MODELLING MECHANISM OF REACTIONS AND ACTIVE SITES IN HETEROGENEOUS CATALYSIS, LOOKING FOR REACTIVITY INDICATORS IN SUPPORTED ZIEGLER-NATTA NANO-SYSTEMS

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Many of the most efficient and selective catalysts for a wide range of energy and environmental applications are composed of nanometer-sized particles exposing different surface sites and involve multiple components mutually interacting each other. Since the experimental characterization of the surface and properties of nano-catalysts is usually quite challenging and generally averaged on multiple sites, theoretical calculations represent a powerful tools in discriminating between surface sites and identifying the role of components in a specific environment. Thanks to an efficient highly parallelized code and HPC facilities we attempted to correlate the catalysts structure of Ziegler-Natta (ZN) at the nano-scale with their activity and selectivity and to understand the role of each component the reaction mixture representing the ultimate target in industrial catalysis. In fact, modern $MgCl_2$-based ZN catalysts may be seen as prototypes of complex nanometer-sized materials, their realistic description required advanced DFT methods accounting for dispersion and employing hybrids or highly parameterized m-GGA exchange-correlation functionals to describe metal catalytic sites. All these calculations were performed by using *ab-initio* CRYSTAL code (http:// www.crystal.unito.it/) based on LCAO approach. Notably, the use of an atom-centered basis set permits the accurate and easy evaluation of the exact HF exchange so that the code is particularly well suited to treat hybrid functionals with extremely high efficiency for periodic systems. Moreover, a massive parallel (MPP) version of CRYSTAL is available on HPC resources that has been specifically tailored to achieve an excellent scalability in terms of both speed-up and memory usage; it can treat very large unit cell systems with large memory requirements. Any modeling of ZN catalysts took into account: 1) the presence of multiple sites on different $MgCl_2$ surfaces and on defective positions (edge and corners); 2) the fact that adducts of catalytic interest have very low degree of coverage. We modelled **low dimension systems: surfaces, edges and energetically stable primary particles** consisting of $MgCl_2$ nano-crystals capped with $TiCl_x$ species , internal donors and Al-alkyls and simulated their vibrational properties. Those ternary and quaternary adducts represent reliable models of ZN catalysts of spread use in polymer industry. The results provide a razionalization of the structure of active sites with a potential positive outcome on productivity and stereospecificity of the industrial catalysts as well as the reduction of their health and environmental impact. Our simulations on systems of thousand atoms were feasible only thanks to HPC resources we got thanks to PRACE Project.