Catalysis Today 152 (2010) 88–92

Contents lists available at ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

Ethylene glycol interaction on alkaline earth oxides: A periodic DFT study

Monica Calatayud [a,b,*]

[a] UPMC Univ Paris 06, UMR 7616, Laboratoire de Chimie Théorique, F-75005, Paris, France
[b] CNRS, UMR 7616, Laboratoire de Chimie Théorique, F-75005, Paris, France

ARTICLE INFO

Article history:
Available online 24 October 2009

Keywords:
Diol
Alcohol
Basic catalyst

ABSTRACT

The present paper describes the interaction of ethylene glycol $CH_2OH–CH_2OH$ with alkaline earth oxide basic catalysts MO (M = Mg, Ca, Sr, Ba) from periodic DFT calculations. The geometry of adsorption depends on the nature of the metallic site: on MgO the alcohol groups bind to the metal sites on quasi-top positions, while on CaO, SrO and BaO the molecule is located on bridging positions. The adsorption is exothermic and the strength correlates with the basicity of the alkaline earth oxide, the more basic the substrate, the more exothermic the adsorption energy: MgO < CaO < SrO < BaO. The glycol molecule deprotonates to form surface alkoxy groups bound to the metal sites. The extent of such deprotonation is also correlated to the basicity of MO:MgO (completely protonated) < CaO (partially protonated) < SrO (completely deprotonated) = BaO (completely deprotonated). Defects, modeled for a stepped CaO slab, are found to enhance the strength of the interaction and the deprotonation extent, inducing a different adsorption mode. The step is found to be more reactive than the most basic BaO regular surface, in agreement with experimental observations on glycerol. The implications of these aspects in chemical reactivity are discussed.

1. Introduction

Polyhydric alcohols (polyols) are regarded as potential green energy platform molecules in biorefinery schemes [1]. They are obtained from sugars or sugar alcohols as by-product in the biodiesel production and find a large number of applications in the pharmaceutical, cosmetic or petroleum industries. In the last years an effort has been made to develop heterogeneous catalysts able to optimize the industrial transformation process. Alkaline earth oxides are an important class of materials with promising application in polyol conversion. They are inexpensive and easily accessible basic catalysts with application in a variety of chemical transformations including isomerization, carbon–carbon and carbon–oxygen bond formation, and hydrogen transfer reactions [2].

Recently, alkaline earth basic homogeneous catalysts have successfully been used for the etherification of glycerol ($CH_2OH–CHOH–CH_2OH$) [3]. In that work, MgO, CaO, SrO and BaO materials are used as solid catalysts in the synthesis of di-, tri- and/or polyglycerol, of importance as polymer additives (lubricants, plasticizers, emulsifiers, stabilizers and dispersants). Glycerol conversion is found to increase with increasing catalyst basicity. Furthermore, Lewis acidity seems also to play an important role since differently prepared CaO materials show different glycerol etherification activity, which even may surpass that of BaO. On the other hand, ethylene glycol ($CH_2OH–CH_2OH$ or 1,2-ethanediol) transesterification reactions lead to esters with superior lubricant properties [4]. The advantage in the use of alkaline earth basic catalysts for this reaction comes from the fact that the alkoxides obtained are insoluble in organic solvents, thus easily separated. In both etherification and (trans)esterification reactions, alkoxy species are key intermediates. It is thus of primary importance the understanding of the first stage in the mechanism, which is the alcohol interaction with the catalyst. The present paper aims at providing fundamental knowledge on the interaction of a simple diol with a basic solid surface by means of *ab initio* calculations. The ethylene glycol molecule and its interaction with basic solid catalysts MO (M = Mg, Ca, Sr and Ba) are modeled by periodic density functional theory (DFT). The geometry, strength of adsorption and deprotonation extent of the molecule will be analyzed as a function of the substrate basicity. Moreover, the role of surface defects will be studied in the case of CaO. The implications of the above mentioned aspects in reactivity are discussed.

