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Methanol decomposition on the β-Ga_2O_3 (1 0 0) surface: A DFT approach

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Abstract

Density functional theory (DFT) cluster model calculations on methanol reactions on the β-Ga_2O_3 (1 0 0) surface have been realized. β-Ga_2O_3 structure has tetrahedral and octahedral ions and the results of gallia–methanol interaction are different depending on the local surface chemical composition. The surface without oxygen vacancies is very reactive and produces the methanol molecule decomposition. The unsaturated surface oxygen atoms strongly oxidize the methanol molecule. CO_2 and H_2O molecules are produced when methanol reacts with a free oxygen vacancy surface on octahedral gallium sites. On the other hand, H_2CO is found after the reaction of this molecule with a free O vacancy surface on tetrahedral gallium sites. A weak interaction between the remaining CO_2 molecule and the oxide surface was found, being this molecule easy to desorb. Otherwise, H_2CO has a stronger surface bond and it could suffer a later oxidation.

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Keywords: DFT; Gallia surface; Methanol decomposition; Catalysis

1. Introduction

Oxides show acidic and basic sites in the surface; thus, making the formulation of catalytic reaction pathways for a large variety of chemical reactions possible, including hydrogenations, dehydrogenations and oxidations [1]. The mechanism of the selective catalytic production of hydrogen over the Pd–Ga_2O_3 system was recently investigated by Collins et al. [2]. They studied the superficial intermediates during the methanol decomposition over pure β-Ga_2O_3 and Pd/β-Ga_2O_3 by means of temperature programmed surface reaction experiments, followed by in situ Fourier transform infrared spectroscopy (FTIR) [2]. CO and CO_2 are produced by non-stoichiometric transformation of formates, leading to the release of atomic hydrogen on the surface of the oxide, as detected by the Ga–H stretching infrared band, and surface anion vacancies. It was concluded that relevant carbonaceous species during the methanol dehydrogenation are bonded to the gallium oxide surface.

An experimental and theoretical study of methanol adsorption on β-Ga_2O_3 was recently published [3]. In this work, it was shown that the interaction of methanol molecule with the gallia surface strongly depends on the local surface chemical environment. The β-Ga_2O_3 (1 0 0) surface without oxygen vacancies is very reactive and produces the oxidative decomposition of the methanol molecule. On the other hand, the methanol molecule is non-dissociatively adsorbed by means of two ionic bonds on the gallia surface with oxygen vacancies. Three neighbouring oxygen vacancies on tetrahedral gallium sites produce the dissociation of the methanol molecule and the formation of a bridge bond between two surface gallium atoms and the methoxy group.

Whereas our previous work [3] was focused to treat the adsorption of a methanol molecule on gallia surface sites with oxygen vacancies, in the present one, a detailed analysis of the decomposition mechanisms of the same molecule on non-defective surface sites was performed. For that purpose, density functional theory (DFT) quantum-mechanical calculations

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were carried out for methanol decomposition over selected clusters of (1 0 0) β-Ga_2O_3 by using Gaussian basis set and the B3LYP method.

2. Computational method

The adsorption of methanol molecule on a perfect (1 0 0) face of β-Ga_2O_3 was modeled. Tetrahedral (Ga^{IV}) and octahedral (Ga^{VI}) gallium atoms, as it was previously mentioned, are present in the β-Ga_2O_3 crystalline structure. The (1 0 0) plane is the more frequent and stable surface produced upon cleavage of β-Ga_2O_3 and it is the normal growth axis of single crystals [4]. This plane consists only of oxygen atoms.

Cluster models have been widely used to study the adsorption and reaction of molecules with oxide surfaces and there is a large body of evidence that they properly describe the physics of local surface processes [5–7].

Two different clusters were considered, $Ga_{14}O_{21}$ and $Ga_{12}O_{18}$. In the first case, a central oxygen atom linked to tetrahedral gallium atoms of the first layer is exposed. On the other hand, the second cluster has a central oxygen atom linked to an octahedral gallium atom. They are designed as T0 and O0, respectively. In addition to these central oxygen atoms, their first oxygen neighbours of both symmetries were included. In this way, the co-adsorption of different species produced after the dissociation is allowed. These clusters are fully stoichiometric. As the β-Ga_2O_3 is a non-ionic oxide, the effects due to the Madelung Potencial should not be relevant. These clusters are the same as those used in Ref. [3] and their atomic structure corresponds to the perfect lattice of bulk β-Ga_2O_3.

