1 Propylene Adsorption On a Nonstoichiometric VSbO₄(110) Surface2 Hernán Seitz,[†] Carla Luna,[†] Alfredo Juan,^{*,†} Graciela Brizuela,[†] and Beatriz Irigoyen[‡]3 [†]Departamento de Física & IFISUR (UNS-CONICET), Av. Alem 1253, 8000 Bahía Blanca, Argentina4 [‡]Departamento de Ingeniería Química, Universidad de Buenos Aires, Pabellón de Industrias. Ciudad Universitaria, C1428EGA

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ABSTRACT: Density functional theory calculations were performed to investigate propylene adsorption on the nonstoichiometric VSbO₄(110) surface. V and Sb sites and two extreme ways of propylene approximation to the surface were considered. Among the six computed configurations, the most stable geometry corresponds to a parallel approach on the surface on a Sb site. This geometry makes possible a simultaneous adsorption of NH₃ on a V site during the ammoxidation reaction to acrylonitrile. Sb(5s and 5p orbitals) interactions with C(2p) from double bond C=C were found, and no interactions with H atoms of CH₃ and CH₂ were produced.

1. INTRODUCTION

The selective oxidation process is one of the most important technologies in the present day chemical industry. During the past six decades, one of the most important applications of these reactions has been the functionalization of olefins and aromatic hydrocarbons to produce monomers of great interest to the polymer industry.

These processes are essential in today's society, because they produce about 25% of the most important organic compounds used in the industrial production of consumer goods.^{1–15} Such compounds include ethylene oxide, propylene oxide, acrylonitrile, acrylic acid, acrolein, methacrylic acid, maleic anhydride, phthalic anhydride, 1,2-dichloroethane, cyclohexanol, cyclohexanone, phenol, and MTBE (methyl *tert*-butyl ether). In most cases, the processes are carried out in a heterogeneous phase, although a considerable number of processes still are made using homogeneous catalysis processes.

Acrylonitrile is one of the main chemicals, with a worldwide production of about 6 million tons in 2003. Some of the major applications of this compound are the production of acrylic, thermoplastic fibers (ABS, SAN), rubber, adiponitrile, and special polymers. The use of acrylonitrile also extends to the automotive, pharmaceutical, textile, electronics, telecommunications, paper, mineral processing, water treatment, and appliance industries, among others. About 90% of the globally produced acrylonitrile is obtained by ammoxidation propylene:

The reaction is highly exothermic ($\Delta H = -123$ kcal/mol), and it is carried out in the gaseous phase over a suitable catalyst, at temperatures of 300–500 °C and pressures that range from 1.5 to 3 bar, in reactors with fixed or fluidized bed, and adequate cooling. The catalyst employed depends on the technology used. The first catalyst commercially used was Bi₂O₃·MoO₃.¹⁶ Since then, many chemical formulations have been patented. At present, the most widely used catalysts contain molybdenum or antimony oxide mixed with other transition metals (Fe, Ni, Co, V).^{1,11,17–20}

The reaction rate is sufficiently high so as to achieve an almost complete conversion step, for the stoichiometric ratio of reactants. Furthermore, the high selectivity toward acrylonitrile still remains a challenge. Currently, the best catalysts achieve acrylonitrile yields of about 80–82%.

In recent years, the use of propane has been proposed as a feedstock, instead of propylene. This is motivated by the lower cost of propane (which is 15–20% less expensive than propylene). The conversion of ethane and propane into useful chemical compounds has the potential to transform the

Received: January 3, 2015

Revised: February 8, 2015

Figure 1. (a) Trirutile type tetragonal VSbO₄ structure. (b) VSbO₄(110) nonstoichiometric surface.

chemical industry.²¹ That is why, in the last 20 years, the synthesis of new materials to be used as catalysts in the partial oxidation of alkanes has been intensively studied, both from a fundamental and from an applied point of view. For this purpose, those materials capable of incorporating different active centers in appropriate environments, at the same time, would be required to carry out the selective oxidation process of alkanes in a single step. In particular, the partial oxidation of hydrocarbons, such as light alkanes, C₂, and C₃, is of great interest due to the low cost and wide availability of such raw material for the production of value-added chemical intermediates.

