

Theoretical description of ammonia adsorption at different low-indices V₂O₅ surfaces.

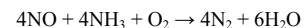
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Introduction

Vanadia-based catalysts are of a great importance in an abatement of NO_x from waste gases. Their resistance to SO₂ poisoning also causes the interest of using these catalysts in industry. The reduction of nitrogen oxides proceeds in the presence of ammonia according to the equation:



The mechanism of the simple reaction, in which nitrogen oxide is reduced to pure N₂ and water, although investigated extensively by both experimentalist as well as theoreticians is still unclear. In last few years some attempts to understand this process were done and as results Eley-Rideal, Langmuir-Hinschelwood and the hybrid of Eley-Rideal and Langmuir-Hinschelwood type of mechanisms were proposed to be responsible for SCR reactions. In all mechanisms the presence of pre-adsorbed NH₃ species in form of NH₄⁺ ions is postulated as obligatory to reduce NO_x species, however, the identification of active centers that are involved is still a matter of controversy.

The crystallites of V₂O₅ catalysts may exhibit different types of faces: surfaces built of chemically saturated atoms (the (010) netplane) and those built of unsaturated cations and anions ((001) and (100) netplanes) (see Fig.1). All surfaces show different behavior in catalytic reactions by performing a complex multi-step operation on the reacting molecule through activation of some of the bonds within reactant and hindering those interactions, which could result in unwanted product. In these study, the adsorption of ammonia on all Brønsted acidic centers present at low-indices V₂O₅ surfaces is discussed.

Methods

The calculations are carried out by means of *ab initio* DFT within the RPBE exchange-correlation functional. As models the local clusters are used, which are cut off from all three surfaces with assumed existing hydroxyl groups as models for Brønsted acidic sites. The electronic structure is described by atomic charges gained from Mulliken population analyses and by Mayer bond indices. Adsorption energies were calculated from the total energies of appropriate systems

Results

The results of the performed calculations indicate spontaneous stabilization of NH₃ at any surface hydroxyl groups with the adsorption energy in the range of 0.8 to 1.3 eV. Ammonia becomes adsorbed in various geometries and the reaction proceeds according to different

mechanism depending on the type of oxygen forming OH group and on the type of surface. In all cases the significant role of hydrogen O...H...N bonds of different strengths is found. The NH₃ becomes in some cases mono, bi- or tri-furcated to the surface and the OH groups can play the role of H-donors or H-acceptors.

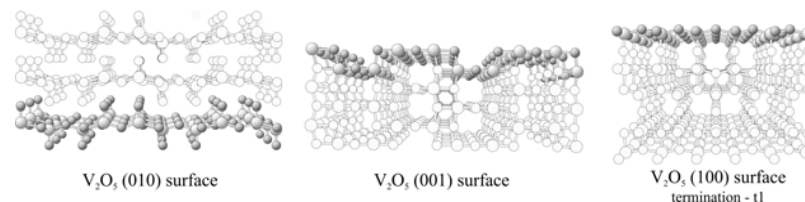


Figure 1. V₂O₅ surfaces – (010), (001) and (100) with termination t1 (the most stable termination).