All the calculations reported in this work were performed using the gradient-corrected Density Functional Theory (DFT) [8] and the hybrid exchange-correlation functional B3LYP [9,10].

The oxide O atoms were described with a locally dense 6-31G basis set and the Ga atoms were treated with a small core ECP (see Ref. [3]). The methanol molecule was treated at the all-electron level using the 6-31G** basis set.

The adsorption energies were computed as the difference between the energy of the methanol/gallia system and the sum of the energies of the separated fragments.

The methanol molecule was fully geometrically optimized. The oxide oxygen atoms involved in the surface reaction were also included in the optimization. The vibrational frequencies were computed by determining the second derivatives of the total energy with respect to the internal coordinates.

The charge distributions in the adsorption complexes were calculated using the approach proposed by Reed et al. [11]. All the calculations were performed using the Gaussian-03 program package [12].

3. Results and discussion

As it was previously shown [3], the surfaces without oxygen vacancies, i.e., T0 and O0, are more reactive than the others. The methanol molecule oxidizes on these surfaces, forming H_2CO, in the first case and CO_2 and H_2O in the second one. In both situations, surface hydroxyls are also produced (see Figs. 1d and 2f). These molecules remain linked with the surface oxide. The E_{ads} obtained for the T0 and O0 sites are very large: 5.74 eV and

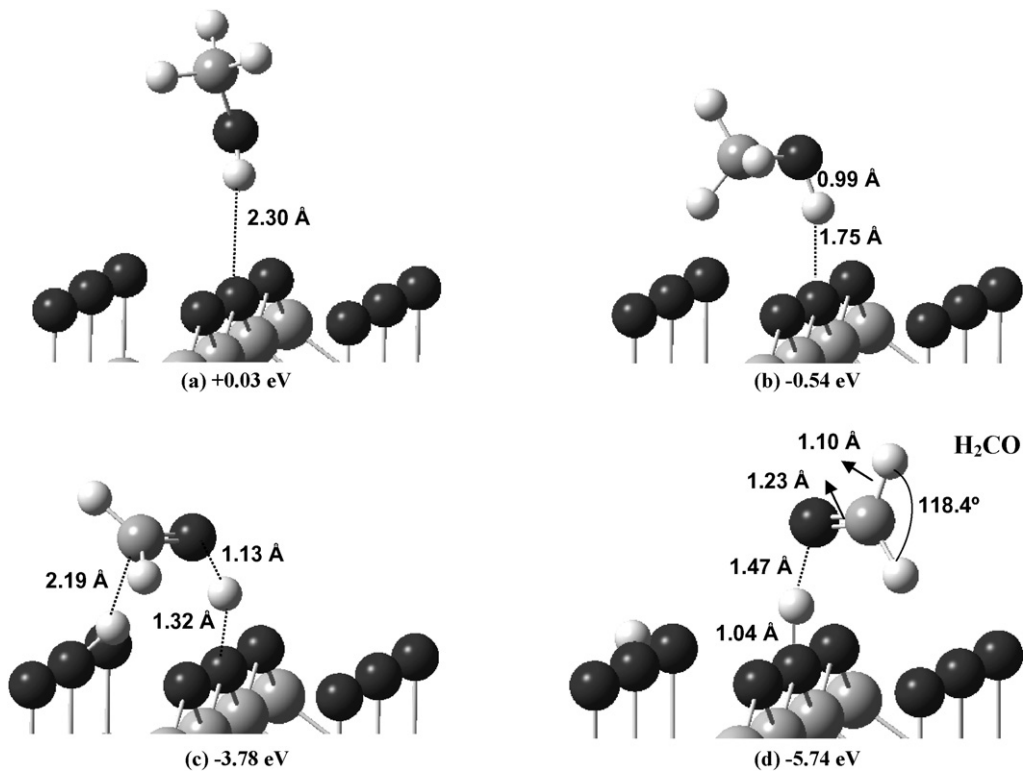

Fig. 1. Steps of oxidation process of the methanol molecule on T0 site. Adsorption energy values for each configuration are also shown.