The ammoxidation of propylene into acrylonitrile is globally described in eq 1, but it involves a complex reaction mechanism. Knowledge of the reaction mechanism is important in the design process. First, only the methyl groups with activated olefins can undergo ammoxidation reactions into nitriles. Otherwise, oxidative dehydrogenation is the production method preferred. For example, among C₄ isomers, only isobutene can produce methacrylic nitrile. Second, the role of ammonia (NH₃ chemisorbed species) is essential in the reaction, as it begins the catalytic cycle instead of propylene.

The adsorption of propylene has been explored through experimental and theoretical techniques, on several catalytic surfaces: Pt/alumina,²² Ag (111),²³ zeolites,²⁴ and catalyst Mo–V–Te–Nb–O.²⁵ The use of different materials aims at both the production of value added products by a specific reaction and the purification of products (propylene production requires the separation of uncured propylene for maximum purity). Recently, the use of various catalysts has been reported for the purpose of environmental remediation (removal of volatile organic compounds, including propylene).²⁶ That is why the adsorption of propylene remains a very topical issue and has become the subject matter of various studies.

Semiempirical and DFT theoretical studies have been performed for the VSbO₄ system.^{27–31} In addition, the adsorption of NH₃ on this solid has been analyzed.^{32,33} On the contrary, there are no extensive DFT studies about propylene adsorption on a cation-deficient VSbO₄(110) surface. The objective of this work is to compute the adsorption energy and geometry, and to analyze the changes in the electronic structure of both the propylene molecule and the solid after adsorption.

2. THEORETICAL METHODS AND MODELS

In this paper, we reported quantum chemical calculations performed by using self-consistent DFT theory as implemented in the Vienna Ab-Initio Simulation Package (VASP).^{34–36} Kohn–Sham equations were solved by using the generalized gradient approximation (GGA) with exchange–correlation functional PW91.³⁷ Core electrons were represented by the projector augmented wave (PAW) method.³⁸ Valence electrons V(4s², 3d³), Sb(5s², 5p³), O(2s², 2p⁴), C(2s², 2p²), and H(1s) were described by plane waves. A truncation energy value of 408 eV was used, and the tolerance for the total free energy change was set to 10^{−3} eV. For geometry optimizations and total energy calculations, we applied the Gaussian smearing scheme with a smearing width of 0.2 eV and we used spin polarization in all cores. The integrals over the Brillouin zone were sampled with a 2 × 3 × 1 *k*-point grid according to the Monkhorst–Pack scheme.³⁹

The calculations were performed using a surface supercell formed by 22 V cations, 22 Sb cations, and 96 oxygen atoms derived from the trirutile-type conventional cell (Figure 1a), which represents the geometric optimization of the VSbO₄(110) surface with 16% cationic vacancies.²⁷ There are relevant experimental reasons to choose this exposed surface and this vacancy concentration. The VSbO₄ oxide was

synthesized by Birchall and Sleight, who reported a rutile-type crystal structure.⁴⁰ V and Sb cations would be present in this phase as V^{3+} and Sb^{5+} , respectively. The calcination of equimolar Sb_2O_3 and V_2O_5 mixtures in air produces a cation-deficient $VSbO_4$ solid.^{41,42} The Rietveld method was applied to XRD data of this structure and indicates the $V_{0.28}^{3+}V_{0.64}^{4+}Sb_{0.92}^{5+}\square_{0.16}O_4$ formula with 16% cationic defects ($\square$ represents vacancies), leading to the presence of vanadium cations in the oxidation state V^{4+} .⁴¹ 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 us to establish a correlation between the nonstoichiometry of the catalyst and its reactivity.⁴³ Metal-cation defects also facilitate the formation of redox couples V^{4+}/V^{3+} , enhancing the catalytic activity of antimonate in hydrocarbon selective oxidation reactions.^{31,44} In a previous study, we modeled the 16% cation-defective $VSbO_4$ introducing two metal cations (Sb and V) obtaining the $V_{0.292}^{3+}V_{0.625}^{4+}Sb_{0.916}^{5+}\square_{0.167}O_4^{2-}$ composition for the non-stoichiometric slab.²⁷ This composition is in good agreement with that corresponding to the experimental $V_{0.28}^{3+}V_{0.64}^{4+}Sb_{0.92}^{5+}\square_{0.16}O_4$ formula.⁴¹

