



Theoretical study of the influence of cation vacancies on the catalytic properties of vanadium antimonate

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ARTICLE INFO

Article history:

Received 21 August 2007

Accepted 16 March 2008

Available online 22 March 2008

Keywords:

Oxidation catalysts
Vanadium antimonate
Oxygen vacancies
Antimonium

ABSTRACT

We have theoretically studied the influence of antimony and vanadium cation vacancies in the electronic structure and reactivity of vanadium antimonate, using molecular orbital methods. From the analysis of the electronic properties of the VSbO₄ crystal structure, we can infer that both antimony and vanadium vacancies increase the oxidation state of closer V cations. This would indicate that, in the rutile-type VSbO₄ phase the Sb and V cations defects stabilize the V in a higher oxidation state (V⁴⁺). Calculations of the adsorption energy for different toluene adsorption geometries on the VSbO₄(1 1 0) surface have also been performed. The oxidation state of Sb, V and O atoms and the overlap population of metal–oxygen bonds have been evaluated. Our results indicate that the cation defects influence in the toluene adsorption reactions is slight. We have computed different alternatives for the reoxidation of the VSbO₄(1 1 0) surface active sites which were reduced during the oxygenated products formation. These calculations indicate that the V cations in higher oxidation state (V⁴⁺) are the species, which preferentially incorporate lattice oxygen to the reduced Sb cations. Thus, the cation defects would stabilize the V⁴⁺ species in the VSbO₄ structure, determining its ability to provide lattice oxygen as a reactant.

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1. Introduction

The vanadium oxide based catalysts, pure or mixed with other metallic oxides, have been used in numerous industrial processes. So they have acquired great commercial and technological importance. Particularly, the Sb–V based oxides emerge as efficient catalysts for the propane to acrylonitrile ammoxidation reaction [1].

The catalytic performance of the vanadium antimonate during toluene partial oxidation reactions has been evaluated in our laboratory. It has been found that benzaldehyde production is a possible alternative, although its yield is still commercially low [2]. In this sense, our quantum-chemical calculations have shown that toluene partial oxidation reactions over VSbO₄(1 1 0) surface involve several reaction steps: hydrocarbon molecule adsorption, hydrogen abstraction, oxygen insertion in the hydrocarbon molecule (the catalyst surface becomes reduced from this step), and surface reoxidation [3,4].

During toluene parallel adsorption over Sb–V surface sites, the aromatic ring interaction with a vanadium cation facilitates the electronic transference from the methyl group to the solid,

weakening one of the C_{methyl}–H bonds. This weakening involves the participation of an Sb cation, and leads to the C–H bond breaking. The toluene dehydrogenation process finally ends with the formation of a benzyl-type species. After that, the step involving oxygen insertion in the hydrocarbon fragment proceeds with the formation of the aldehyde precursor species. It has also been observed that an oxygen surface atom two-coordinated with antimony (OSb₂□; where the symbol □ indicates a cation vacancy) takes part in the benzaldehyde formation.

Finally the benzyl-type species desorption leaves an oxygen vacancy on the VSbO₄(1 1 0) surface, which requires a fast solid reoxidation step to keep active the catalyst.

The theoretical calculation also shows that carbon oxides formation occurs because of toluene interactions with the V–V moieties on the catalyst surface. Thus, the performance of the VSbO₄ rutile-type phase as a good catalyst for toluene partial oxidation reactions would be explained by the fact that Sb cations interpose between the V–O moieties, breaking V–O–V chains in its structure. Thus, to obtain high benzaldehyde yields it is important an adequate balance of these functionalities in the catalyst formulation.

It has been reported that the VSbO₄ phase has a rutile-type structure with the antimony cation presents in the oxidation state Sb⁵⁺; while vanadium is formally V³⁺ [5]. It has also been concluded, based in X-ray and neutron diffraction measurements,

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that the calcination of equimolar Sb_2O_3 and V_2O_5 mixtures in air produces a cation deficient rutile-type structure [6,7]. The refinement of this structure by the Rietveld method, indicates that the metal site in $\text{V}_{0.92}\text{Sb}_{0.92}\square_{0.16}\text{O}_4$ contains a mixture of 46% of Sb, 46% of V and 8% of cation vacancies (\square). The sum of metal bonds valences indicates an antimony oxidation state of (+5), and vanadium oxidation states of (+3) and (+4). From these studies, the composition $\text{V}_{0.28}{}^{3+}\text{V}_{0.64}{}^{4+}\text{Sb}_{0.92}{}^{5+}\square_{0.16}\text{O}_4$ has been assigned to the vanadium antimonate rutile phase.

In the rutile structure, each metal atom coordinates with six oxygen atoms, while each oxygen atom coordinates with three metal atoms (coordination 6:3). Thus, the oxygen local surrounding is formed by three metal positions occupied by a selection of Sb^{5+} , V^{3+} and V^{4+} , and a vacancy.

From the calculations of the valences sum of the oxygen bonds to different metal cations and vacancies, Hansen et al. have reported that the O atoms connected with cation vacancies are sub-bonded preferentially to antimony [6]. Thus, it has been established the following order of preference for an oxygen atom associated with a cation metal defect: $\text{OSb}_2\square$, $\text{OSbV}\square$, $\text{OV}_2\square$.

It is known that the chemistry of transition metal oxides strongly depends on the quantity and properties of the surface defects and that these imperfections can also influence the chemical adsorption reactions and the catalytic properties. The comparison of the structural, surface and reactivity characteristics for different samples of rutile Sb–V oxides, in the propane to acrylonitrile ammoxidation reaction, has allowed to establish a correlation between the non-stoichiometry of the catalyst and its reactivity [8].