2. Computational methods and models

Total energy calculations were carried out with the periodic *ab initio* code VASP [5,6]. The PW91 functional was used together with

---

* Correspondance address: Laboratoire de Chimie Théorique, UPMC 4, Pl. Jussieu case 137, F-75252 Paris, France. Tel.: +33 1 44 27 26 82; fax: +33 1 44 27 41 17.
E-mail address: calatayu@lct.jussieu.fr.

0920-5861/$ – see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.cattod.2009.08.011

Table 1
Selected geometrical parameters used in the DFT calculations for different alkaline earth metal oxides with rocksalt bulk structure. *a*: cell parameter, d_{M-M}: the shortest distance between two metal sites.

	MgO	CaO	SrO	BaO
Bulk				
a calculated (Å)	4.25	4.82	5.20	5.60
a experimental (Å)	4.21	4.80	5.20	5.52
(0 0 1) Plane				
$\sqrt{2}a$ (Å)	6.01	6.82	7.35	7.92
d_{M-M} (Å)	3.00	3.41	3.67	3.96
$\sqrt{2}\times\sqrt{2}$ area (Å^2)	36.15	46.49	54.00	62.69

a plane wave basis set (cutoff 400 eV). The core electrons were replaced by PAW generated pseudopotentials [7,8], as in Ref. [9]. This methodology was tested for the bulk rocksalt structures leading to excellent agreement with experimental results, as can be seen in Table 1.

The regular surfaces have been modelled by cutting the optimized bulk structure through the most stable (0 0 1) plane. The CaO stepped surface is modelled by a (5 0 1) terminated slab. A five layer thick slab was used, the two bottom layers being fixed to the bulk optimized positions, the rest being allowed to relax. A vacuum of at least 10 Å prevents interaction between successive slabs. The distance between k-points in the reciprocal space was ~0.02 Å^{-1}. A $\sqrt{2}\times\sqrt{2}$ R45 unit cell was used for the adsorption systems on the regular surfaces; one ethylene glycol molecule is computed per unit cell. The adsorption energy is calculated as the energy of the molecule plus the substrate minus the interaction complex, and is positive for an exothermic adsorption. This scheme has been employed for a similar system (glycerol etherification on alkaline earth oxides) in good agreement with experimental results [3,9]. Implications of the sites studied in catalytic reactivity are discussed below. The extent of deprotonation of ethylene glycol is considered – note that "protonated" is used in the text to denote the presence of $O_{gly}H$ groups (not $O_{gly}H_2^+$), in contrast to "deprotonated" which denotes O_{gly}^- groups.

3. Results

3.1. Ethylene glycol adsorption on MO (M = Mg, Ca, Sr and Ba) (0 0 1) surfaces

The interaction of one ethylene glycol molecule on the $\sqrt{2}\times\sqrt{2}$ R45 unit cell of the different substrates implies a coverage of one molecule per four surface metal (or oxygen) sites. Different orientations of the molecule (perpendicular or parallel to the surface, on top of the metal sites or bridging two sites) have been explored for each substrate. Deprotonation of one or two alcohol groups has been considered following the reaction:

$$R{-}OH \rightarrow R{-}O^- + H^+ \qquad (1)$$

Fig. 1 shows the most favorable adsorption modes obtained from the calculation, Table 2 summarizes the main results. For all the substrates ethylene glycol adsorbs parallel to the surface, the alcohol groups in interaction with the surface. On MgO the molecule OH groups are located on quasi-top positions of the surface Mg sites. The molecule is completely protonated and the alcohol groups bind to the surface by hydrogen bonds. The $M-O_{gly}$ distances are in the range 2.2–2.5 Å. On the CaO surface the molecule lies on bridging positions between two surface Ca atoms. It is partially deprotonated forming an alkoxide $Ca-OCH_2CH_2OH$ with a Ca–O distance of 2.279 Å. On SrO the molecule is located in bridging positions. It completely deprotonates forming two alkoxide $Sr-OCH_2$ groups bridging two Sr surface sites each one. The $Sr-O_{gly}$ distances are around 2.5 Å. On BaO a similar picture is

