

Adsorption of Trace Elements and Sulfur Dioxide on Ca-Based Sorbents

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With the reduction of natural gas and petroleum sources and subsequent increases in their costs, energy from coal is becoming increasingly popular. However, coal is not a clean technology, so with this demand comes a demand to make this energy source more environmentally friendly. Trace elements, such as mercury, arsenic, and selenium, are highly volatile and are known to escape into the atmosphere from coal combustion flue gas.

Ab initio quantum mechanical tools were used to explain the adsorption mechanism of trace elements on a calcium oxide surface in the gas phase. Density functional theory was used to calculate binding energies of elemental mercury, oxidized mercury, selenium dioxide and sulfur dioxide molecules with a calcium oxide sorbent using the software programs, Gaussian 03 and Vienna *Ab initio* Simulation Package (VASP). Super cells with periodic boundary conditions versus cluster approaches were compared to illustrate the potential mechanisms of adsorption. Further, effects of hydrogen chloride on the

adsorption of oxidized mercury are investigated to determine how hydrogen chloride plays a role in activating the calcium oxide surface to increase potential trace element adsorption.

Our predictions calculated in the gas phase indicate SO_2 , HgCl_2 and SeO_2 molecules are capable of adsorbing onto calcium oxide and hydrated calcium oxide surfaces. However, elemental mercury does not adsorb onto calcium oxide unless it is first oxidized. Moreover, HCl inhibits the adsorption of HgCl_2 on the CaO surface. These results are in good agreement with the current data in the literature.

Keywords: mercury, selenium, hydrogen chloride, calcium oxide, DFT, *ab initio*

Introduction

The American Coal Ash Association (ACAA) estimated that 122.5 millions tons of coal utilization by-products (CUB) were produced in the United States in 2004 and only 35 % of the CUBs were recycled to concrete (fly ash), structural fill material (bottom and fly ash) and wallboard manufacture (FGD gypsum) [1]. CUBs contain hazardous trace elements such as mercury, selenium, arsenic, boron, aluminum, cadmium and lead. Among all of these trace elements mercury causes the highest concerns, since it has more hazardous effects when compared to the others. Within the United States alone, in 1996 [2] 75 tons per year of mercury was emitted from coal burning with only 40% of mercury being removed. Regulations for mercury emissions are getting stricter and in 2005, the Environmental Protection Agency adopted the Clean Air Mercury Rule to reduce

mercury emissions from coal-fired power plants [3] which will ultimately reduce the US emissions of mercury by 70 %.

With these expectations, companies using CUBs started searching ways to remediate mercury from their products. The most economical way to increase mercury retention is to develop existing particulate control devices and flue gas desulfurization (FGD) scrubbers [4]. One of the current technologies uses calcium-based sorbents to capture trace elements along with sulfur dioxide in wet chemical scrubbers. The spent calcium oxide is then treated for recycling in the manufacture of wallboard. However, recycling of flue gas desulfurization (FGD) waste byproducts could be a critical environmental concern since it may release the trace elements during the treatment stage; therefore, it is required to develop a system for capturing mercury and selenium, and sulfur selectively. Kellie et al. reported that mercury could be found in both the elemental and oxidized forms in the flue gas depending upon the coal chlorine content or the amount of hydrogen chloride (HCl) in the flue gas. It is known that elemental mercury vapor is the dominant form compared to the oxidized form; however, elemental mercury reacts with acid species to form oxidized mercury [5] and Gullet et al. [6] verified in their experimental work that alkali earth metals have the capacity to adsorb gaseous oxidized mercury (Hg^{+2}). On the other hand, Sakai et al. [7] mentioned SO_x and NO_x inside the coal combustion flue gas could be adsorbed by calcium-based sorbents. In addition to mercury, other trace elements such as selenium and arsenic are captured by calcium-based sorbents as well. Diaz-Samoano et al. [8] concluded that arsenic and selenium could be removed from the flue gas environment at temperatures between 350 and 750 °C

when limestone sorbents are used. Accordingly, in flue gas remediation processes SO_x , NO_x , mercury, arsenic and selenium are retained simultaneously inside wet or dry scrubbers and the selective capture of these trace species has yet to be achieved. In addition it has been known that HCl has a big effect on mercury oxidation, however HCl effects on adsorption of HgCl_2 on calcium oxide (CaO) continues to remain an unresolved issue.

