COMMUNICATION

A Molecular Approach for Unraveling Surface Phase Transitions: Sulfation of BaO as a Model NO_r Trap

Nikola Rankovic,^{*[a, c]} Céline Chizallet,^{*[b]} André Nicolle,^[a] and Patrick Da Costa^[c]

Understanding and modeling the way oxides interact with their environment is of crucial interest for various domains of chemistry, for example, geoscience,^[1] material science,^[2] and catalysis.^[3] Despite the great attention that basic solids have received in the past years,^[4] important questions about their reactivity still remain open.^[5] The basicity and the chemical behavior of the alkaline earth oxides is governed by the chemistry and the local environment of surface oxygens and cations.^[6] Among them, BaO stands out as a potential candidate for industrial depollution applications for its remarkable affinity to adsorb amphiphilic molecules.^[7,8] More precisely, BaO is a prominent storage material for commercial-vehicle NO_x abatement systems^[9,10] and for fuelcell applications.^[11] A challenge for its large-scale implementation is represented by sulfur poisoning, leading to BaSO₄ formation. Thus, understanding the way BaO interacts with SO₃ is of great interest for environmental chemistry, given the presence of sulfur compounds in fossil fuels and the harmful effects that SO₃ has on health, the environment, and infrastructures.^[12] First-principle modeling provides a powerful framework for describing and eventually controlling chemical reactions.^[13,3] However, no modeling study fully assessing SO₃ adsorption thermodynamics or the effect of adsorption-site topology on BaO has been previously reported. One of the first studies in the field by Pacchioni et al.^[14] targeted SO₂ adsorption on MgO and CaO. Chemisorption was found to take place by anchoring the sulfur atom to a surface oxygen atom. Density functional theory

[a]	Dr. N. Rankovic, Dr. A. Nicolle
	IFP Energies nouvelles
	1 et 4 avenue de Bois-Préau
	92852 Rueil-Malmaison (France)
	Fax: (+33)1-4752-7068
	E-mail: nikola.rankovic@ifpen.fr
[b]	Dr. C. Chizallet
	IFP Energies nouvelles
	Rond-point de l'échangeur de Solaize
	BP 3, 69360 Solaize (France)
	Fax: (+33)4-3770-2066
	E-mail: celine.chizallet@ifpen.fr
[c]	Dr. N. Rankovic, Prof. P. Da Costa
	Institut Jean Le Rond d'Alembert
	UPMC Paris 6, CNRS UMR 7190
	2 place de la gare de ceinture
	78210 Saint-Cyr-l'Ecole (France)
	Supporting information for this article is available on

the WWW under http://dx.doi.org/10.1002/chem.201103950.

(DFT) computations by Schneider et al.^[15,16] showed that both SO₂ and SO₃ adsorb as Lewis acids on a basic O_{5C} site on BaO(100) to form pyramidal-like sulfite (SO₂) and tetrahedral-like sulfate (SO₃) surface species. Similarly, Karlsen et al.^[17] performed ab inito calculations that confirmed an increasing affinity toward SO_x adsorption with increasing alkaline earth oxide basicity. Although they provide a consistent picture of SO_x chemistry on alkaline earth oxides, the existing studies only deal with low coverages, never assessing the effect of potential repulsive lateral interactions, crucial to draw a picture of the NO_x trap in realistic operating conditions.

In the present work we use periodic DFT calculations and ab initio molecular dynamics (MD) at the generalized gradient approximation (GGA) level and energies corrected from Hartree-Fock exchange. We have investigated BaSO₄ formation through SO₃ adsorption on ideal BaO(100) terrace surfaces and on two types of surface irregularities: monoatomic steps and kinks. Remarkable surface reconstruction phenomena were observed at high SO₃ coverage. The affinity of the (100) surface for SO₃ surprisingly appears to be lower than that of bulk BaO. Based on DFT results, a thermodynamic model was conceived, completing the image of BaO particle evolution in the presence of SO₃. In a broader sense, SO₃ can be regarded as a multidentate ligand in which all three O atoms together with the S atom represent coordination sites. Its reactivity is a consequence of the affinity of O atoms to coordinate a maximum number of Ba atoms and the oxophilic S atom to create a tetrahedral sulfate-like environment.

