Catalysis Today 139 (2008) 209–213

Contents lists available at ScienceDirect

Catalysis Today

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

Combining theoretical description with experimental *in situ* studies on the effect of alkali additives on the structure and reactivity of vanadium oxide supported catalysts

Anna E. Lewandowska [a], Mònica Calatayud [b], Enrique Lozano-Diz [a], Christian Minot [b], Miguel A. Bañares [a,*]

[a] *Laboratorio de Espectroscopia Catalítica, Instituto de Catálisis y Petroleoquímica, CSIC, Marie Curie 2, E-28049 Madrid, Spain*
[b] *Univ. Paris 06, UMR CNRS 7616 LCT, Paris F-75005, France*

ARTICLE INFO

Article history:
Available online 20 June 2008

Keywords:
DFT
Alkali
Vanadia–titania
In situ Raman
Operando

ABSTRACT

A periodic model has been selected to model the structure and reducibility of vanadia/titania catalysts and the effect of alkali doping for Li, Na and K. Alkali interact with both the surface vanadia units and the support. The calculated changes on vanadia structure are consistent with the changes evidenced by Raman spectroscopy. Reducibility is modeled by adsorption of one hydrogen atom, forming hydroxyl groups with the bridging V–O–Ti present in the model. The adsorption energy decreases in the series Li > Na > K, in agreement with experimental TPR results.

1. Introduction

Vanadium oxide, as an active species, is present in most of the catalysts for selective oxidation of alkanes [1–3], which allows achieving a high productivity at moderate temperature. A rational model of catalysts needs information on the nature of the active centers and their role in the catalytic system. The catalytic properties of the supported vanadium oxide species for the selective oxidation processes are strongly affected by the vanadia loading, preparation method, nature of the support and type of promoter. The vanadium content determines type of the metal oxide species present on the surface. The surface VOx species occur in the isolated form at low loading evolving into polymerized forms when increasing the vanadia content until the monolayer coverage is reached. The segregate V_2O_5 crystalline phase dominates on the surface support above monolayer coverage. Among the catalysts promoters, alkali metals are usually mentioned as promoters for industrial catalysts since they provide a higher selectivity for partial oxidation reactions [4,5]. The molecular structure of supported vanadium oxides and oxide supports (e.g. TiO_2) has been studied by different experimental techniques [6–8]. The theoretical calculation and modeling permit to describe the structure, spectra characteristics and reactivity [9–14]. An interaction of the alkali cations with the oxide supports has been detailed studied by experimental [15–17] and theoretical [18–20] techniques. However, the role of alkali dopants on the structure and properties of supported vanadium oxide is not fully understood. Titania-supported vanadia catalysts exhibit a noticeable dependence on the preparation method or the coverage level of the support. Below monolayer coverage, supported species do not form the aggregates of the V-alkali-O phases. However, the evident interaction, which results in the weakening of the vanadyl group and in the changes of the reactivity exists [15–17].

The present work aims to provide a molecular description of the structure and reactivity of the vanadium oxide catalysts supported on titanium oxide and the importance of alkali doping on their structure and reactivity by a combined theoretical and experimental studies. The surface features have been determined by complementary studies of theoretical modeling (DFT) and experimental *in situ* Raman spectroscopy and temperature-programmed reduction (TPR). The structural and reactive features are contrasted with those described by theoretical calculation. The results obtained will be important for understanding the changes occurring during the catalytic act as well as will be complementary tools to describe the structures and activity observed during *operando* studies.

---

[*] Corresponding author. Tel.: +34 91 585 4788; fax: +34 91 585 4760.
E-mail address: banares@icp.csic.es (M.A. Bañares).

0920-5861/$ – see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.cattod.2008.04.049

2. Experimental

2.1. Computational studies

The periodic DFT calculations have been performed with the VASP code [21,22] using the Perdew–Burke–Ernzerhof functional [23,24] for the total energy determination. Spin-polarized calculations have been performed for the open shell systems (hydrogenated and alkali doped systems). The valence electrons have been described by plane waves based functions (cutoff energy = 400 eV) with the following electrons treated explicitly: O: s^2p^4, Ti: s^2d^2, V: s^2d^3, M: s^1 (M = Li, Na), K: s^1p^6. The *core* electrons are replaced by PAW generated pseudopotentials [25,26]. The reciprocal space is sampled with a Monkhorst-Pack $3 \times 3 \times 1$ grid. All atoms of the models are relaxed and the optimization of the geometry is carried out by the conjugated gradient algorithm.