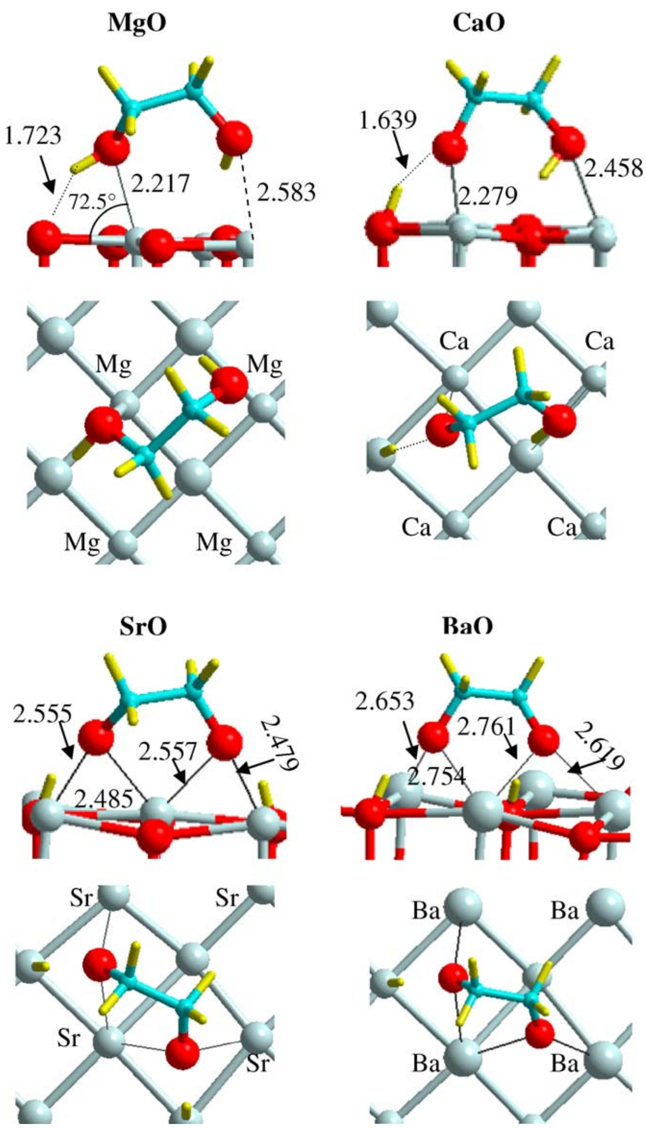

Fig. 1. The most stable adsorption modes for glycol interaction with MO (0 0 1) surfaces, top and side views. Selected distances in Å, angles in degrees.

Table 2
Coverage *θ*, shortest distance between two adsorbed species in two neighboring cells *d*(gly–gly), and adsorption energy E_{ads} obtained for all the metal oxide surfaces studied, positive values indicate exothermicity. The extent of deprotonation of the ethylene glycol molecule in the most favorable mode is reported (protonated means $O_{gly}H$ group, deprotonated O_{gly}^- group), together with the average $M-O_{gly}$ bond distance $d(M-O_{gly})$.