In our calculations, we have selected the (110) plane because it appears to be one of the most stable crystal faces of rutile oxides⁴⁵ and results from breaking the smallest number of M–O bonds. This plane has been recently used to represent the active surface of vanadium antimonate catalysts and calculate ammonia adsorption,³³ and light hydrocarbon ammoxidation and oxidative dehydrogenation processes,³¹ uncovering the involved reaction mechanism. Noteworthy, the 16% cation-deficient $VSbO_4(110)$ surface model exhibits an oxygen extra plane and contains the most probable Sb–V combinations reported by Hansen et al.⁴¹ Moreover many V sites are separated by Sb ions in agreement with the principle of site isolation, an important concept developed by Callahan and Grasselli to improve the selectivity of catalytic oxidation reactions.⁴⁶ The $VSbO_4(110)$ catalytic surface was modeled with a slab of $13.316 \times 9.286 \times 28 \text{ \AA}^3$, which consisted of 12 atomic layers and a vacuum space of about 15 Å, to avoid interactions between successive images (Figure 1b). For all energy calculations, the atomic positions of V, Sb, and O ions located in the six uppermost layers of the slab were allowed to fully relax, whereas those of the six lowermost layer ions were kept fixed to their bulk positions.

The atom projected density of states (PDOS) was calculated by projecting one-electron states onto spherical harmonic atomic orbitals centered on atomic sites. A qualitative study of the bonding between different atoms was also performed using the overlap population (OP) concept,⁴⁷ as implemented in the SIESTA code.⁴⁸ We adopted the generalized gradient approximation (GGA) to treat the electronic exchange and correlation effects, as described by Perdew–Burke–Ernzerhof.⁴⁹ In all procedures, a split-valence double- ζ basis set of localized numerical atomic orbitals was used, including polarization functions (DZP), with an energy shift of 50 meV and a split norm of 0.15.⁵⁰ We used a $2 \times 3 \times 1$ Monkhorst–Pack k -point set and an energy cutoff of 150 Ry for the grid integration was chosen to represent the charge density.⁵¹ Standard norm-conserving Troullier–Martins pseudopotentials,⁵² in their fully separable form,⁵³ were used to describe the electron–ion interaction. The following electronic states were considered as valence in the pseudopotential description

of the atoms: Sb, $5s^25p^3$; V, $3d^34s^2$; O, $2s^22p^4$; C, $2s^22p^2$; H, 1s. Spin-polarized calculations were performed in all cases.

The propylene molecule consists of three carbon atoms, linked by two binding types: a single bond (C_1-C_2) and one double ($C_2=C_3$) (Figure 2). The atoms have the following

Figure 2. Propylene molecule. The carbon and hydrogen atoms are shown in gray and blue, respectively.

tags: in the propylene molecule C_1 represents the terminal carbon atom of the methyl group (CH_3), C_2 represents the secondary atom linked to the methyl group, and C_3 corresponds to the remaining terminal carbon atom, which forms the methylene group ($=CH_2$). The C_2 and C_3 atoms present sp^2 hybridization, so the $C_1-C_2=C_3$ bond should submit an angle $\beta = 120^\circ$. The real value of the angle is slightly distorted by the imbalance between adjacent CH_2 and CH_3 groups, with $\beta = 124^\circ 43'$.

Several geometric configurations were considered (Table 1), depending on the type of approach for the propylene molecule.