The models contain both the support, a plane (0 0 1) of TiO_2 anatase found in the powder commercial samples, and the active phase, a V_2O_5 unit [27]. The final model of the surface is shown in Fig. 1. A unit cell of dimension 7.57 Å × 7.57 Å × 1.7 Å is used. A vacuum space of 8 Å is sufficient to avoid an interaction between successive layers.

The alkali dopant effect is considered by the addition of a neutral atom M to the vanadia–titania slab. The alkali atom is localized between different vanadia units, according to Fig. 1. The M:V:$Ti_{surface}$ atomic ratio in the model is 1:2:4, which is close to the experimental preparation [17,28,29]. Therefore, the model possesses both acidic centers and redox centers (vanadium atoms) as well as centers (vanadyl group and bridging oxygen atoms) accessible for the reaction. Detailed description of the geometry of doped systems is presented below.

2.2. Preparation of samples

The catalysts were prepared by sequential impregnation of titanium (IV) oxide (Alfa Aesar, 100% anatase, S_{BET} = 166 m^2/g). At the beginning, TiO_2 was modified by the solution of alkali hydroxides. Dissolution of alkali metal precursors was performed by stirring an aqueous solution during 10–20 min. The suspension was evaporated in rotatory evaporator at 65 °C. The obtained materials were dried at 110 °C for 16 h and the samples were calcined at 450 °C for 4 h in air (heating rate = 5 °C min^{-1}). Vanadia supported on alkali-doped titania catalysts were prepared by impregnation with an aqueous solution of ammonium metavanadate (Sigma, 99.99%). Oxalic acid (Panreac, 99.5%) was added to an aqueous solution of NH_4VO_3 to facilitate dissolving the salt. Dissolution of vanadium precursor mixture was carried out by stirring at 50 °C for 50 min. The solid obtained after impregnation was dried and calcined at the same conditions like modified supports.

The total vanadium content corresponds to half monolayer (4 V atoms/nm^2 of TiO_2 support). The concentration of alkali cations was selected by a mode that a V/alkali metal atomic ratio was 4/0.6. Catalysts are labeled as xV/yK/TiO_2, where “x” and “y” indicate the number of atoms per nm^2 of vanadia and alkali metal, respectively.

2.3. Temperature programmed reduction (H_2-TPR)

The reducibility properties of the alkali-doped vanadia catalysts were studied by H_2-TPR. The reduction was performed in a “U” shaped fixed-bed quartz reactor with a Micromeritics TPD/TPR 2900 analyzer equipped with a thermal conductivity detector (TCD). The reduction was carried out with 10 vol.%. of H_2/Ar mixture with a flow rate 40 cm^3 min^{-1}. 30 mg of sample placed in the reactor was dehydrated in a synthetic air flow at 400 °C (heating rate = 5 °C min^{-1}). Subsequently, the sample was cooled to room temperature, and then it was reduced at a heating rate 10 °C min^{-1} to 950 °C under 10% H_2/Ar. The water produced during the reduction was condensed in a cold trap dipped in a mixture of isopropanol and liquid nitrogen.

2.4. In situ Raman

Raman spectra were run with a single monochromator Renishaw System-1000 microscope Raman equipped with a cooled CCD detector (−73 °C) and holographic super-Notch filter for removing the elastic scattering. The powder samples were excited with the 514 nm Ar^+ line; spectral resolution was near 3 cm^{-1} and spectrum acquisition consisted of 20 accumulations of 10 s. The spectra were obtained under *in situ* dehydrated conditions in a hot stage (Linkam TS-1500). The samples were dehydrated in synthetic air at 400 °C for 1 h. The rate of the heating was 5 °C min^{-1}. The spectra of dehydrated samples were recorded at room temperature