	MgO	CaO	SrO	BaO	CaO step
θ (mol/nm^2)	2.77	2.15	1.85	1.60	0.84
d(gly-gly) (Å)	3.25	4.03	4.67	6.00	6.75
E_{ads} (eV)	0.77	1.34	1.66	2.55	2.73
Glycol protonation	Fully protonated	Partially protonated	Deprotonated	Deprotonated	Deprotonated
$d(M-O_{gly})$ (Å)	2.2–2.5	2.3–2.5	2.5–2.6	2.6–2.8	2.3–2.5

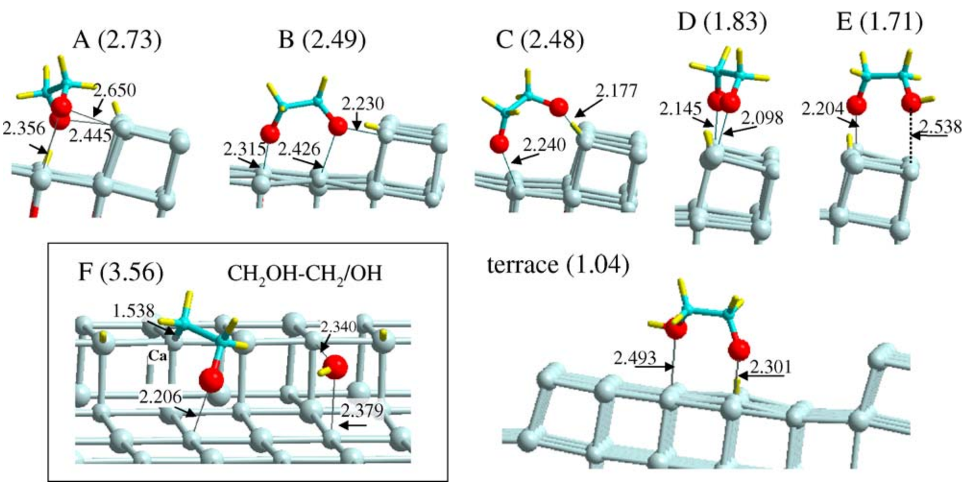

Fig. 2. Selected structures for ethylene glycol interaction with a stepped CaO (5 0 1) surface, top and side views. Selected distances in Å. In parentheses, adsorption energy in eV.

found: the formation of two Ba–OCH_2 alkoxide groups upon complete deprotonation of the alcohol groups. The Ba–O_{gly} distances are in the range of 2.6–2.8 Å.

Regarding energetics, the interaction of ethylene glycol with the MO surfaces is exothermic. The adsorption energy increases in the order MgO (0.77 eV) < CaO (1.34 eV) < SrO (1.66 eV) < BaO (2.55 eV).

3.2. Ethylene glycol adsorption on a stepped CaO surface

The coverage considered is one molecule per 10 surface Ca atoms, two of them belonging to the step. A set of six initial geometries has been calculated involving ethylene glycol in interaction with the step, or on the terrace. Fig. 2 shows some representative structures obtained together with their adsorption energy. Deprotonation of one or two alcohol groups has been considered following the reaction (1) (structures A–E).

The most favorable geometry upon deprotonation (A) involves the ethylene glycol molecule in close interaction with the step, flat on the surface and parallel to the step. The molecule oxygen atoms bind to two undercoordinate Ca sites: one of the step (4-fold) and one of the terrace (5-fold), as an extension of the step. The molecule is deprotonated, with a preference for the formation of hydroxyl groups on the step. The Ca–O_{gly} distances lie in the range between 2.3 and 2.9 Å. Some other structures with direct interaction with the step and the terrace are also stable (B and C). The structures where ethylene glycol is on top of the step (D and E) are less favorable by 1 eV. Adsorption on the terrace is the least favorable among those studied (1.04 eV), and involves partial protonation of the molecule, as found with the (0 0 1) regular slab model. The difference in the calculated interaction energy with the (0 0 1) regular surface comes from the lower coverage.

