

QUANTUM CHEMICAL MODELING OF VANADYL COMPLEXES WITH N,O-CHELATING SCHIFF BASES GRAFTED TO SILICA SURFACE

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Introduction

There are wide variety of reactions that are catalyzed by complexes of vanadium with Schiff bases, and in particular, polymerization, bromination, coupling, degradation, epoxidation, hydroxylation, oxidation, sulphoxidation, dehydrogenation, dehydroperoxidation reactions etc. The most promising catalysts are those containing complexes immobilized on solid matrices, due to their easy separation from the reaction mixture. However, establishing the real structure of immobilized complexes is an important and at the same time a difficult task due to the ambiguity of the interpretation of indirect physical research methods. Therefore, the application of theoretical quantum chemical methods to determine the structure of complexes on which the catalytic activity depends, and the agreement with the experimental results is of particular importance.

Models and methods

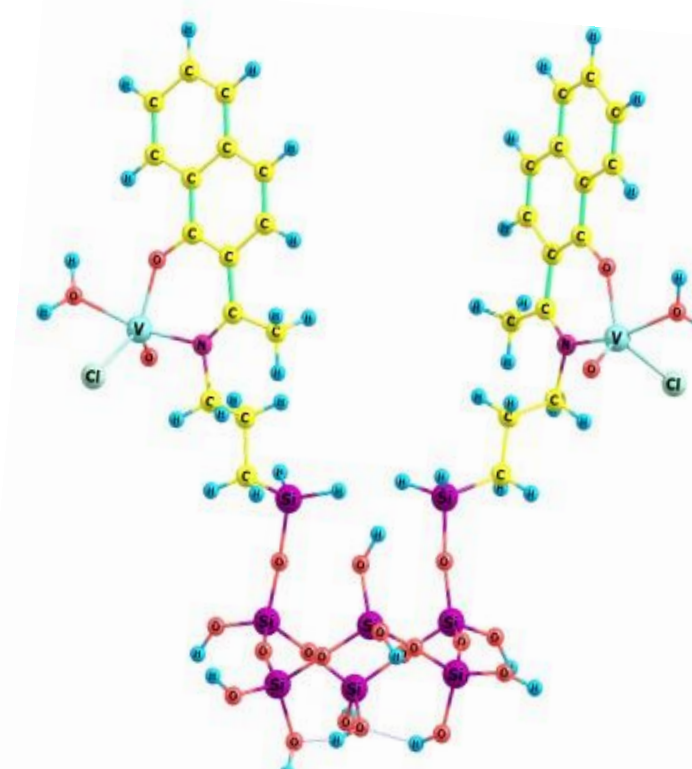
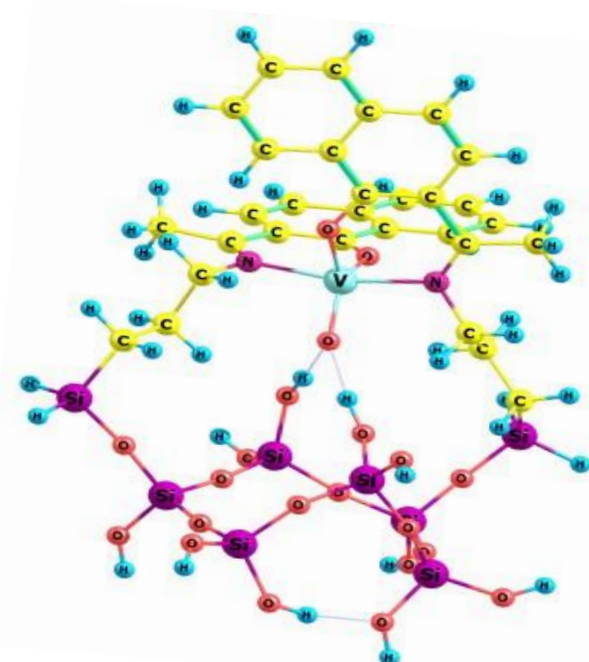
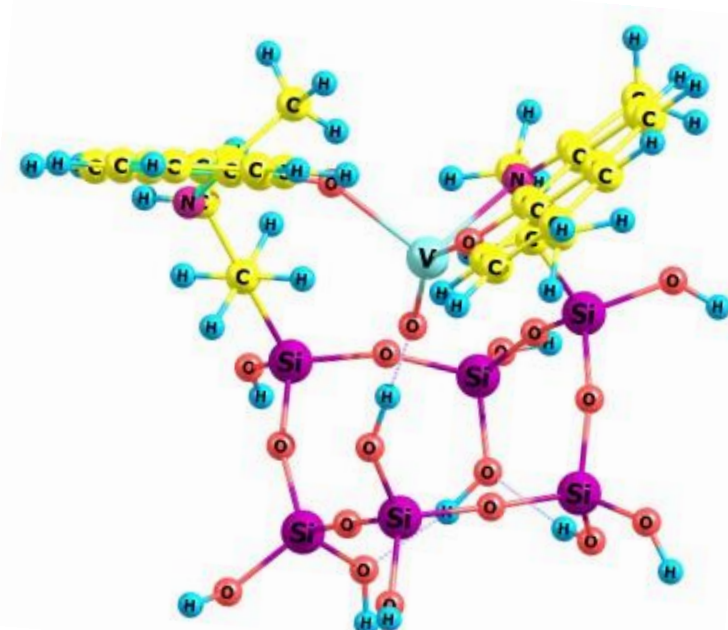
The restricted Hartree-Fock method for open shells (ROHF) with the SBKJC basis set has been used to establish the structure of model vanadyl complexes with sterically hindered Schiff Base ligand – N-propyl-1'-hydroxy-2'-acetonafonimin, immobilized on silica surface. All calculations were performed using the GAMESS program (Firefly version 8.2.0). A cyclosiloxane ring consisting of six silicon-oxygen tetrahedra in an armchair conformation was chosen as the surface model. This model corresponds to the spatial structure of β -cristobalite, the motifs of which are characteristic of amorphous silica surface. Three types of structures are considered: (1) 2 ligands are connected to silica surface by $-(\text{CH}_2)_3-$ spacers and surround one vanadyl ion (total formula $\text{VSi}_6\text{C}_{30}\text{N}_2\text{H}_{40}\text{O}_{19}$); (2) 2 ligands are connected to the silica surface by $-(\text{CH}_2)_3\text{-SiH}_2\text{-O-}$ spacers and surround one vanadyl ion, (total formula $\text{VSi}_8\text{C}_{30}\text{N}_2\text{H}_{44}\text{O}_{21}$); (3) 2 ligands are connected to silica surface by spacers of the composition $-(\text{CH}_2)_3\text{-SiH}_2\text{-O-}$ and surround two distant vanadyl ions (there is only one ligand, a water molecule and a chloride ion near each ion), (total formula $\text{V}_2\text{Si}_8\text{C}_{30}\text{N}_2\text{H}_{48}\text{O}_{24}\text{Cl}_2$). Models (1) and (2) correspond to a doublet state, whereas model (3) could be in singlet or triplet states.