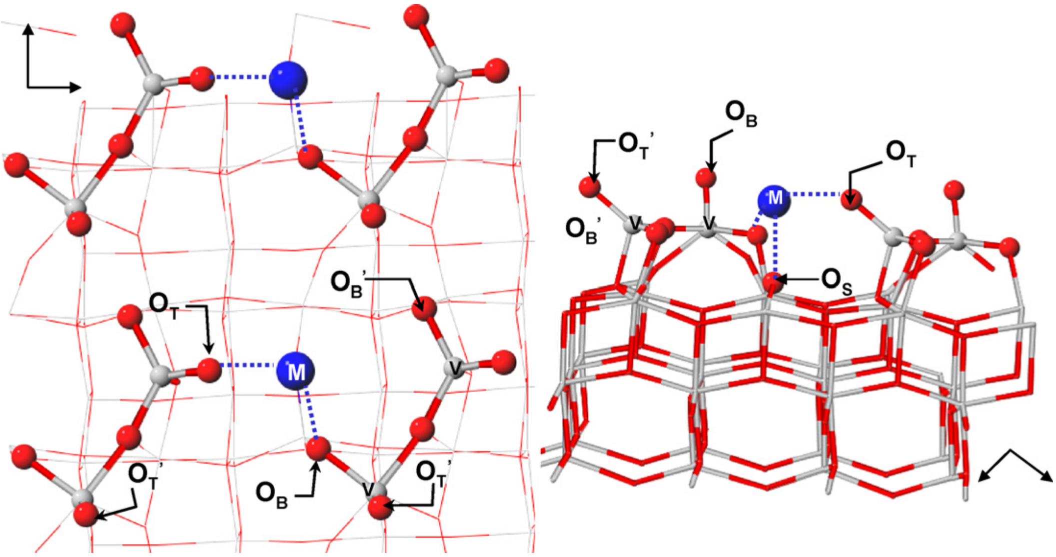

Fig. 1. Periodic model of the alkali modified vanadia/titania catalysts: O_T, terminal oxygen; O_B, bridging oxygen; O_S, support oxygen; M, alkali atom.

after cooling the samples. The spectra of hydrated samples were obtained at room temperature in a flow of humid air.

3. Results and discussion

3.1. Geometry

The presence of alkali atoms disturbs the vanadia–titania system geometry in different aspects. On the one hand, the alkali atoms form a strong ionic bond with both the vanadium and the support units. The alkali atom binds to two vanadium oxide units dispersed on the titania surface in our model. In accordance to this model, alkali atom forms bonds with a bridging oxygen O_B in V–O–Ti and the other one to a terminal oxygen O_T in V═O group, as is presented in Fig. 1. The M–O distances obtained from the optimization are summarized in Table 1. At the same time, alkali atoms interact with the support oxygen, which is visible from the M–OX bond length. The bond distance (M–OX) increases with the size of the alkali metal with the following order: ca. 1.90 Å for Li, ca. 2.20 Å for Na and ca. 2.80 Å for K. The largest alkali atom, K, is in interaction with a third vanadium oxide unit (not shown).

The second important geometry effect is the vanadyl group (V═O) bond elongation due to the close presence of alkali metals. The V═O bond is lengthened from 1.615 Å to 1.652 Å with a movement of the corresponding Raman band toward minor energies. The Raman band position of the vanadyl mode is extremely sensitive to the length of the bond [30]. This elongation would affect the activity of the material if the vanadyl group were involved in the reaction.

3.2. Raman

The Raman spectra of alkali-free and titania-supported vanadium oxide species are shown in Fig. 2. The Raman band at 1020 cm^{-1} corresponds to the vibration of the terminal vanadyl group (V═O). The addition of the alkali promoters to the catalysts induces mainly a red shift of the vibration frequency related to V═O bond. It indicates a weakening of the V═O double bond. A dependence between bond distance and bond order with V═O vibration Raman frequency was clearly demonstrated previously [30]. The experimental results obtained confirm the prediction of V═O bond elongation by alkali promoters addition to the vanadia/titania system described by modeling.

3.3. Hydrogenation

At last, the hydrogenation was modeled to probe the redox properties of the alkali-modified systems. Hydrogen interacts with surface oxygen sites forming a strong O–H bond:

$$H + O_{surf}{}^{2-} \rightarrow O_{surf}H^{-} + 1e^{-}$$

The electron is transferred to the surface vanadium sites reducing them. Hydrogen atom is anchored to different oxygen sites in the model. Two oxygen sites in the vanadia unit were explored in the theoretical system: bridging V–O–Ti (O_B) and terminal (O_T). The (O_B) site is preferable for the hydrogenation according to the results observed for previous studies of undoped surface areas [11].

