the zinc atoms belonging to the hexagonal rings of the oxide structure. The electronic rearrangement due to the appearance of such bond counterbalance the increase in energy due to framework deformation, resulting in a barrier at least one order of magnitude lower than the ones commonly observed for such phenomena.

The transport properties along the hexagonal channels of a novel sodalite-like nanoporous ZnO polymorph (SOD-ZnO), predicted as an accessible synthesis target via the self-assembly of fulleroid-shaped $(ZnO)_{12}$ nanoclusters [1], have been investigated. Specifically, atomic hydrogen, observed as an isolated non-interacting species when lying in the center of the interstitial SOD-ZnO sites, has been used as a probe to model the barrier for transport through the hexagonal ring linking two adjacent interstitial cavities.

Energies, structures and electronic states were calculated within the framework of Density Functional Theory (DFT), using the PW91 exchange-correlation potential [2] and the Projector-Augmented Wave (PAW) method [3]. The VASP code was used throughout [4]. Barriers were computed by constrained minimization approach, and minimum energy path was checked by manual perturbation of selected barrier points.

Going from the center of the cavity to the center of the six-member ring (barrier maximum), the Local Density Of States (LDOS) projected on the hydrogen 1s orbital evolve from a situation consistent with a single electron residing on the hydrogen 1s orbital, to a bonding/antibonding system, where the bonding and antibonding states are found to be completely occupied and completely unoccupied, respectively. The first appearance of this new feature is associated with the total minimum of the barrier (fig.1).

In analogy to similar situations where hydrogen multicenter bond has also been predicted [5], in the present case the formation of such system can be described in terms of an interaction between hydrogen 1s orbital and a totalsymmetric linear combination of the empty 4s orbitals of the zinc atoms forming the hexagonal ring (fig.2).

Being positioned very deep in energy in respect to the Fermi level (~ -6eV), correspondent to the top of the Valence Band (VB), the bonding state behave as a localized acceptor: while one of the two electrons is donated from the hydrogen 1s orbital, the other falls directly from the top of VB. The big drop in energy associated with the donation of this second electron counterbalance nearly completely the natural increase in energy due to framework deformation induced by the impurity passage, resulting in the very small barrier observed (~ 0.05eV).

Because of these unconventional features, the SOD-ZnO material is thus proposed as a fast transport membrane and a valid alternative to Pd-based membranes, for which transport barriers are calculated to be at least one order of magnitude higher [6].

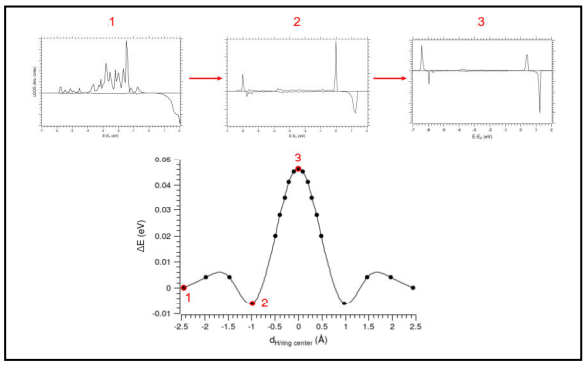

Figure 1: Evolution of the H 1s LDOS for hydrogen (top) going from the center of the cavity (point 1) to the center of the hexagonal ring (point 3), and calculated barrier for transport (bottom), shown as relative energy versus distance of the H atom from the hexagonal ring center.

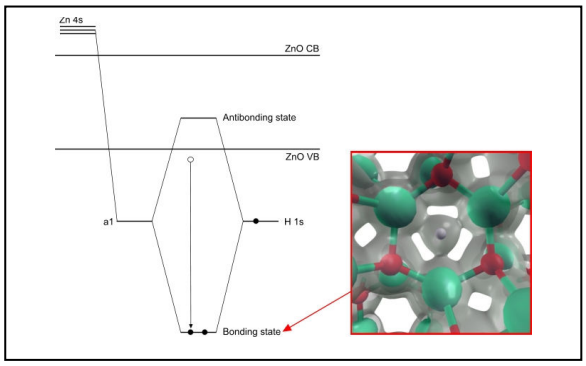

Figure 2: Schematic of the formation of hydrogen multi-center bond (left), and charge density isosurface plot of the multicenter bonding state taken at the top of the barrier (right). Hydrogen, oxygen and zinc atoms are printed in white, red and green, respectively.

References

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