

Nanostructured surfaces

Formation of molybdena species on the surface of SiO₂ nanoparticles

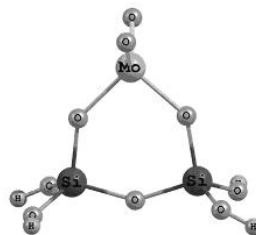
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Dispersed molybdena based pigments are promising alternatives to the conventional toxic hexavalent chromium analogues used with environmental restriction for metal corrosion protection. Novel monolayer molybdena pigments of “core-shell” structure with SiO₂ core ($D_{\text{core}} = 7$ nm) attracts special attention. The present work was focused at characterisation of model surface molybdena nanostructures in such SiO₂ core pigments.

Quantum chemical simulation of the reaction between MoO₃ and SiO₂ surface was carried out by *ab initio* examination of respective cluster models. All calculations were carried out by non-empirical spin-restricted Hartree-Fock method within SCF MO LCAO approximation by means of GAMESS program package (version Firefly 8.0.0 by A.Granovsky). In order to shorten the computing time, the valent basis set SBKJC (Stevens-Basch-Krauss-Jasien-Cundari) was used which needs application of respective effective core potential.

The interaction of MoO₃ molecules with cluster model for SiO₂ surface (H₆Si₂O₇) has been considered. The model for MoO₃ structure on SiO₂ surface included a MoO₃ tetrahedron with two covalent bonds with SiO₂ surface ($E_{\text{total}} = -218.46236$ Hartree). The calculated value of the Gibbs free energy for the reaction between MoO₃ and H₆Si₂O₇ cluster appeared to be negative in 300–1100 K temperature interval and the process of interaction between MoO₃ and silica surface is energetically favourable.



$$E_{\text{total}} = -218.46236 \text{ Hartree}$$

The thermal treatment of mechanical blends of MoO₃ and SiO₂ support (Mo content within 1–20 Mo wt. %) at 400 °C resulted in the appearance of strong absorption in the range of 200–400 nm because of the ligand to metal $O^{2-} \rightarrow Mo^{6+}$ charge transfer in Mo⁶⁺ surface oxo-species. The different coordination environments of Mo⁶⁺ ions in surface oxo-species, namely Mo⁶⁺ in tetrahedral (T_d) and octahedral (O_h) coordination were distinguished of which the band at 230 nm is common for both Mo⁶⁺ (T_d) and Mo⁶⁺ (O_h) whereas absorption in 280–295 nm region is connected only with Mo⁶⁺ (O_h).