Table 1
Bond distances in the alkali modified vanadia/titania systems, in Å

Distance (Å)	Without additive	Li	Na	K
$d(M–O_B)$	–	1.906	2.262	3.129
$d(M–O_T)$	–	1.859	2.199	2.769
$d(M–O_S)$	–	2.033	2.341	2.744
$d(V═O_T)$	1.615	1.658	1.652	1.652

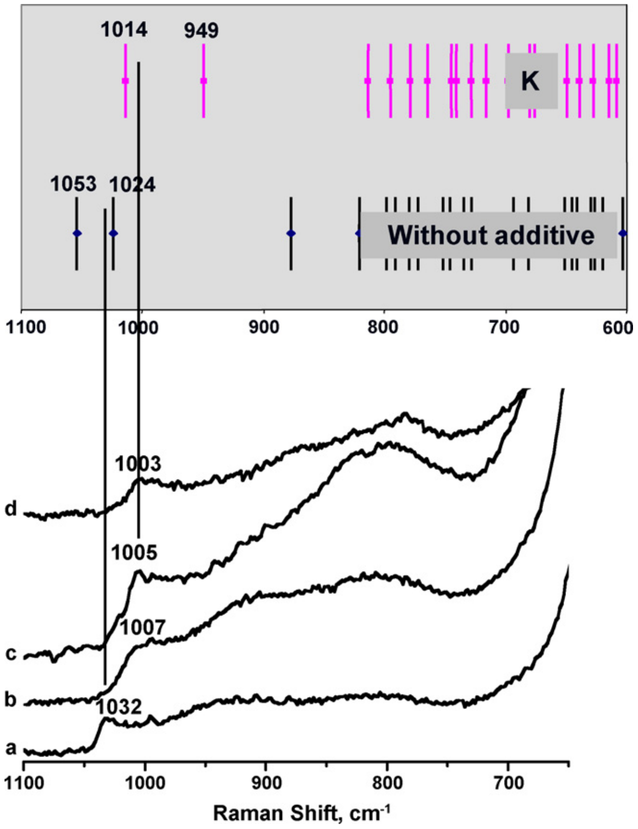

Fig. 2. Raman spectra of dehydrated vanadia/titania catalysts without and with alkali promoter: (a) without promoter; (b) with Li; (c) with Na; (d) with K (bottom). Calculated Raman frequencies for the material with V/K = 2 atomic ratio (top).

The hydrogenation process is exothermic [31] and more favorable for undoped systems according to the values shown in Fig. 3, Table 2. For the same V–O–Ti (O_B) site, the alkali-doped systems show a decrease of the first hydrogen adsorption energy in the order undoped (2.97 eV) > Li (2.70 eV) > Na (2.63 eV) > K (2.54 eV). In view of these results, the catalyst doped with lithium is more reducible than doped with potassium. It is important to note that the studied model considers a neutral alkali atom, which reduces the vanadium site immediately and forms a cationic species M^+. Even if the alkali atom is found as a cation, the fact that the catalyst is already reduced before considering hydrogenation

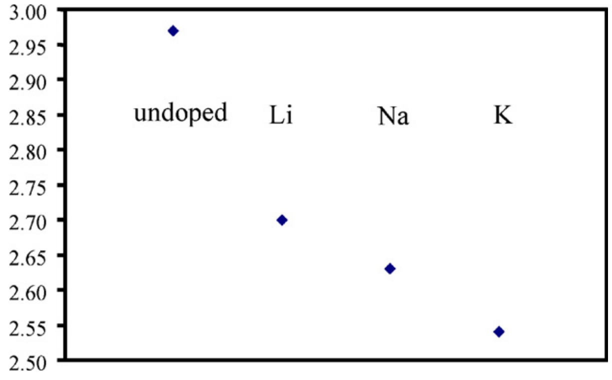

Fig. 3. Hydrogen adsorption energy (in eV), calculated as $E_{ads} = E_{slab} + E_H - E_{slab+H}$. Positive value indicates exothermic process. The reducibility decreases in the sequence undoped >Li > Na > K.

Table 2
Adsorption energy for the hydrogenation of the M model, calculated as $E_{ads} = (E_{slab} + nE_H - E_{slab+nH})/n$

	Bare	Li	Na	K
1st H on O_B	2.97	2.70	2.63	2.54
2nd H on O_B'	2.88	2.48	2.43	2.41

Positive values indicates exothermic process for each individual hydrogenation.

could affect the results. A parallel study demonstrates that the use of MOH units instead of M units, at the same V:Ti:M atomic ratio, points to the same conclusion [32]. In that model the alkali atom is cationic and no electron transfer occurs between the MOH and the catalyst. The decrease of the reducibility in the series Li > Na > K therefore seems to be related to the presence of the cationic alkali, and recovers the same trend found for the neutral M model.