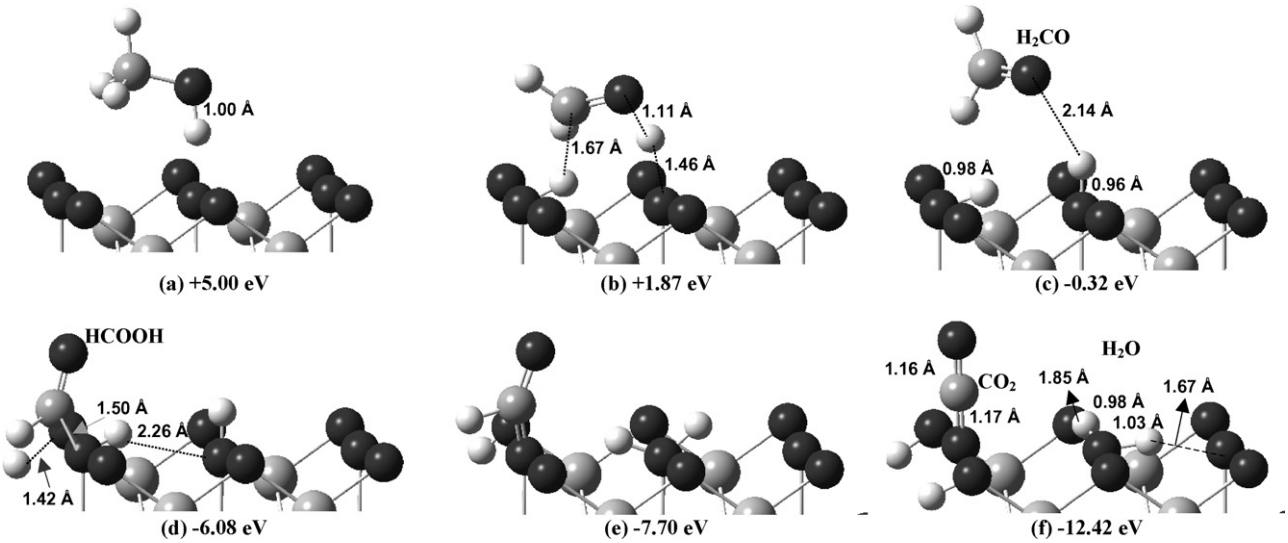

Fig. 2. Steps of oxidation process of the methanol molecule on O0 site. Adsorption energy values for each configuration are also shown.

12.42 eV, respectively. These results indicate that the (1 0 0) gallia surface without vacancies is especially reactive, leading to the total decomposition of the methanol molecule.

Next, the evolution of the oxidative reaction processes that the methanol molecule undergoes on the oxide surface without oxygen vacancies are analyzed. Fig. 1 shows the methanol molecule decomposition sequence on a T0 site (Ga^{IV}). To begin with, the methanol molecule was located near the surface with the optimized free molecule configuration (Fig. 1a). The molecule rotates and the methyl group approaches the surface (Fig. 1b). Then, the methyl group deforms losing a hydrogen atom which binds to a neighboring octahedral oxygen (Fig. 1c), therefore, the carbon changes its hybridization from sp^3 to sp^2. Later, the alcoholic hydrogen is attracted by the central oxygen (T0 site) to generate a second surface hydroxyl; thus, acetaldehyde remains at the surface bound by a hydrogen bond (1.47 Å) through the last OH generated group (Fig. 1d). For the sake of comparison, the adsorption energies of each of the intermediate species in this reaction sequence were calculated. The E_{ads} values are shown under each configuration. Notice that they show monotonically decreasing behavior. It is obvious that we are dealing with an exothermic reaction without activation barrier; besides, an important energy decrease in step c can be observed where the surface oxygen anion takes a methylic hydrogen.

Fig. 2 shows the methanol decomposition reaction on an O0 site (Ga^{VI}). Just as before, the calculation is begun by locating the methanol molecule with the optimized free geometrical configuration (Fig. 2a). Then, the methyl group also leans towards the surface and it is a methylic hydrogen the first one to stick to the surface (Fig. 2b). Immediately after to the breaking of the CH bond and the formation of the first surface hydroxyl, the C atom changes its hybridization from sp^3 to sp^2. Then, the OH alcoholic bond is broken and the second surface hydroxyl is formed (Fig. 2c). The remaining surface formaldehyde, H_2CO, is not stable and the oxidation process continues. Other hydrogen atom is taken by an oxide oxygen anion neighboring to the oxygen which had previously captured the first hydrogen to generate acetic acid (HCOOH), (Fig. 2d). At the same time, the acetic acid formed gives the acid hydrogen to neighboring oxygen generating a water molecule (Fig. 2e). Finally, the acetate group gives the last hydrogen to other neighboring oxygen anion remaining CO_2 on the surface (Fig. 2f). The adsorption energy decreases monotonically, but in this case, a significant activation barrier (~5 eV) appears when the methanol molecule is brought nearer the surface. Nevertheless, it must be considered only as an upper limit. Notice that the initial geometry was selected imposing severe constraints (fixed molecule-surface distance, molecule orientation and free molecule parameters) that lead to an unstable situation. The minimization of internal molecule coordinates would produce a decrease of this activation barrier.