Table 1. Geometric Configurations for Adsorption of Propylene on a Nonstoichiometric $VSbO_4(110)$ Surface

Configuration	Geometry	Figure
1	$H_3C_1 \cdots V$ Perpendicular	3a
2	$H_2C_3 \cdots V$ Perpendicular	3b
3	$H_3C_1 \cdots Sb$ Perpendicular	4a
4	$H_2C_3 \cdots Sb$ Perpendicular	4b
5	$H_2C_3 \cdots C_2H$ Parallel	5a
6	$H_2C_3 \cdots C_2H$ Parallel	5b

Configurations 1–4 represent the perpendicular adsorption of the propylene molecule on a nonstoichiometric $VSbO_4(110)$ surface, to V and Sb surface atoms, via terminal carbon atoms C_1 and C_3 , whereas configurations 5 and 6 correspond to a parallel approach to the surface via the double bond $C_2=C_3$, to V and Sb atoms, respectively. A study using similar approaches was performed by Rojas et al.³¹ Additional calculations changing the approximation and azimuthal angle and the rotation of the molecule do not improve the lower adsorption energy found in configuration 6 (see next).

The adsorption energy ($\Delta E_{\text{ads,propylene}}$) was calculated as the difference between the $V_{0.92}Sb_{0.92}\square_{0.16}O_4(110)$ surface energy with an adsorbed propylene molecule ($E_{\text{propylene/surf}}$) and the energies of the clean surface (E_{surf}) and propylene molecule in vacuum ($E_{\text{propylene}}$):

$$\Delta E_{\text{ads propylene}} = E_{\text{propylene/surf}} - E_{\text{surf}} - E_{\text{propylene}}$$

3. RESULTS AND DISCUSSION

Figures 2–4 show the optimized geometries with their corresponding values of adsorption energy.

Figure 3. Perpendicular adsorption of propylene on a VSbO₄(110) nonstoichiometric surface. V site, (a) C₁–V geometry and (b) C₃–V geometry.

In the case of propylene perpendicular adsorption on V (Figure 3), a higher stability is observed in configuration 2 (Figure 3b), being 1.32 eV more stable than configuration 1. For configuration 2, there is a distortion in the surface. The Sb atom on which propylene is adsorbed (exposed cation-chain Sb–Sb–V–Sb) is removed from the surface and located just over 1 Å toward the propylene molecule. This could be a clue for the α -H abstraction belonging to the C₁ methyl group. However, none of the three H–C₁ bonds presents any bond weakening, as measured by changes in their overlap population (from 0.91 to 0.90). Moreover, angle β shows no difference compared to isolated propylene in configuration 1, although a slight increase of 0.4% is observed in configuration 2.

Comparing configurations 3 and 4 (Figure 4) shows the latter is more stable (Figure 4b, 1.22 eV lower energy value). In both configurations, the surface shows a little distortion, but in configuration 4 the propylene molecule rotates around the ($\bar{1}10$) axis, showing a tendency to parallel adsorption. The propylene molecule presents a slight increase in the angle β of about 0.5% in configuration 4, whereas the hydrogen atoms of the (C–H₁) methyl group slightly weaken their bonds.

Configurations 5 and 6 parallel to the surface and on V and Sb atoms, respectively (Figure 5) are quite different from each other. Configuration 6 is the most stable of all adsorption geometries considered (1–6), with an adsorption energy value of –1.6 eV, showing, as in configuration 2, a distortion of the surface Sb atom, which moves 0.78 Å away from the surface toward the propylene molecule. In this case, the distance between the α -hydrogen atoms (C₁ methyl group) and the Sb site is shorter than the distance present in configuration 2. The

Figure 4. Perpendicular adsorption of propylene on a VSbO₄ (110) nonstoichiometric surface. Sb site, (a) C₁–Sb geometry and (b) C₃–Sb geometry.

Figure 5. Parallel adsorption of propylene on a VSbO₄ (110) nonstoichiometric surface, (a) V site (C₂–V–C₃ geometry) and (b) Sb site (C₂–Sb–C₃ geometry).

hydrogen atoms of the methyl group show no bond weakening with the C₁ atom, following the same trend seen in configuration 2. The angle β shows an increase of 0.5%. Configuration 6 (propylene parallel adsorption on the Sb atom) is the most stable, on the basis of the results, assuming that the double bond, C₂=C₃, where the π orbitals are along

the (110) axis, should be the more reactive. Additionally, this configuration makes NH_3 adsorption feasible on a nearby V site, the preferential adsorption site of NH_3 .⁵⁴ This makes the simultaneous adsorption of propylene and NH_3 possible, which is a required condition for the ammoxidation reaction to produce acrylonitrile. Moreover, it is important to note that in configuration 6 (Figure 5b) the molecule approximation occurs in such a way that the above-mentioned formation of the allyl complex would be possible.