3.4. H_2-TPR profiles

The effect of the alkali metal addition to the vanadia/titania catalysts on the reduction profiles is shown in Fig. 4. All catalysts keep the same V/alkali ion atomic ratio. The presence of the Li ion decreases the reducibility of dispersed vanadium oxide species compared to the undoped system. The reduction becomes more difficult with the period of the alkali atom in the periodic table. Hence, the sequence of the experimental reducibility, undoped >Li > Na > K, agrees with the predicted modeling tendency of the reactivity of titania-supported vanadium oxide catalysts.

The structure and reactivity modeling of the solid materials reflects a close interaction between alkali additives and both supported oxides and matrices. The alkali atom affects more than one vanadium center; therefore it can explain a major complexity of the reduction profiles of the materials doped with Na and K.

It is worthy to notice the vanadyl bond weakening with the addition of alkali metal; hence it diminishes the reducibility of the supported vanadium species (Figs. 3 and 4) and activity in the oxidation reactions [15–17]. It was widely discussed in the literature if the V=O group is an active center for the oxidation reaction. However, there exist important experimental evidences suggesting that V=O bond is not involved in the critical step of the hydrocarbon oxidation reactions [1]. Previous studies pointed out a great importance of the type of matrices utilized. The change of the support modifies the V=O bond, which again does not correspond to the activity changes, but rather points to the oxygen center associated to an interface between supported oxide and support (V–O-support bond) [33,34]. Unfortunately, the study of that oxygen centers is not experimentally facile. The theoretical calculations carried out in this work allow valuing reactivity by a comparison of the two oxygen centers. The results presented in this work demonstrate that the reducibility does not correspond to the strength changes in V=O bond and preferred sites for the hydrogen interaction are the bridging oxygen (O_B) in V–O–Ti bond. This has a direct implication for the understanding of different parafins and olefins oxidation reactions, ammonia oxidation or selective catalytic reduction, among others.

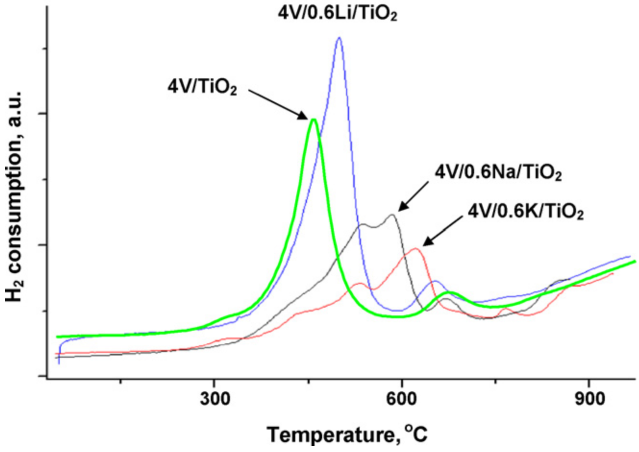

Fig. 4. H_2-TPR profiles of the of V_2O_5/TiO_2 catalysts with different alkali additives: Li, Na, and K.

The dispersion of the active phase is crucial for the catalytic activity and should be carefully studied. Alkali doping appears to minimize vanadia polymerization due to the strong interaction with the support and alkali sites at the interface; this is particularly important for larger alkali units, such as potassium. Modelling highly dispersed catalysts is technically difficult and needs large unit cells. However, the reactivity of dispersed systems is found to depend critically on the surface concentration of vanadia [35].

4. Conclusions

The combination of theoretical and experimental studies describes in a consistent way the effect of the alkali additives on the titania-supported vanadium oxide catalysts. The alkali atoms bind to both vanadia units and support forming strong ionic bonds. The vanadia/titania materials modified by alkali atoms possess a lower reducibility than the undoped catalyst. The bridging oxygen V–O–Ti is more reactive than the terminal oxygen of vanadyl group (V=O). It determines – a priori – which can be an active site. The reducibility of the vanadium oxide species decreases according to a sequence undoped > Li > Na > K.

Acknowledgements

This work has been supported by the COST ACTION D36 (Working Group D36-006-06) and has been accomplished in the frame of the French GDR "Dynamique moléculaire quantique appliqué à la catalyse". Computational facilities by CCRE and IDRIS are acknowledged. Support was provided by the Spanish Ministry of Education and Science CTQ2005-02802/PPQ. AEL acknowledges Spanish Ministry of Education and Science for a "Juan de la Cierva" postdoctoral position, and ELD acknowledges Comunidad de Madrid project (DETOX_H_2S) for an associated contract.