4. Discussion

4.1. Geometry

The adsorption mode for ethylene glycol adsorption on regular (0 0 1) slabs is flat, parallel to the surface, the oxygen groups binding one (MgO) or several (CaO, SrO, BaO) surface metal sites. The average M–O_{gly} distances increase in the series Mg–O < Ca–O < Sr–O < Ba–O, as corresponds to an increase in the atomic radii. Two sets of M–O_{gly} distances are observed when protonated/deprotonated modes coexist, as for CaO: a short one when the O_{gly} site is deprotonated (formation of an alkoxide, 2.279 Å), and a longer one when O_{gly} is protonated (2.458 Å). The deprotonation of the glycol molecule leads to the formation of surface hydroxyl groups, that may interact by hydrogen bonds with the alkoxide moiety stabilizing bridging positions. In the case of total or partial protonation of the molecule (MgO or CaO respectively), the molecule alcohol groups interact with the surface oxygen sites by hydrogen bonds. In the presence of a step, ethylene glycol completely deprotonates and binds bridging the step and the terrace, with two M–O_{gly} bonds per oxygen (Fig. 2A). In all the configurations considered, the protons form hydroxyl groups in the step showing high stability for these species. This is in agreement with the results obtained by Chizallet et al. [10].

4.2. Energetics

The interaction energy is exothermic for all the surfaces studied. The interaction between the adsorbate and the surface is mainly of electrostatic character as expected from the different electronegativity of the atoms involved (M–O_{gly} and O_{surf}–H). The most favorable interaction energy obtained for all the systems (regular and defective sites) upon deprotonation is depicted in Fig. 3. The interaction is found to increase in the series

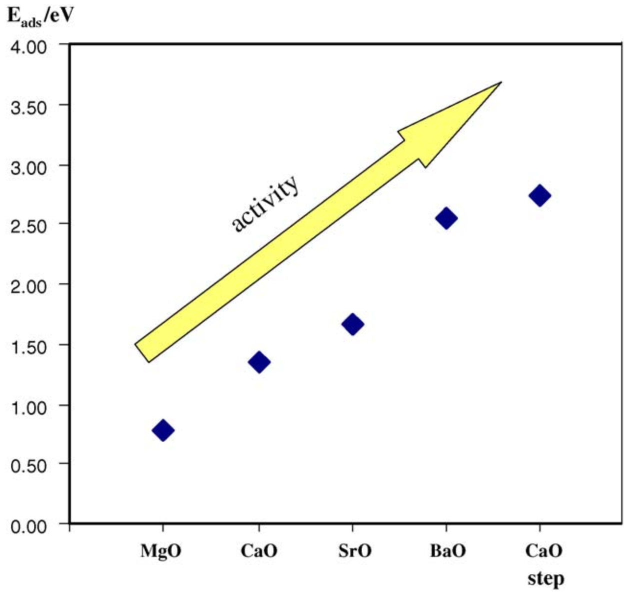

Fig. 3. calculated adsorption energy (eV) as a function of the material. The interaction increases in strength in the series MgO < CaO < SrO < BaO < CaO-step, and correlates with the activity of the material.

MgO < CaO < SrO < BaO, in correlation with the increasing basicity of the materials. The basic character of alkaline earth oxides has been related to their electrostatic nature. Pacchioni et al. [11] have shown that the different reactivity for MgO and CaO comes from the different Madelung potential of the ionic crystal. The oxygen anion is stabilized in the surface by the charge distribution of the crystal, the smaller the potential, the lower the stabilization, the higher the basicity. Therefore, the different basicity observed is correlated to the atomic size: the smaller the atom, the stronger the Madelung potential, the higher the anion stabilization, the lower basicity. The results presented in the present work clearly follow this rule. The poor reactivity of MgO towards dissociation has been explained in the case of water adsorption by the large barriers involved in the separation of proton-hydroxyl structure [12]. This probably applies to the case of ethylene glycol and other alcohol molecules which do not dissociate on regular MgO.

4.3. *Defects*

According to the conclusion derived above, the stepped CaO surface should be more reactive than the most basic material BaO, since it presents the highest adsorption energy for the deprotonation reaction (2.73 vs 2.55 eV). This finding is in agreement with the observed reactivity in glycerol etherification over alkaline-earth oxide materials [3], where some CaO based catalysts showed better reactivity than BaO materials. According to our previous [9] and present results, this might be due to a higher density of defects.