In configurations 2 and 6 (Figures 3b and 5b) a similar behavior is observed for the surface Sb atom, which tends to move away from the surface toward the propylene molecule. This Sb atom may have a role, acting as cation Sb^{3+} , in the activation and abstraction of $\alpha\text{-H}$, as reported in the literature, in the adsorption of propylene on mixed oxides¹¹ and toluene on VSbO_4 .³⁰

Adsorption geometries are displayed in Table 2. The values obtained are in good agreement with those reported by Rojas et al.³¹

Table 2. Adsorption Energy, Bond Distances, and Angles Calculated for Propylene Adsorption Configurations on the $\text{VSbO}_4(110)$ Nonstoichiometric Surface

configuration	$\text{C}_1\text{---C}_2\text{=C}_3$ angle (β)	E_{ads} (eV)	interaction	distance (Å)
1	$124^\circ 51'$	−0.25	$\text{C}_1\text{---V}$	3.48
2	$125^\circ 13'$	−1.57	$\text{C}_1\text{---V}$	3.56
3	$124^\circ 32'$	−0.3	$\text{C}_1\text{---Sb}$	3.30
4	$125^\circ 20'$	−1.52	$\text{C}_3\text{---Sb}$	3.63
5	$124^\circ 55'$	−1.08	$\text{C}_3\text{---V}$	3.22
6	$125^\circ 18'$	−1.6	$\text{C}_3\text{---Sb}$	2.85
			$\text{C}_2\text{---Sb}$	3.23

Adsorption energy values indicate that the perpendicular adsorption of propylene by a methyl group results in physical adsorptions on both V and Sb cations (configurations 1 and 3), whereas the perpendicular adsorption through the methylene group produces more stable adsorption on V and Sb (configurations 2 and 4). Meanwhile, the parallel adsorption of propylene on V and Sb sites, exposing the double bond $\text{C}=\text{C}$, give place in both cases to the most stable adsorptions (configurations 5 and 6), the double bond interaction with the Sb site (configuration 6) being the most important one. The adsorption energy values obtained are lower than those reported in the literature for the same system.³¹ These changes can be attributed to the $\text{VSbO}_4(110)$ surface model, which shows a different distribution of cationic vacancies. Additional calculations are needed to elucidate the trends in adsorption energies at other propylene coverages. Similar V–Sb sites must be considered and the fact that neighboring sites present different energies and different cation combinations. Unfortunately, there is no surface science characterization of propylene adsorbed on VSbO_4 at different coverages. TPD experiments of propylene adsorption on $\text{V}_2\text{O}_3(0001)/\text{Au}(111)$ surfaces⁵⁵ show a shift to lower desorption temperatures from coverages from 0.1 to 1 langmuir. DFT and Monte Carlo calculations of temperature dependence of coverage for ethylene desorption on Pd and Pt (111) study predict the same shift in TPD peak.⁵⁶

3.1. Electronic Structure of Propylene before and after Adsorption. DOS curves for propylene are shown in Figure 6. The density of states of the isolated propylene (Figure

Figure 6. Total DOS of propylene: (a) isolated, (b) perpendicular adsorption on $\text{VSbO}_4(110)$ (configuration 2), and (c) perpendicular adsorption on $\text{VSbO}_4(110)$ (configuration 6).

6a) shows peaks located at fixed energy levels, as expected for a molecule. At lower energy values, $\text{C}(2s)$ states dominate, with small contributions from $\text{C}(2p)$ and $\text{H}(1s)$ orbitals, showing peaks at −13.5 and +11 eV. Starting from −8 eV, the trend reverses and several peaks appear from $\text{C}(2p)$ and $\text{H}(1s)$ orbitals. Particularly, from −6 to −2 eV, $\text{C}(2p)\text{---H}(1s)$ interactions forming the C–H bond can be noted. Near the Fermi level, a peak from a nonhybridized $\text{C}(2p)$ state appears, which does not interact with the $\text{H}(1s)$ orbital and forms part of the $\text{C}_2\text{=C}_3$ bond. In the most stable configurations found, 2 and 6 (Figure 6b,c, respectively), the results show less intense peaks of density. The composition of orbitals is similar to that observed in an isolated propylene molecule. Furthermore, in both configurations, the peaks move to slightly lower energy values, thus indicating stabilization after adsorption. In configuration 6, this shift is more evident, and the band at −9 eV is slightly broadened. Also, the incipient appearance of an additional band around −2 eV with $\text{C}(2p)$ character can be observed.