There are many experimental studies on the adsorption of sulfur dioxide (SO_2), mercury and selenium on calcium-based sorbents and how HCl affects the adsorption of these trace elements. Jozewicz et al. [9] expressed that SO_2 can be adsorbed by calcium hydroxide (Ca(OH)_2) or calcium oxide sorbents. Moreover, when silica or alumina is mixed with calcium sorbents, high SO_2 adsorption capacity can be achieved since a larger surface area is available. Lee et al. [10] studied SO_2 adsorption of sorbent materials obtained from coal fly ash, coal bottom ash, oil palm ash and incinerator ash. They used a BET-specific surface area analyzer to investigate their adsorption capacity and concluded that Ca-based sorbents have the ability to adsorb SO_2 . Furthermore, a bench-scale mechanistic study conducted by Gullet et al. [6] indicated that alkaline earth metal sorbents are capable of capturing mercuric chloride (HgCl_2). They explained the reason for adsorption is due to Lewis acid/base and van der Waals interactions occurring between the surface and adsorbent species. Another possible reason is due to the formation of surface complexes with the interaction of acidic sites (Ca^{2+}) and basic sites (O^{2-}). Ghosh-Dastidar et al. [11] investigated mineral sorbents used to capture selenium inside the flue gas and proved that the adsorption mechanism of selenium dioxide (SeO_2)

by a CaO sorbent is not a physical adsorption, but rather a chemical reaction between SeO_2 and CaO. In addition, Hutson et al. [5] conducted bench-scale experiments to investigate whether HgCl_2 has effects on surface mechanisms in the sorbent. They declared calcium to be a mercury capture inhibitor with HCl. Also, Niksa et al. [4] through a statistical analysis, studied Hg retention and found that Hg remediation is sensitive to HCl levels. However, none of these studies investigated the adsorption energies of flue gas components on CaO.

There has been only one theoretical study performed on mercury and selenium adsorption with calcium-based sorbents. Pacchioni et al. [12] used a cluster approach supported by point charges to study the adsorption of CO_2 and SO_2 at the surfaces of MgO and CaO. They calculated interaction energies of the structures by changing the distance between sorbent and adsorbent materials. They have illustrated that CaO reacts with SO_2 to form a sulfite species. In addition, there are some other previous studies which investigate CaO clusters. Wang et al. [13] studied the stability of CaO clusters using the Chen-Mobius lattice inverse technique. They concluded that the bigger the cluster size, the more stable the clusters are. Malliavin et al. [14] also showed cubelike $(\text{CaO})_n$ clusters to have improved stability. Nonetheless, none of the previous studies have investigated the adsorption behavior of elemental mercury (Hg^0), oxidized mercury, and SeO_2 on CaO sorbents. Therefore, this will be the first theoretical research study to examine the adsorption of trace elements on CaO, hydrated CaO sorbents and how HCl affects the adsorption of HgCl_2 .

The purpose of this study is to understand mechanisms associated with adsorption of SO₂, Hg⁰, HgCl₂ and SeO₂ on CaO (001) and hydrated CaO (001) surfaces on a molecular level and to see the effects of HCl on HgCl₂ adsorption. Both cluster and periodic calculations have been performed to calculate binding energies and a comparison has been made from a modeling point of view.

Computational Methodology

Calculations for obtaining binding energies of trace elements on calcium oxide surfaces have been done in both the Gaussian 03 software package [15] and the Vienna *Ab Initio* Simulation Package (VASP) [16-18].

Cluster calculations have been carried out using the Gaussian 03 simulation package by using Density Functional Theory (DFT). Because of its simplicity and accuracy, a DFT-based algorithm can successfully be applied for ionic materials [19-21]. Moreover, Konigstein et al. compared calculated and experimental binding energies of metal peroxides concluding density functional theory techniques have the best prediction for peroxide bonds. Furthermore, Effective Core Potentials (ECP), which describe the inner core electrons and semi-empirically accounts together for relativistic effects, have been preferred to define atoms having a larger number of electrons such as mercury and selenium. Hence, Beck's three-parameter functional with a Lee-Yang-Parr gradient-corrected correlation functional (B3LYP) with an LANL2DZ basis set was used to optimize the structures and to predict the chemical properties.