It must be emphasized that CO_2 and H_2O molecules involve oxide oxygen anions and its release from the surface would generate two oxygen vacancies. CO_2 molecule is weakly surface bound with O–Ga bond of ~2.3 Å. The water-surface link is also weak with O–Ga bond of ~2.1 Å, however, in this case the hydrogen bonds formed with neighboring oxygen anions (see Fig. 2f) make a stronger link with the substrate than the CO_2 one.

The main geometrical parameters of methanol decomposition products on T0 and O0 sites were compared with those for the isolated molecules (see Figs. 1d and 2f). In the case of the T0 site, the H_2CO molecule linked with the surface shows a shorter C–H bond (1.10 Å) and a longer C–O bond (1.23 Å) than the corresponding bonds of the free molecule (1.11 Å and 1.21 Å, respectively). Moreover, the HCH angle becomes greater (118.4° and 115.2°, respectively). Regarding the decomposition products on the O site, the adsorbed H_2O has its O–H bonds longer than those of the free molecule (0.98 Å/ 1.03 Å and 0.96 Å, respectively). It shows an important interaction with the surface; in fact, the O–H bond nearest to the surface is more elongated. On the other hand, the CO_2 structure is the same for the free and adsorbed molecules, which indicates a very weak interaction with the substrate.

Table 1
NBO atomic charges of the methanol decomposition products on the (1 0 0) Ga_2O_3 surface and the isolated species: T and O design tetrahedral and octahedral gallium atom sites and the subindexes the number of oxygen vacancies

	Q(H_2CO)	Q(H)	Q(C)	Q(O)
T0	+0.12	+0.16/+0.20	+0.29	−0.53
Free	–	+0.14/+0.14	+0.22	−0.49
	Q(CO_2)	Q(C)	Q(O)	
O0	+0.08	+1.12	−0.57/−0.47	
Free	–	+1.04	−0.52/−0.52	
	Q(H_2O)	Q(H)	Q(O)	
O0	+0.02	+0.53/+0.53	−1.04	
Free	–	+0.47/+0.47	−0.94	

The NBO atomic charges of methanol decomposition products on the β-Ga_2O_3 (1 0 0) surface are exposed in Table 1. The same parameters for the isolated species were also calculated. The residual molecule of the oxidation reaction occurred on T0 site, H_2CO, is positively charged (+0.12e). A major charge polarization can be observed when H_2CO is linked with the surface, i.e, the atoms which have positive charge in the isolated species have a greater charge than those in the adsorbed molecule. The same occurs with the negative charged atoms. The products of the reaction on O0 site, CO_2 and H_2O, were only slightly charged. Also, in these species a charge polarization when the molecule is linked with the substrate was found.

Table 2 summarizes the calculated vibrational frequencies corresponding to the fundamental modes of the methanol decomposition products on the T0 and O0 sites of gallia surface. These values were scaled down using the above-mentioned 0.97 renormalizing factor [3].

The calculated IR results to the isolated species are in excellent accord with the experimental data. Analyzing H_2CO molecule; (i) we see that both antisymmetrical and symmetrical stretching modes are greater for the adsorbed molecule than the ones for the isolated molecule, ~140 cm^{-1} and ~80 cm^{-1}, respectively, consistent with the C–H bond shortening. However, for the linked molecule, υ(CO) is shorter, ~90 cm^{-1}, confirming the weakness and the lengthened of this bond with respect to the free molecule. The symmetrical CH_2 bending mode, $\delta_s(CH_2)$, practically does not change. These IR frequency changes together with the geometrical results and NBO analysis indicate a significant interaction between H_2CO and the gallia surface.