Site topology is expected to strongly influence the adsorption energy.^[18] Surface defects (structures detailed in the Supporting Information) exhibit a stronger affinity to adsorb SO_3 in comparison to the ideal (100) terraces. The molecule adsorbs over a tetracoordinate step surface oxygen atom to form a tetrahedral environment for the sulfur atom. Two SO₃ oxygen atoms fit in the crease of the step to coordinate step (Ba_{4C}) and lower-surface (Ba_{5C}) sites (Figure 1), leading to a remarkable stability of the adsorbed state with the adsorption energy $\Delta_{ads}U$ of -513 kJ mol^{-1} . The presence of a second SO₃ molecule per supercell leads to saturation of the O_{4C} sites. Lateral interactions of two adjacent SO₃ molecules on the step lower the adsorption energy for the second molecule to -425 kJ mol^{-1} . A subsequent MD on the saturated step does not alter the results obtained for a static optimization. Surface sulfate is slightly more stable

© 2012 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

🕅 WILEY 师

These are not the final page numbers!



Figure 1. SO_3 differential adsorption energies and optimized geometries on various BaO surfaces as a function of the fractional coverage. Enlarged structures of the insets are available in Supporting Information.

 $(-531 \ kJ \ mol^{-1})$ over an intrinsically more reactive kink O_{3C} site.

When adsorbed over a (100) terrace at low coverage (0.125 ML; ML = monolayer), the most stable (-484 kJ mol⁻¹) adsorption mode corresponds to a sulfate-like species in which the electrophilic S atom sits above an O_{5C} center. Additional interactions with Ba_{5C} orient the molecule in such a way that two out of three O atoms are slightly rotated away from the Ba_{5C} sites. Our findings are in line with literature data on SO₃ adsorption over O_{5C}.^[15,17]

The rationale for exploring higher SO₃ surface coverages is based on the high adsorption energy obtained at 0.125 ML. Once on the surface, we observe that SO₃ can penetrate and restructure its environment to form amorphous bulk BaSO₄. We gradually increased the number of adsorbed molecules to explore geometries and energies for various fractional coverages (0.25, 0.5, 0.75 and 1 ML). When more than one molecule adsorbs simultaneously, it is possible to imagine several co-adsorption structures. For the case of two molecules co-adsorbed on the supercell (0.25 ML), we conclude that the most stable conformation is the one in which two SO₃ molecules are adsorbed onto two neighboring O_{5C} sites (Figure 1). The (100) terrace is not reconstructed yet, and the adsorption energy of -434 kJ mol⁻¹ per SO₃ molecule leading from 0.125 to 0.25 ML is about 50 kJ mol⁻¹ higher compared to the adsorption on bare surface.

With an increase in fractional coverage, a former (100) terrace undergoes radical structural transformations. When four SO₃ molecules are co-adsorbed per cell (0.5 ML), the initial geometry optimization yields a stable structure in which SO₃ molecules form a square around a barium ion that is extracted from the surface (Figure 2). A subsequent MD simulation leads to the final reconstructed state with an adsorption energy of -423 kJ mol⁻¹ per SO₃ molecule for the 0.25 to 0.5 ML transition. In this most stable configuration, three Ba atoms are extracted and two S atoms have diffused at the surface level. These are the beginnings of a surface versus bulk sulfation transition.

MD calculations were repeated for higher fractional coverages of 0.75 and 1 ML. Interestingly, for the stoichiometric SO₃ coverage of 1 ML, all attempts to simulate a (100) surface entirely covered with SO₃ were unsuccessful, leading to a desorption of one or more SO₃ molecules from the surface. We overcame the steric hindrance by constructing the upper layers as a result of an epitaxial growth of bulk BaSO₄ on the top of the BaO(100) surface (Figure 2). Adsorption energies given in Figure 1 suggest that from a thermodynamic point of view, adsorbing SO₃ onto surface terraces will lead to radical surface reconstruction and the





Figure 2. Side view of the geometries obtained after SO_3 adsorption on BaO(100) at 0.5 ML (upper) and 1 ML (lower). Left: initial geometries, middle: first geometry optimization, right: quenched geometries after MD.

BaO(100)–SO₃ system will tend to stabilize at stoichiometric coverage of $\theta_{SO_3}=1$ ML. In other words, all intermediary coverages are metastable.

