Molecular dynamics modeling of half-metallocene titanium(IV) ethylene polymerization catalysts.

Łukasz Piękoś, Artur Michalak

K. Gumiński Department of Theoretical Chemistry, Faculty of Chemistry, Jagiellonian University, Kraków, Poland

In the present work results of molecular dynamics simulations of half-metallocene titanium(IV) catalysts are presented. Molecular systems under consideration include non-bridged half-metallocene titanium complexes with aryloxo ligand acting as catalysts in ethylene polymerization process. Catalysts with various ligands and at various catalytic process stages are considered.

Methodology includes Born-Oppenheimer molecular dynamics on the semiempirical level (MSINDO software package) and Car-Parinello molecular dynamics on the *ab initio* DFT level (CPMD software package). Despite lower accuracy semiempirical approach is still useful due to 3.5 orders of magnitude difference in performance comparing to *ab initio* approach. Such performance allows for simulations with timescale far beyond reach of *ab initio* methods. Free molecular dynamics is used to study spontaneous transitions (including conformational changes and ethylene insertion reactions). Constrained molecular dynamics in slow-growth approach is used to obtain free energy profiles of ethylene insertion reaction.

Presented results include spontaneous conformational transitions affecting catalyst reactivity. Example where six stable conformations (including several transitions between them) can be observed in one simulation is also presented. Spontaneous insertion of ethylene is observed, followed by conformational changes which make catalytic cycle in one simulation.
Sections of trajectory (plots of selected coordinates) as well as its snapshots (structures of molecular systems) are presented.