The acido-basic properties of defective sites on MgO have been studied by Chizallet et al. [10] by considering water adsorption. It is concluded that undercoordination leads to an enhanced reactivity, in agreement with our previous [13,14] and present results. The presence of defects has proven to significantly increase the reactivity of water and methanol due to the presence of undercoordinated sites, as confirmed by other theoretical works [10,15–17]. Note however that the higher reactivity of defects may lead to the formation of other sites, such as hydroxyl groups by water splitting, also involved in catalytic activity, not considered in the present work.

4.4. *Reactivity*

The key intermediate in the main reactions of transformation of alcohols (such as etherification or esterification) is the alkoxide species. Its formation takes place through the deprotonation of the alcohol, and its stability determines the subsequent steps. The role of the solid surface is to stabilize such alkoxide species. In this work it is shown that the formation of ethylene glycol alkoxides is favored when increasing the basicity of the materials, in the series MgO (no alkoxide) < CaO < SrO < BaO. The interaction energy accounts for the stability of the adsorbed species. The poor reactivity of MgO compared to other alkaline-earth oxides has also been evidenced from calculations for water [12,18,19], methanol [20,21] or CO [22] adsorption.

Regarding the role of the solid surface in the reaction mechanism, it has been found that for the glycerol etherification [3] not only the basicity, but also the Lewis acidity was determinant for the activity of some CaO materials. A possible molecular explanation might be the activation of a glycerol alcohol group as leaving group by adsorption on the substrate Lewis acid sites [9]. This was supported by the stability of adsorption modes presenting protonated alcohol groups. Such groups are also present in the case of ethylene glycol adsorption on CaO. It is thus possible that the same mechanism applies to similar reactions.

In order to check this possibility, the formal dissociation of ethylene glycol by a C–O bond break has been considered:

$$CH_2OH{-}CH_2OH \rightarrow CH_2OH{-}CH_2^+ + OH^- \qquad (2)$$

The $CH_2OH–CH_2^+$ fragment adsorbs on a surface oxygen site, while the hydroxyl group adsorbs on a surface Ca site. It may also deprotonate to $^-OCH_2–CH_2^+$. The stability of such adsorption mode would be in line with the mechanism evoked above, where the surface Lewis acid sites stabilize the hydroxyl groups activating the molecule for a nucleophilic attack. This adsorption mode following Eq. (2) has been found less favorable than the one following Eq. (1) for all the regular surfaces MO (M = Mg, Ca, Sr, Ba). However, it is the most stable mode in the case of the stepped CaO model (3.56 eV, Fig. 2F). The reason is the stabilization of the hydroxyl group in bridging positions between the step and the surface. This feature is also found of high stability in the case of water dissociation on MgO monatomic steps [10]. Surprisingly, the initial geometry involving the $CH_2OH–CH_2^+$ fragment on a step oxygen site evolves during the optimization: starting from the deprotonated moiety $^-OCH_2–CH_2^+$ (the proton H^+ binds to the step oxygen), the formation of a Ca–C bond takes place. The role of the $Ca–CH_2–CH_2O^-$ species would need further investigation.

Finally, some caution must be taken when relating stability (in the present case basicity) and chemical reactivity: the stabilization of key intermediates should be enough to allow the species exist, but not too much to make the intermediate too stable to react, or to avoid parallel reactions. In this sense, the structures having intermediate stability might be potentially more interesting for reactivity than those showing high stability.