Table 2
Selected frequency modes for methanol decomposition products on the (1 0 0) Ga_2O_3 surface, (i) H_2CO, (ii) H_2O and (iii) CO_2

	Isolated	Exp.	Adsorbed
(i) H_2CO			
υ_{as}(CH) (cm^{-1})	2871	2874[a]	3009
υ_s(CH) (cm^{-1})	2817	2780[a]	2897
υ(CO) (cm^{-1})	1793	1743[a]	1701
$\delta_s(CH_2)$ (cm^{-1})	1505	1503[a]	1492
(ii) H_2O			
υ_{as}(OH) (cm^{-1})	3803	3756[b]	3426, 2613
υ_s(OH) (cm^{-1})	3691	3657[b]	–
$\delta(H_2O)$ (cm^{-1})	1612	1595[b]	1684
(iii) CO_2			
υ_{as}(CO) (cm^{-1})	2362	2349[c]	2382
υ_s(CO) (cm^{-1})	1329	1285[c]	1343

[a] Gaseous H_2CO [13].
[b] Water vapour [14].
[c] Gaseous CO_2 [15].

The H_2O spectrum (ii) shows that the antisymmetrical stretching mode, υ_{as}(OH), has a smaller value when the molecule is linked to the surface. These changes indicate an important interaction of water molecule with the oxide surface. On the other hand, υ_s(CO) and υ_{as}(CO) for the CO_2 molecule are slightly greater than the those of the isolated molecule. The latter results are in agreement with the above comment that the CO_2 molecule has a weak interaction with the substrate.

4. Conclusions

The surfaces without oxygen vacancies are more reactive than the others and produce the methanol decomposition. The methanol molecule oxidizes on these surfaces, forming H_2CO on tetrahedral sites (T0), and CO_2 and H_2O on octahedral sites (O0). All these molecules remain linked with the surface oxide. The E_{ads} obtained for these sites are large: ~6 eV and ~12 eV, respectively. Hence, the high basicity of these surfaces brings about the loss of hydrogen atoms by steps; while formate is the final species on T0 site, this molecule undergoes the dehydrogenation to CO_2 on O0 site.

Both geometrical parameters and infrared results indicate a weak interaction between CO_2 molecule and the substrate being this molecule easy to desorb. Otherwise, H_2CO has a stronger surface bond and it could suffer a later oxidation before desorption.

Acknowledgements

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References

[1] K. Tanabe, M. Misono, Y. Ono, H. Hattori, New solid acids and bases. Their catalytic properties, in: B. Delmon, J.T. Yates (Eds.), Studies in Surface Science and Catalysis, vol. 51, Kodansha/Elsevier, Tokyo/Amsterdam, 1989.
[2] S.E. Collins, M.A. Baltanás, A.L. Bonivardi, Appl. Catal. A: Gen. 295 (2005) 126.
[3] M.M. Branda, S.E. Collins, N.J. Castellani, M.A. Baltanás, A.L. Bonivardi, J. Phys. Chem: B 110 (2006) 11847.
[4] D. Kohl, Th. Ochs, W. Geyer, M. Fleischer, H. Meixner, Sens. Actuators B 59 (1999) 140.
[5] Cluster Models for Surface and Bulk Phenomena, G. Pacchioni, P.S. Bagus, F. Parmigiani (Eds.), NATO ASI Series B, vol. 283, Plenum Press, New York, 1992.
[6] M.M. Branda, R.M. Ferullo, P.G. Belelli, N.J. Castellani, Surf. Sci. 527 (1–3) (2003) 89.

[7] M.M. Branda, C. Di Valentin, G. Pacchioni, J. Phys. Chem: B 108 (2004) 4752.
[8] W. Kohn, A.D. Becke, d.R.G. Parr, J. Phys. Chem. 100 (1996) 12974.
[9] A.D. Becke, J. Chem. Phys. 98 (1993) 5648.
[10] C. Lee, W. Yang, R.G. Parr, Phys. Rev. B 37 (1988) 785.
[11] E. Reed, L.A. Curtiss, F. Weinhold, Chem. Rev. 88 (1988) 899.
[12] M.J. Frisch, et al., Gaussian03, Gaussian Inc., Pittsburgh, PA, 1998.
[13] G. Herzberg, Infrared and Raman Spectra of Polyatomic Molecules, D. Van Nostrand Co., Inc., Princeton, NJ, 1949.
[14] P.F. Bernath, Phys. Chem. Chem. Phys. 4 (2002) 1501.
[15] V.B. Kazansky, V.Yu. Borovkov, A.I. Serykha, M. Bulow, Phys. Chem. Chem. Phys. 1 (1999) 3701.