



Effect of the adsorption of 3d transition metals on the oxidation of the Si(001) surface

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Motivation

We report the results of a comparative theoretical study of the interaction of molecular oxygen with the silicon surface coated by submonolayer 3d transition metal (M - Ti, Cr, Mn) films. Investigating the effect of transition metal adsorption on surface oxidation is important for technological applications because such systems can be used in conventional silicon technologies. Recently, the promoting effect of adsorbed metals on the silicon surface oxidation was found [1,2].

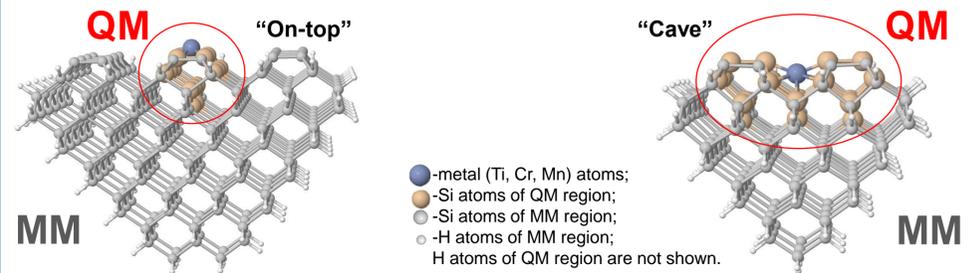
This work aims to compare the oxidation of the M/Si(001) systems (M - Ti, Cr, Mn). Our investigation includes determining the adsorption energies of single and multiple O atoms on the M/Si(001) surface for different spin states of the system and simulation of the step-by-step interaction of the M/Si(001) with the O₂ molecules.

References:

- [1] I.P. Koval', Yu.A. Len', M.G. Nakhodkin, et al., Ukr. J. Phys. 60 (2015) 46.
[2] K.O. Butariev, I.F. Koval', Yu.A. Len', et al., J. Nano-Electron. Phys. 5 (2013) 01025.

Methodology

The simulations were carried out using a hybrid quantum mechanical-molecular mechanical (QM/MM) method and embedded clusters - SIMOMM (Surface Integrated Molecular Orbital Molecular Mechanics) with GAMESS/TINKER software.

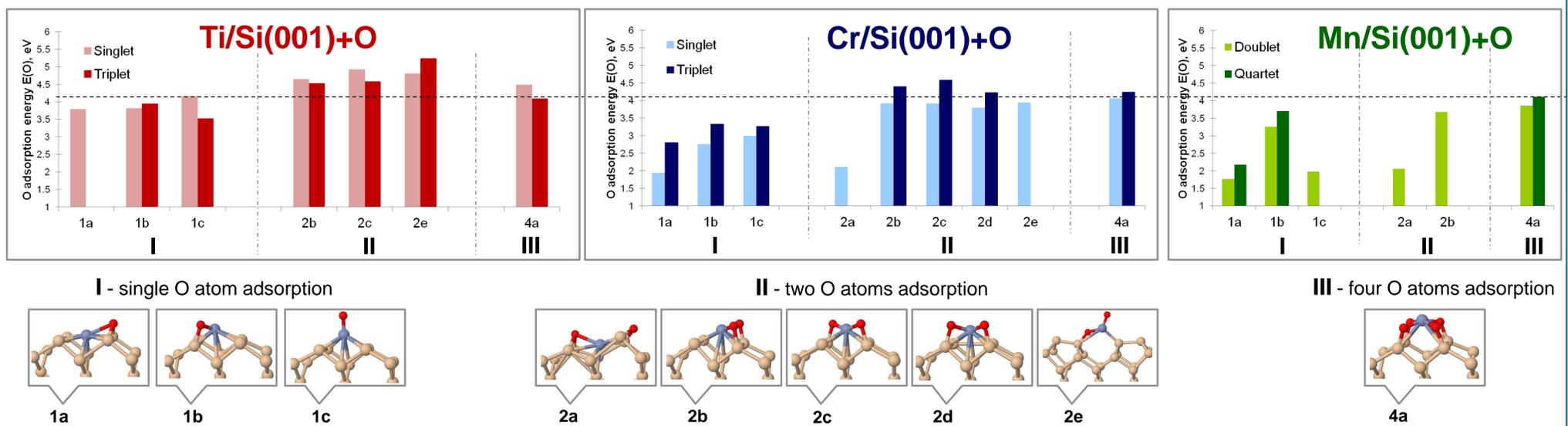


QM: B3LYP/6-31G**, M₁Si₁₅H₁₆
MM: MM3 Force Field, M₁Si₂₈₉H₁₂₀

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Two of the most favourable adsorption sites ("on-top" and "cave") of transition metal atoms on the Si(001) surface were obtained. The site on top of surface dimer rows on the Si(001) is energetically preferred.