5. Conclusions

Ethylene glycol adsorption on MO (0 0 1) surfaces of alkaline earth metal oxides involves the interaction with acid–base surface sites. The basicity of lattice oxygen is correlated to the adsorption energy in the following order MgO (0.77 eV) < CaO (1.34 eV) < SrO (1.66 eV) < BaO (2.55 eV). The more basic the character of the oxide, the stronger the interaction. The deprotonation of the alcohol groups follows the same trend: MgO (not dissociated) < CaO (partially dissociated) < SrO (completely dissociated) = BaO (completely dissociated). The molecule adsorbs flat, parallel to the surface, stabilized by electrostatic interaction with the surface. MgO shows preference for quasi-top adsorption sites, the two alcohol groups binding to the lattice oxygen sites by hydrogen bonds. In the case of deprotonation, $M–O_{gly}$ alkoxide groups are formed (M = Ca, Sr, Ba), stabilized by hydrogen bonds with surface hydroxyl groups. The presence of steps in CaO enhances the interaction with ethylene glycol (2.73 eV) so the final system is more reactive than BaO. Moreover, the step favors a different dissociative mode where the $C–O_{gly}$ bond breaks, stabilizing hydroxyl groups bonded both to the step and the terrace Ca sites, as well as the formation of a Ca–C bond.

Acknowledgements

The author thanks A. Ruppert and B. Weckhuysen (Utrecht University, The Netherlands) for stimulating discussions. This work was performed using HPC resources from GENCI-CINES/IDRIS (Grant 2009-82131).

References

[1] N. Yan, C. Zhao, W.J. Gan, Y. Kou, Chin. J. Catal. 27 (2006) 1159.
[2] A. Corma, S. Iborra, Adv. Catal. 49 (2006) 239.
[3] A.M. Ruppert, J.D. Meeldijk, B.W.M. Kuipers, B.H. Erne, B.M. Weckhuysen, Chem. Eur. J. 14 (2008) 2016.
[4] S. Gryglewicz, Appl. Catal. Gen. 192 (2000) 23.

[5] G. Kresse, J. Hafner, Phys. Rev. B 47 (1993) 558.
[6] G. Kresse, J. Hafner, Phys. Rev. B 49 (1994) 14251.
[7] G. Kresse, D. Joubert, Phys. Rev. B 59 (1999) 1758.
[8] P.E. Blöchl, Phys. Rev. B 50 (1994) 17953.
[9] M. Calatayud, A.M. Ruppert, B.M. Weckhuysen, Chem. Euro. J. 15 (2009) 10864.
[10] C. Chizallet, G. Costentin, M. Che, F. Delbecq, P. Sautet, J. Phys. Chem. B 110 (2006) 15878.
[11] G. Pacchioni, J.M. Ricart, F. Illas, J. Am. Chem. Soc. 116 (1994) 10152.
[12] J. Carrasco, F. Illas, N. Lopez, Phys. Rev. Lett. 100 (2008) 016101.
[13] M. Calatayud, A. Markovits, M. Ménétrey, B. Mguig, C. Minot, Catal. Today 85 (2003) 125.
[14] M. Calatayud, A. Markovits, C. Minot, Catal. Today 89 (2004) 269.
[15] D. Costa, C. Chizallet, B. Ealet, J. Goniakowski, F. Finocchi, J. Chem. Phys. 125 (2006) 054702.
[16] M.L. Bailly, C. Chizallet, G. Costentin, J.M. Krafft, H. Lauron-Pernot, M. Che, J. Catal. 235 (2005) 413.
[17] W. Langel, M. Parrinello, Phys. Rev. Lett. 73 (1994) 504.
[18] W. Langel, M. Parrinello, J. Chem. Phys. 103 (1995) 3240.
[19] W.S.A. Halim, A.S. Shalabi, Appl. Surf. Sci. 221 (2004) 53.
[20] A.H. Rodriguez, M.M. Branda, N.J. Castellani, J. Phys. Chem. C 111 (2007) 10603.
[21] I.D. Gay, N.M. Harrison, Surf. Sci. 591 (2005) 13.
[22] W.S.A. Halim, Appl. Surf. Sci. 253 (2007) 8974.