3.2. Electronic Structure of $\text{VSbO}_4(110)$ after Propylene Adsorption. Figure 7 shows the total DOS curves for configurations 2 (Figure 7a) and 6 (Figure 7b), including the contributions of the adsorbed propylene. Both configurations have similar features and a composition that shows bands located at different values of energy. Between −21 and −17 eV, the contributions observed correspond to $\text{Sb}(5s)$ and $\text{Sb}(5p)$ states, with a significant contribution from the $\text{V}(3d)$ orbital at the top of the band. The small band located at −14 eV comes primarily from $\text{C}(2s)$ states, with small contributions

Figure 7. Total DOS for adsorption of propylene on VSbO₄(110): (a) perpendicular to V site (configuration 2) and (b) parallel to Sb site (configuration 6).

3.3. Electronic Structure of Perpendicular Adsorption of Propylene on V. In the perpendicular adsorption of propylene on V (configuration 2), the main interaction is produced between the atom H₃, belonging to the methylene group of C₃, and the nearest surface Sb atom. Particularly, this interaction occurs between Sb(5p) and H₃(1s) orbitals, at energy values of −5 and −3 eV (Figure 8). However, although

Figure 8. DOS of selected atomic orbitals of Sb and H₃. Adsorption of propylene, perpendicular to V (configuration 2).

minor, Sb(5s)–H₃(1s) contributions can be observed at −8 eV. There are no important H₃–V and C₃–V interactions. The C₃–H₃ bond does not suffer any distortion, because the Sb–H₃ interaction is small compared to the C–H bond of the methylene group.

Moreover, the geometric distortion of the surface Sb atom is a result of the decrease in the bond strength between Sb and the oxygen atom of the next lower layer; the orbital overlap decreases more than 90%, stretching the bond from 2.15 to 3.54 Å.

Finally, no interaction between any of the hydrogen atoms of the methyl group with the Sb atom was observed.

3.4. Electronic Structure of the Parallel Adsorption of Propylene on Sb. The Sb/C₂/C₃ environment is shown in Figure 9, with the Sb–Sb–C₂ and C₃ distances.

Figure 9. Sb/C₂/C₃ environment for parallel propylene adsorption on the VSbO₄(110) surface (Sb site), configuration 6.

from H(1s) and C(2p) orbitals. Between −12 and +8 eV, Sb(5s) states dominate. Within this energy range, C(2s) and H(1s) orbitals are located at the bottom and at the top of this band (−11.5 and −8.5 eV), whereas C(2p) states are present only at the top of the band. Between −8 eV and the Fermi level, O(2p), C(2p), H(1s), and V(3d) states appear, with small contributions from Sb(5p) states and even smaller from Sb(5s) states. At this energy range, the fact that V(3d) and O(2p) bands are broader than Sb(5s) and Sb(5p) bands indicates that the strength of the Sb–O bond, in terms of orbital overlap, would be, on average, lower than the strength of the V–O bond (OP average values are 0.36 and 0.5 for Sb–O and V–O bonds, respectively). This would explain the distortion suffered by the surface Sb atom near the propylene adsorption site in both configurations.

At −1 eV, configuration 2 shows a peak corresponding to C(2p) states (Figure 7a). The same peak is shown in configuration 6 (Figure 7b), but unlike configuration 2, the peak is due to C(2p) states mixed with Sb(5s) and Sb(5p) orbitals, and it would indicate the C₃–Sb interaction that is responsible for the adsorption of propylene on the Sb site.