Thus, the study of cation vacancies influence in the catalytic properties of the $\text{VSbO}_4(1\ 1\ 0)$ surface active centers emerges as an interesting challenge. Taking into account that the catalytic properties of the transition metal oxides strongly depend on their ability to provide oxygen as a reactant, it is also important the elucidation of the involved mechanisms in the catalyst surface reduction and reoxidation steps.

In this work, we have performed quantum-chemical calculations to study the influence of the Sb and V cation vacancies in the electronic structure of the rutile-type vanadium antimonate phase. We have also studied the influence of these defects on toluene– $\text{VSbO}_4(1\ 1\ 0)$ interactions, and particularly on the catalyst reduction and reoxidation mechanisms.

2. Solid and surface active sites models

We have studied the influence of the Sb and V cation vacancies on the catalytic properties of vanadium antimonate. For this purpose we have evaluated the electronic properties of the crystal structure and the toluene adsorption energy for different hydrocarbon interactions on the catalyst surface, for a stoichiometric and non-stoichiometric VSbO_4 structures.

In order to give an adequate theoretical description of the vanadium antimonate structure and reactivity we require reasonable models for:

- (i) The oxide bulk: we used a three-dimensional (3D) structure, which represents the VSbO_4 and $\text{V}_{0.92}\text{Sb}_{0.92}\square_{0.16}\text{O}_4$ catalysts.
- (ii) The oxide surface: we used a cluster, which represents the $\text{VSbO}_4(1\ 1\ 0)$ surface. In our calculation we have selected the (1 1 0) surface, because it is the most stable among the rutile-type transition metal oxides surfaces.
- (iii) The toluene– $\text{VSbO}_4(1\ 1\ 0)$ interactions: this model takes into account the hydrocarbon perpendicular and parallel approaches to the catalyst surface active sites.
- (iv) The catalyst surface active sites reduction and reoxidation processes.

We also require an adequate theoretical treatment for the toluene–catalyst interactions described before. In the following section we describe the models used in this work.

2.1. The bulk model

- (i) The stoichiometric bulk model: the vanadium antimonate VSbO_4 three-dimensional structure (3D) has been modeled with a rutile-type tetragonal super-cell. This super-cell was built taking into account the experimental parameters reported for the vanadium antimonate in Ref. [9]: $a = b = 4.636\ \text{\AA}$ and $c' = 3c$ ($c = 3.048\ \text{\AA}$).
- (ii) The non-stoichiometric bulk model: we also used an extended super-cell ($a = b = 4.636\ \text{\AA}$, and $c'' = 4c'$) to obtain a model representative of the $\text{V}_{0.92}\text{Sb}_{0.92}\square_{0.16}\text{O}_4$ structure. This model reproduces not only the crystal rutile-type structure but also the most probable metal–oxygen combinations, which have been reported in Refs. [6,7].

2.2. The surface model

- (i) The stoichiometric $\text{VSbO}_4(1\ 1\ 0)$ surface has been modeled with the $\text{V}_{30}\text{Sb}_{35}\text{O}_{163}$ cluster, which has 228 atoms (see Fig. 1). The charge of this cluster is (–61). This electron excess has been assigned to keep the oxygen anions in the oxidation state O^{2-} .
- (ii) The non-stoichiometric $\text{VSbO}_4(1\ 1\ 0)$ -NE surface has been modeled with the same cluster, but in this case we introduced point defects (see Fig. 2). The clusters obtained after the introduction of a V or Sb vacancy resulted in ($\text{V}_{29}\text{Sb}_{35}\text{O}_{163}$) and ($\text{V}_{30}\text{Sb}_{34}\text{O}_{163}$) compositions, respectively.

2.3. The toluene– $\text{VSbO}_4(1\ 1\ 0)$ interactions model

The toluene–catalyst interactions have been studied, approaching the hydrocarbon molecule to the catalyst surface with the aromatic ring perpendicular or parallel to the different active sites exposed in the (1 1 0) surface: O, Sb and V. Thus, we studied two main toluene interactions on the vanadium antimonate (1 1 0) surface:

- (i) Perpendicular adsorption, where the methyl group (CH_3) can face O, Sb or V sites.
- (ii) Parallel adsorption, where the methyl (CH_3) and phenyl (C_6H_5) groups can interact with the O–O, Sb–Sb, Sb–V or V–V sites. In Fig. 3, we show the schemes for toluene parallel adsorption on Sb–Sb (left), Sb–V (center) and V–V (right) sites.

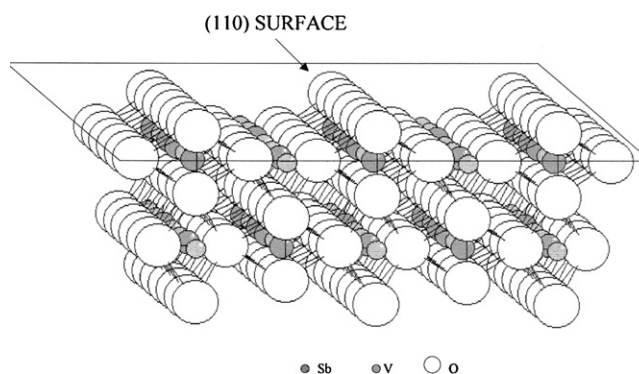


Fig. 1. The cluster $\text{V}_{30}\text{Sb}_{35}\text{O}_{163}$, which represents the stoichiometric $\text{VSbO}_4(1\ 1\ 0)$ surface.

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