A density functional pseudopotential and Monte Carlo investigation of the thermodynamics of the adsorption of Pt on ZrO_2

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Metal oxide interfaces, in particular, platinum on zirconia are promising systems for many technological applications such as sensors, solid oxide fuel cells and catalysis. One way of investigating the metal-oxide interaction is by adsorbing Pt atoms on the oxide in order to mimic flat metal layers. For zirconia we have chosen its cubic an tetragonal modifications, i.e the (001) and (110) surfaces of cubic and (001) surface of tetragonal zirconia to calculate the adsorption energies at different coverages. In addition, the calculated adsorption energy parameters were used to determine the statistical thermodynamic properties, i.e the Monte Carlo technique (was used to calculate the adsorption isotherms for 150, 370 and 500 K. The first phase of our calculations were performed using Vienna ab-initio Simulate Package (VASP) which employs density functional theory and expand the electronic structure using plane wave basis set. The calculations were performed in the framework of density functional (DFT) pseudopotential theory using the Projector Augmented Wave (PAW) (as well as the Perdew and Wang 91 (PW91) and PBE approximation to the exchange-correlation functional. We used a converged (2x2) 4 slab model of ZrO_2, corresponding to a height of 10 Å, with a kinetic energy cuttoff of 550 eV. For each surface system the first two slab of ZrO_2 are relaxed. We make the adsorption of Pt atoms in different non-equivalents symmetry sites for each surface (with a coverage of 0.5) in order to calculate adsorption energies for each site. We subsequently used these these adsorption energies and a Monte Carlo (Grand-canonical ensemble) in order to calculate the adsorption isotherm for the tetragonal (001) termination. We use a square lattice with 1000x1000 sites where the average of the properties were taken every 105 Monte Carlo steps in order to ensure that the properties where calculated in an equilibrium configuration. We observe from Fig. 1, that for T=150K, regarding the formation of different adsorption phases, the first step belongs to the bridge2 site phase. Increasing the chemical potential, another phase appears which correspond to the ontop1 site. Saturation, i.e all the remaining ontop2 sites are occupied, is achieved when there is a large pressure in the system. In the saturation region the coverage is 1. When temperature is increased the curves become flat for all pressures. This happens because for high temperatures all the sites are quite similar and the Pt atoms are able to occupy most of the sites.

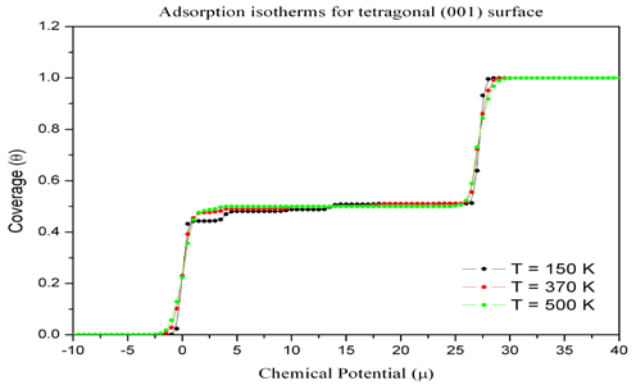

Fig. 1 Adsorption isotherm for the tetragonal surface (001) of ZrO_2

[1] G. Kresse and J. Furthmüller, Comput. Mat. Sci. 6, 15-60 (1996).