DFT Calculations on $(V_2O_5)_n$ Clusters with n = 1–8

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Crystalline divanadium pentaoxide has a layered structure with pentacoordinated vanadium atoms within a layer and an additional weak inter-layer coordination. The main question addressed in the present study is whether such a structure is recognizable in smaller $(V_2O_5)_n$ clusters, and from what size? For this purpose, DFT calculations using various functionals (B3LYP, BP86) and basis sets (double- and triple-ζ) were performed on such clusters (n = 1,2,4,8).

For the V_2O_5 cluster, a doubly bridged structure is more favorable than a singly bridged one. For V_4O_{10}, a tetrahedral configuration, which resembles the analogous P_4O_{10} structure, is the most stable, followed by two structures with quadrangular and linear arrangement of V atoms. A configuration which corresponds to the atom arrangement within one layer of the crystal is energetically the highest. Thus, small $(V_2O_5)_n$ clusters (n = 1–2) show a clear trend to *tetrahedrally coordinated vanadium* and to *avoid triply coordinated oxygen* whenever possible.

Also in larger clusters, pentacoordinated V atoms are only stable in sheet-shaped $V_{16}O_{40}$ or bigger clusters. Triply coordinated O atoms are found in smaller clusters, but only to avoid vanadium coordination numbers less than four.

The DFT-optimized structures of selected $(V_2O_5)_n$ clusters are applied to fit parameters of a classical shell-model ion-pair potential. The potential includes three-body terms and is more suitable for cluster calculations than for solid. It is intended to be used by simulated annealing to rapidly generate plausible starting structures for DFT optimizations of larger clusters.