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Theoretical Study of Cleavage Surfaces and Water Adsorption on B-Nb_2O_5

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Abstract: Niobium oxide (Nb_2O_5) based systems play an important role in many catalytic processes, mainly when high acidity and water tolerance are needed in the processes. In this report, the structural and energetic results of the B phase cleavage surface study of niobia (B-Nb_2O_5) are presented. The cleavage and surface energies have been calculated indicating that the (010)-2 surface is the most favored. The order of stability for the relaxed surfaces is: (010)-2>(110)>(100)>(010)-1>(001). The Projected Density of States (PDOS) indicates that the Nb atom is the preferred adsorption site (Lewis acidic sites). Water molecules adsorb molecularly at the surface. However, the dissociative adsorption of water is just slightly higher in energy. Therefore, one can argue that at the surface both mechanisms (molecular and dissociative) may be present.

1. Introduction

Nb_2O_5 is also known as niobia, exists in many polymorphic forms depending on the starting materials, pressure and temperature. According to the phase diagrams of Nb_2O_5, their crystallographic phases are classified in three groups: low-temperature (~700 to 900 K), medium-temperature (~900 to 1200 K) and high-temperature (~1223 K).[1] Among the applications of niobia, there is a growing interest in niobium containing materials with potential applications in heterogeneous catalysis, mainly when high acidity and water tolerance are needed in the processes.[2] The phase chosen for the study of water adsorption was B-Nb_2O_5,[3,4] a phase of medium-temperature. There is no report concerning the favorable cleavage plane of B-Nb_2O_5. In the present work the different cleavage surfaces and the different water adsorption mechanism were investigated. Various geometric configurations were examined for the water adsorption. For the dissociative mechanism for the water adsorption, it was assumed that the dissociated hydrogen atom remains chemisorbed on the surface oxygen atom. All the calculations were carried out by using the Quantum Espresso program package (pWscf).[5] The calculations were performed using PBE XC functional, with an energy cutoff of 60 Ry and at the gamma (Γ) point. A vacuum layer of 15 Å normal to the surface was used.

2. Results and discussion

The proposed cleavage planes were that with low Miller index. The five different surfaces were labeled as: (100), (010)-1, (010)-2, (001), (110) and (111), (Fig.1a). Considerable relaxation occurred on all surfaces (up to 63% reduction in energy). The (010)-2 surface is more likely to cleave (1.37 J m^{-2}) among the proposed plans. The

order of stability for the relaxed surfaces is: (010)-2 > (110) > (100) > (010)-1 > (001). Fig.1b shows the (010)-2 optimized surface. The niobium cations are all unsaturated with coordination number equal to five (Nb^{5c}) and oxygen ions have coordination number equal to two forming a bridge with the niobium atoms. In addition there are two types of oxygen atoms, those that are more exposed (O^{up}) and those that are less exposed (O^{down}).

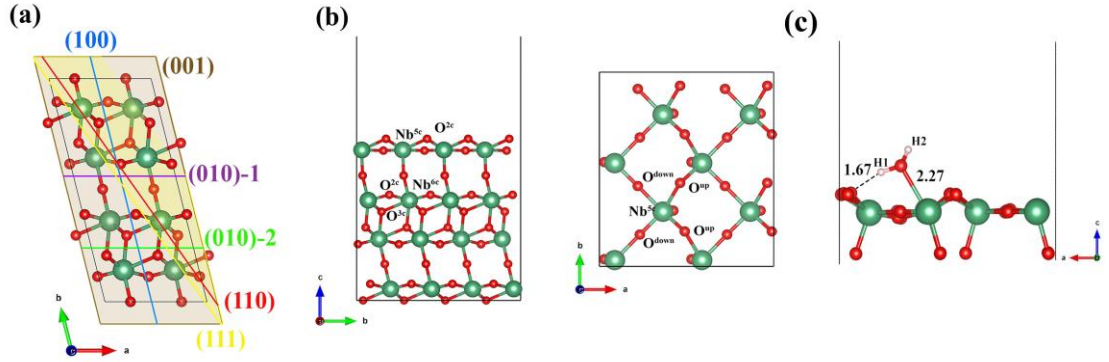

Figure 1: (a) Optimized structure of the B-Nb_2O_5 bulk, and the six different cleavage planes, (b) optimized structure of B-Nb_2O_5 (010)-2 surface and (c) water molecule adsorbed on (010)-2 surface.

The calculation of PDOS was performed and showed that the Nb atom is the preferred adsorption site (Lewis acidic sites). The adsorption of a water molecule on the optimized (010)-2 surface was carried out in several configurations. The most favorable adsorption mechanism is molecularly with adsorption energy of 25.6 kcal mol^{-1}. The adsorption occurs on the niobium adsorption sites (Fig.2c). In addition, one of the hydrogen of the water molecule (OH1) is pointing toward one oxygen atom, O^{up}, forming a hydrogen bond.

3. Conclusions

In summary, the cleavage of the B-Nb_2O_5 along the (010)-2 direction is preferred. The calculations of adsorption energies showed that the molecular adsorption on (010)-2 surface is more favorable than the dissociative. The PDOS of (010)-2 surface showed that the conduction band is composed mainly of *d* orbitals of the niobium atoms. This fact explains the preference for adsorption on the niobium atom, the most electrophilic center. The dissociative mechanism leads to structures that are, at least, 4.4 kcal mol^{-1} less favorable than the molecular adsorption. This study suggests that the two states compete in energy and, therefore, the authors believe two configurations are expected to coexist on B-Nb_2O_5 (010) surface. The effect of the full coverage of water molecules on the surface has been investigated and will be discussed in details.

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