References

[1] M.A. Bañares, Catal. Today 51 (1999) 319.
[2] E. Heracleous, M. Machli, A. Lemonidou, I. Vasalos, J. Mol. Catal. A 232 (2005) 29.
[3] S. Albonetti, F. Cavani, F. Trifirò, Catal. Rev. Sci. Eng. 38 (4) (1996) 413.
[4] A. Klisinska, K. Samson, I. Gressel, B. Grzybowska, Appl. Catal. A: Gen. 309 (2006) 10.
[5] A. Klisinska, S. Loridant, B. Grzybowska, J. Stoch, I. Gressel, Appl. Catal. A: Gen. 309 (2006) 17.
[6] G. Ramis, G. Busca, F. Bregani, P. Forzatti, Appl. Catal. 64 (1990) 259–278.
[7] B. Grzybowska-Swierkosz, Appl. Catal. A: Gen. 157 (1997) 263.
[8] N.-Y. Topsøe, Science 265 (1994) 1217.
[9] M. Calatayud, A. Beltran, et al. J. Phys. Chem. A 105 (2001) 9760.
[10] M. Calatayud, B. Mguig, C. Minot, Surf. Sci. Rep. 55 (2004) 169.
[11] M. Calatayud, C. Minot, J. Phys. Chem. B 108 (2004) 15679.
[12] O.L.J. Gijzeman, J.N.J. van Lingen, J.H. van Lenthe, S.J. Tinnemans, D.E. Keller, B.M. Weckhuysen, Chem. Phys. Lett. 397 (2004) 277.
[13] A. Klisinska, A. Hara, K. Samson, M. Witko, B. Grzybowska, J. Mol. Catal. A 210 (2004) 87.
[14] N. Magg, B. Immaraporn, J.B. Giorgi, T. Schroeder, M. Baumer, J. Döbler, Z. Wu, E. Kondratenko, M. Cherian, M. Baerns, P.C. Stair, J. Sauer, H.-J. Freund, J. Catal. 226 (2004) 88.
[15] L. Kiwi-Minsker, D.A. Bulushev, F. Rainone, A. Renken, J. Mol. Catal. 184 (2002) 223.
[16] L. Lietti, P. Forzatti, G. Ramis, G. Busca, F. Bregani, Appl. Catal. 3 (1993) 13.
[17] G.G. Cortéz, J.L.G. Fierro, M.A. Bañares, Catal. Today 78 (2003) 219.
[18] T. Bredow, E. Aprà, M. Catti, G. Pacchioni, Surf. Sci. 418 (1998) 150.

[19] J. Muscat, N.M. Harrison, G. Thornton, Phys. Rev. B 59 (1999) 15457.
[20] M.A. San Miguel, C.J. Calzado, J.F. Sanz, J. Phys. Chem. B 105 (2001) 1794.
[21] G. Kresse, J. Hafner, Phys. Rev. B 47 (1993) 558.
[22] G. Kresse, J. Hafner, Phys. Rev. B 49 (1994) 14251.
[23] J.P. Perdew, K. Burke, M. Ernzerhof, Phys. Rev. Lett. 77 (1996) 3865.
[24] J.P. Perdew, K. Burke, M. Ernzerhof, Phys. Rev. Lett. 78 (1997) 1396.
[25] G. Kresse, J. Hafner, Phys-Condens. Mater. 6 (1994) 8245.
[26] G. Kresse, D. Joubert, Phys. Rev. B 59 (1999) 1758.
[27] M. Calatayud, B. Mguig, C. Minot, Surf. Sci. 526 (2003) 297.
[28] X. Wang, I.E. Wachs, Catal. Today 96 (2004) 211.
[29] H. Si-Ahmed, M. Calatayud, C. Minot, E. Lozano-Diz, A.E. Lewandowska, M.A. Bañares, Catal. Today 116 (2007) 96.
[30] F.D. Hardcastle, I.E. Wachs, J. Phys. Chem. 95 (1991) 5031.
[31] M. Calatayud, C. Minot, J. Phys. Chem. C 111 (2007) 6411.
[32] A.E. Lewandowska, M. Calatayud, C. Minot, M.A. Bañares, in preparation.
[33] M.A. Bañares, X. Gao, J.L.G. Fierro, I.E. Wachs, Stud. Surf. Sci. Catal. 110 (1997) 295.
[34] D.E. Keller, S.M.K. Airaksinen, A.O. Krause, B.M. Weckhuysen, D.C. Koningsberger, J. Am. Chem. Soc. 129 (2007) 3189.
[35] M. Calatayud, F. Tielens, F. De Proft, Chem. Phys. Lett. 456 (2008) 59.