To illustrate and compare relative stabilities of different surface and bulk states, we built a phase diagram for the SO_3 -BaO-BaSO₄ system (Figure 3). A critical discussion of the temperature/pressure conditions at which phase transitions occur is given in Supporting Information. This approach reveals that, upon exposure to SO_3 , surface irregular-

COMMUNICATION

ities (kinks and steps) react at the earliest stage. Typically, at $P_{SO_3} = 10^{-10}$ bar, kinks and steps (0.5 ML) are poisoned at temperatures lower than 1350 K. A further increase in SO₃ partial pressure (or a decrease in temperature at constant P_{SO}) leads to restructuring of (100) terraces. However, at this stage, bulk BaSO₄ is thermodynamically more stable than bulk BaO, meaning that the SO₃ ligand prefers encapsulated (concave) bulk environments rather than flat surfaces. Thus, the reconstructed (100) surface is only a metastable intermediate leading to bulk BaSO₄. Step saturation is observed as the final stage of sulfation. In the operating conditions of typical fossil-fuel combustion (10 ppm S, 623-773 K), BaSO₄ is more stable than BaO, leading to the deactivation of the storage material. Thermal desulfation is proposed as one of the regeneration techniques requiring high temperatures (>873 K).^[19] It first leads to a desorption of SO₃ from saturated steps. Subsequently, a decomposition of bulk BaSO₄ to BaO and SO₃ takes place. Surface irregularities, however, are more resistant to SO₃ desorption and remain sulfated after bulk BaSO₄ has decomposed to BaO.

Because of the great stability of bulk BaSO₄ compared to bulk BaO, the role of the (100) terraces is to channel SO₃ to the core of the particle and back to the atmosphere. Our calculations suggest that the oxide–sulfate reconstruction is initiated by the terraces rather than the defects (which do not induce any reconstruction). Therefore, a metastable state in which (100) surfaces are sulfated with BaO as bulk phase only has physical meaning when increasing P_{SO_3} . For the reverse route, SO₃ desorption follows the species thermodynamic stabilities. This dynamic behavior is depicted in



Figure 3. Left: BaO surface and bulk evolution as a function of SO₃ partial pressure and temperature and a comparison with standard operating conditions of a fossil-fuel exhaust. Experimental thermal desulfation conditions (T > 873 K, $P_{SO_3} < 10^{-5}$ bar) are illustrated for comparison. Right: Evolutive model of a BaO particle during sulfation (filled arrows, P_{SO_3} increase/T decrease) and desulfation (white arrows, P_{SO_3} decrease).

Chem. Eur. J. 2012, 00, 0-0

© 2012 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

These are not the final page numbers! 77

www.chemeurj.org

Figure 3 (right), representing an evolution of a BaO particle during sulfation and desulfation.

In summary, we demonstrate a strong affinity of BaO to adsorb SO_3 leading to remarkable surface reconstructions. We propose a thermodynamic model describing the evolution of a BaO particle into $BaSO_4$ through hysteresis of a metastable intermediary. The phase transition is suggested to occur via terraces and not via defects, even if the latter intrinsically interact more strongly with SO_3 . These findings are important for understanding the way SO_3 poisons the adsorbing material and developing more resistant catalyst formulations.

Computational Methods

Periodic DFT calculations were performed in the framework of the GGA-PW91 functional,^[20] as implemented in VASP 4.6 package.^[21,22] The interaction between core and valence electrons was described by the projector augmented waves (PAW) approach,^[23] with a cutoff energy of 400 eV. The convergence criterion for the electronic self-consistent field (SCF) loop was set to 5×10^{-6} eV and geometry optimizations performed until the convergence on forces (0.02 eVÅ⁻¹) was reached. A dipolar correction along the direction perpendicular to the slab was applied. After performing the initial structural relaxation, velocity-scaled molecular dynamics were performed to efficiently investigate surface reconstruction. (see Supporting Information for details). Reaction energies calculated from geometries optimized at the GGA level were rectified at constant geometry by employing the range-separated hybrid Heyd–Scuseria–Ernzehof (HSE06)^[24,25] exchange-correlation functional, implemented in VASP 5.2.

We were interested in two types of values: differential adsorption energy $[\Delta_{ads}U, \text{ Eq. (1)}]$, reflecting an incremental adsorption of SO₃, and mean adsorption energy $[\Delta_{ads}^{mean}U, \text{ Eq. (2)}]$, relative to adsorption of *n* molecules on bare surface. U_{SO_3} , U_{BaO} and $U_{BaO+nSO_3}$ are the energies of SO₃, BaO, and the adsorbed states.

$$\Delta_{\rm ads} U = U_{\rm BaO+nSO_3} - U_{\rm BaO+(n-1)SO_3} - U_{\rm SO_3}$$
(1)

$$\Delta_{\rm ads}^{\rm mean} U = \frac{U_{\rm BaO+nSO_3} - U_{\rm BaO} - nU_{\rm SO_3}}{n} \tag{2}$$

Thermodynamic stability domains were drawn as a function of T and P_{SO_3} by calculating the free energy of sulfation, taking into account the chemical potential variations of SO₃ (modeled as an ideal gas) and of the condensed phases (according to approximations given in Supporting Information).