Results and discussion

From the calculations results, it follows that model (1) could have at least 3 conformations, of which the most energetically favorable is the hypothetical structure where the hydrogen atom is transferred from the silanol group to the oxygen atom of the vanadyl group, thereby reducing the vanadyl ion to vanadium(III). Since the formation of vanadium(III) is not observed in the experiment, the formation of such structures is unlikely. The remaining conformations are very strained and therefore have significantly higher energy. Extending the spacer in model (2) reduces stress. Two possible conformations were found as a result of calculations. The more favorable one is characterized by the presence of two hydrogen bonds between the vanadyl oxygen atom and silanol groups, and the less favorable one is characterized by one hydrogen bond between the oxygen atom of one of the ligands and the silanol group. Structure (3) could be formed with a sufficient amount of vanadyl ions in the reaction mixture. From the results of the calculations, it follows that such structure is characterized by the triplet state, in which the vanadium atoms are very far from each other, while the singlet lies significantly higher on the energy scale, and the vanadium atoms cannot get closer due to steric hindrances.

Conclusions

It follows from the above mentioned that the stable structures of vanadyl complexes could have different compositions depending on the presence of an excess of vanadyl salt in the reaction mixture, and the complexes cannot be in the singlet state due to steric hindrances. However, when the surface is densely filled with ligands, trigonal bipyramidal bischelatate complexes with the orientation of the vanadyl group towards or away from the surface are most likely. The first from them has the lower total energy.



Model 1

Model 2

Model 3

Optimal structures of the models for considered grafted complexes