In both configurations, at higher values than the Fermi level, Sb(5p), C(2p), and O(2p) states appear; also, and to a lesser extent, Sb(5s) orbitals can be observed.

It is worth mentioning that the peaks present at −14, −11.5, and −8 eV (Figure 7a) and −14.5, −12, and −8.5 eV (Figure 7b) are solely from propylene contributions (C(2s), C(2p), and H(1s) states). These peaks are not present in the DOS of the VSbO₄(110) surface.

In the parallel adsorption of propylene on Sb, the main interaction observed corresponds to C_3 –Sb. This interaction is stronger than the Sb– H_3 interaction in configuration 2, an order of magnitude greater in terms of orbital overlap. The energy difference between configurations 2 and 6 may be a direct consequence of this fact.

The DOS of $C_3(2p)$, Sb(5s), and Sb(5p) orbitals are displayed in Figure 10. There are $C_3(2p)$ –Sb(5p) interactions

Figure 10. DOS of C3 and Sb selected atomic orbitals. Adsorption of propylene, parallel to Sb (configuration 6).

at different energy values (−6.5, −5.5, −4, −3.5, and −2 eV). In addition, there is a peak at −1 eV, which represents the interaction between the nonhybridized $C_3(2p)$ orbital with Sb(5s) and Sb(5p) orbitals. The reactivity of the double bond by delocalized π electrons, represented by $C_3(2p)$ orbitals, can be one of the reasons configuration 6 is energetically more stable than configuration 2. The C_3 –Sb interaction does not cause significant distortions in the C_3 – H_3 bond of the hydrocarbon.

No interaction between the C_2 and the Sb atom was observed. In addition, hydrogen atoms from both the methylene and the methyl groups do not interact with the Sb atom.

In configuration 6, the distortion of the Sb atom is caused by reducing the orbital overlap of the Sb atom with the oxygen atom of the layer that is immediately below it. However, the geometric distortion is less than that present in the adsorption perpendicular (configuration 2). The values of the Sb–O overlap decrease almost 90%, whereas the bond distance increases from 3.18 to 2.15 Å.

4. CONCLUSIONS

In this work, the study of the adsorption of propylene on a nonstoichiometric $VSbO_4(110)$ surface was presented. Two types of surface sites (V and Sb), and two ways of approximation to the surface (perpendicular and parallel) were considered. Adsorption energy calculations, bond distances, and geometry optimization were performed. The results indicate that the preferential adsorption geometry corresponds to the parallel approach to the surface, on the Sb site, which turned out to be the most energetically stable one, and presented lower bond propylene–Sb distances. This geometry also allows for the simultaneous adsorption of NH_3 on the V site (the site of preferential adsorption of NH_3), for subsequent ammoxidation of propylene to acrylonitrile.

The calculations of the density of states (DOS) allowed exploring major interactions between propylene and surface atoms for the most stable geometries.

In the case of perpendicular adsorption on the V site, it is observed that the greatest interaction occurs between the 1s orbital of the H atom of the methylene group of propylene and the Sb(5p) orbitals. The C–H bond of methylene group is not distorted because the Sb–H interaction is small (the distance H_3 –Sb is 3.10 Å).

In the case of parallel adsorption on the Sb site, interactions between 2p orbitals of the terminal C atom (that is part of the double bond $C=C$) with Sb (5s) and Sb (5p) states are observed. No interaction was found between the H atoms of the CH_3 and CH_2 groups with the surface Sb atom (the H_3 –Sb distance is 3.07 Å).

In both configurations, a geometric distortion in a superficial Sb atom is present, although in parallel adsorption the distortion is smaller, with a C_3 –Sb orbital overlap being 1 order of magnitude higher than in the case of H_3 –Sb overlapping in perpendicular adsorption. This would cause a lower interaction energy.

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The authors gratefully acknowledge the financial support of Universidad de Buenos Aires (UBACYT-20020110200044), Universidad Nacional del Sur-SGCyT, Comisión de Investigaciones Científicas (CIC-BA) and ANPCyT (PICT-2011-1312 and 2012-2186). H.S. thanks CONICET for a postdoctoral fellowship. C.R.L., A.J., and G.B. are members of CONICET.

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