Acknowledgements

The authors are grateful to Dr. P. Raybaud (IFPEN) for help in performing Phonon calculations. This work was performed using HPC resources from IFPEN and GENCI-CINES (Grant 2011-ifp6134).

Keywords: alkaline earth oxides \cdot barium \cdot density functional calculations \cdot SO₃ adsorption \cdot surface chemistry

- G. E. Brown, V. E. Henrich, W. H. Casey, D. L. Clark, C. Eggleston, A. Felmy, D. W. Goodman, M. Grätzel, G. Maciel, M. I. McCarthy, K. H. Nealson, D. A. Sverjensky, M. F. Toney, J. M. Zachara, *Chem. Rev.* 1999, 99, 77.
- [2] R. P. Stoffel, C. Wessel, M.-W. Lumey, R. Dronskowski, Angew. Chem. 2010, 122, 5370; Angew. Chem. Int. Ed. 2010, 49, 5242.
- [3] J. K. Norskov, T. Bligaard, J. Rossmeisl, C. H. Christensen, Nat. Chem. 2009, 1, 37.
- [4] A. Corma, S. Iborra, Adv. Catal. 2006, 49, 239.
- [5] H. Lauron-Pernot, Catal. Rev. Sci. Eng. 2006, 48, 315.
- [6] M. Che, A. J. Tench, Adv. Catal. 1982, 31, 77.
- [7] C. H. Kim, G. Qi, K. Dahlberg, W. Li, Science 2010, 327, 1624.
- [8] B. M. Weiss, K. B. Caldwell, E. Iglesia, J. Phys. Chem. C 2011, 115, 6561.
- [9] S. Roy, A. Baiker, Chem. Rev. 2009, 109, 4054.
- [10] P. Granger, V. I. Parvulescu, Chem. Rev. 2011, 111, 3155.
- [11] L. Yang, Y. Choi, W. Qin, H. Chen, K. Blinn, M. Liu, P. Liu, J. Bai, T. Tyson, M. Liu, *Nat. Commun.* **2011**, *2*, 357.
- [12] W. W. Kellogg, R. D. Cadle, E. R. Allen, A. L. Lazrus, E. A. Martell, *Science* **1972**, 175, 587.
- [13] M. Salciccioli, M. Stamatakis, S. Caratzoulas, D. G. Vlachos, *Chem. Eng. Sci.* 2011, 66, 4319.
- [14] G. Pacchioni, J. M. Ricart, F. Illas, J. Am. Chem. Soc. 1994, 116, 10152.
- [15] W. F. Schneider, J. Phys. Chem. B 2004, 108, 273.
- [16] W. F. Schneider, J. Li, K. C. Hass, J. Phys. Chem. B 2001, 105, 6972.
 [17] E. J. Karlsen, M. A. Nygren, L. G. M. Pettersson, J. Phys. Chem. B 2003, 107, 7795.
- [18] C. Chizallet, G. Costentin, M. Che, F. Delbecq, P. Sautet, J. Phys. Chem. B 2006, 110, 15878.
- [19] D. H. Kim, J. Szanyi, J. H. Kwak, T. Szailer, J. Hanson, C. M. Wang, C. H. F. Peden, J. Phys. Chem. B 2006, 110, 10441.
- [20] J. P. Perdew, Y. Wang, Phys. Rev. B 1992, 45, 13244.
- [21] G. Kresse, J. Hafner, Phys. Rev. B 1994, 49, 14251.
- [22] G. Kresse, J. Furthmüller, Comput. Mater. Sci. 1996, 6, 15.
- [23] G. Kresse, D. Joubert, Phys. Rev. B 1999, 59, 1758.
- [24] J. Heyd, G. E. Scuseria, M. Ernzerhof, J. Chem. Phys. 2003, 118, 8207; Corrigendum: J. Heyd, G. E. Scuseria, M. Ernzerhof, J. Chem. Phys. 2006, 124, 219906.
- [25] J. Heyd, G. E. Scuseria, J. Chem. Phys. 2004, 121, 1187.

Received: December 16, 2011 Published online: ■■ ■, 0000

www.chemeurj.org © 2012 Wiley-

COMMUNICATION



SO₃-induced surface reconstruction: The SO₃ molecule as a multidentate ligand induces remarkable surface reconstruction phenomena on alkaline earth oxide surface. Using ab initio computations, adsorption properties are derived to elucidate the thermodynamics of the SO₃-BaO system.

Surface Chemistry

N. Rankovic,* C. Chizallet,* A. Nicolle, P. Da Costa

A Molecular Approach for Unraveling Surface Phase Transitions: Sulfation of BaO as a Model NO_x Trap