Adsorption of single and multiple oxygen atoms on the M/Si(001) surface

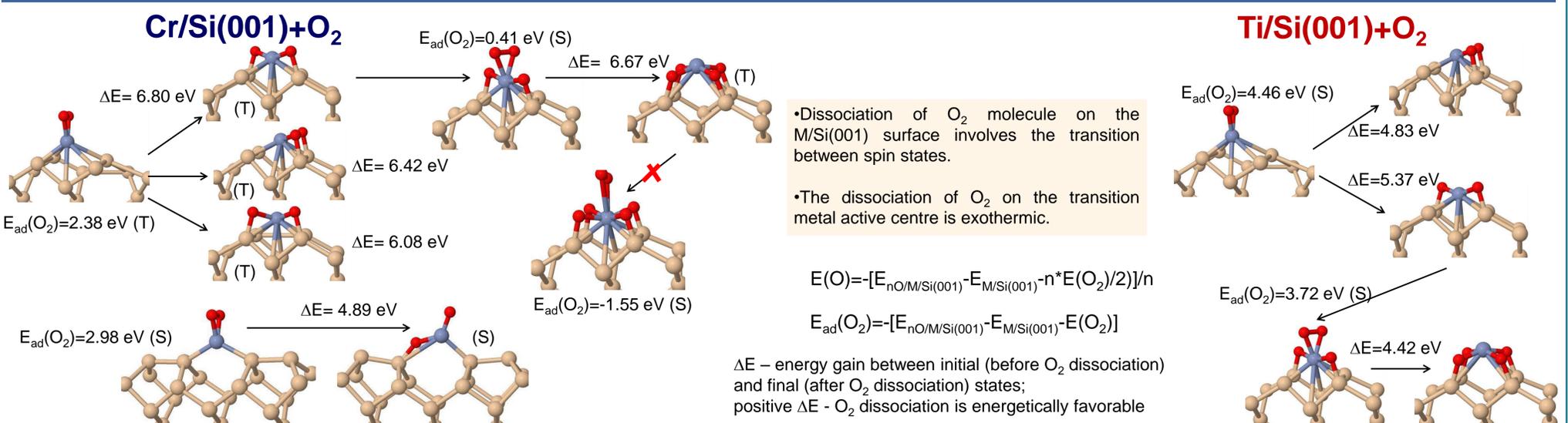


•The stationary states in the Ti/Si(001)+O system are mainly singlet in contrast to the stationary states in the Cr/Si(001)+O system. Quartet and doublet states were obtained for the ground states in the Mn/Si(001)+O system.

•The formation of the M-O-Si bridge structures is more energetically favourable for Cr/Si(001) and Mn/Si(001) systems.

•The adsorption of an oxygen atom near an already adsorbed oxygen atom is energetically favoured than elsewhere in an unoxidized area of Ti/Si(001) and Cr/Si(001) surfaces. Thus, the growth of oxides on Ti/Si(001) and Cr/Si(001) surfaces in the form of islets is energetically favourable. The growth of oxides on Mn/Si(001) had been predicted to be more uniform than on Ti/Si(001) and Cr/Si(001) surfaces.

Dissociation of O₂ molecule



Conclusion

- Oxygen atoms tend to bind with 3d transition metal atoms (M - Ti, Cr, Mn) adsorbed on the Si(001) surface, in agreement with previous experimental results (AES, EELS) [1,2]. Therefore, the transition metal atoms are active centres for the M/Si(001) surface oxidation.
- The adsorption of neighbouring O atoms is energetically preferable to non-interacting inserts of single O atoms. Consequently, at the initial stage of oxidation of the M/Si(001) surfaces, the island growth of oxides is energetically preferable to uniform growth.
- The stationary states in the Ti/Si(001)+O system are singlet in contrast to the stationary states in the Cr/Si(001)+O and Mn/Si(001)+O systems.
- Both atomic and molecular oxygen bind more tightly with Ti atoms adsorbed on the Si(001) surface than with Cr or Mn atoms.
- Dissociation of O₂ molecule on the M/Si(001) surface involves the transition between different spin states.
- The dissociation of molecular oxygen on the metal active centres on the M/Si(001) surface is exothermic.