As for the periodic calculations, the lattice constant of CaO and adsorption energies were estimated by a DFT optimization using the Vienna *Ab Initio* Simulation Package (VASP) in which supercells were used with periodic boundary conditions in all three principal axes to simulate a crystal lattice. Simulations were carried out using a unit cell consisting of eight atoms. Electron exchange correlation functionals were calculated using a Perdew and Wang [22] approximation which was described as a generalized gradient approximation (GGA). A plane wave expansion with a cutoff of 520 eV was used in all of the calculations. For the calculation of total energies residual minimization method for relaxation was performed with a 4x4x4 k points created by Monkhorst-Pack mesh [23]. In addition, for the relaxation of the structure, a Gaussian-smearing width is taken as 0.2 eV to obtain more accuracy. Geometry relaxation calculations employed the conjugate-gradient (CG) algorithm until the forces on the unconstrained atoms were less than 0.03 eV/Å.

Results and Discussion

1. Cluster Calculations

Cluster calculations have been completed using the Gaussian 03 software package. Before calculating the binding energies of SO₂, Hg, HgCl₂ and SeO₂ on a calcium oxide surface, it is important to first optimize the calcium oxide structure. Calcium oxide has a face centered cubic (fcc) structure; therefore, cubic structures including both nine calcium and oxygen atoms were located according to this crystal structure. The DFT-based B3LYP/LANL2DZ level of theory was used to optimize 18 atoms. The energy of the CaO structure was found to be -1000.98 Hartrees with a bond distance between calcium

and oxygen atoms of 2.37 Å compared to the experimental bond distance is 2.406 Å [24]. Furthermore, the optimized structure of calcium oxide was used to calculate binding energies and bond distances of SO₂, HgCl₂, Hg⁰ and SeO₂ on the CaO surface. Binding energies of flue gas components on the CaO surfaces were calculated according to the formula shown in equation 1,

$$\text{Binding Energy} = E(\text{AB}) - [E(\text{A}) + E(\text{B})] \quad (1)$$

where AB, A and B represents adsorbate/substrate, adsorbate and substrate system respectively. Adsorption of SO₂ has been investigated in three different ways. First, oxygen atoms of the sulfur dioxide molecule were bonded to calcium atoms located at the center and edge sites of the cluster, represented in Figure 1a. Second, oxygen atoms of the sulfur dioxide molecule were bonded to the edge sites of the calcium atoms in the cluster, represented in Figure 1b. Lastly, the CaO cluster size increased to 27 atoms and oxygen atoms were bonded to the calcium atoms located at the edge sites, represented in Figure 1c. Optimized structure energetics, binding energies and bond distances of SO₂ adsorbed on CaO clusters were calculated and illustrated in Table 1-2. Since lower ground state energy was obtained in the second complex considered, it was concluded that the SO₂ molecule would prefer to bind to oxygen atoms located at the edge sides of the CaO cluster. As the cluster size increases, calculations become more computationally expensive so that the cluster size was restricted to 27 atoms. This investigation is the first theoretical study that has been reported for calculating binding energies and bond distances of CaO-SO₂ structures. However, Malliavin et al. [14] reported that CaO cubelike clusters have better stability and Wang et al. [13] expressed that the binding energies of CaO decrease as the cluster size increases. These studies are in good

agreement with the results as presented in Table 1-2. However, it would be wise to compare binding energies with periodic calculations as well.

Binding energies of Hg^0 , HgCl_2 and SeO_2 were also calculated. It has been found that Hg^0 is not adsorbed by calcium-based sorbents. It is known that elemental mercury is not soluble in water and cannot be adsorbed by calcium based sorbents [4, 6] until it is oxidized. Calculations involving SO_2 have shown that edge site atoms in the cluster can make stronger bonds than atoms located at the center of the cluster. Hence, HgCl_2 and SeO_2 molecules were adsorbed by edge site atoms in a CaO cluster and their results are illustrated in Table 3.

2. Periodic Calculations

Periodic calculations have been performed using the software, VASP. A unit cell was prepared according to a CaO space group Fm3m to represent the entire CaO structure. Energies of the CaO structure using different lattice constants were calculated to find the minimum energy of the structure. Further, ground state energies have been obtained from plots of energy versus lattice constants as illustrated in Figure 2, by choosing the minimum energy. The lattice constant of the CaO structure was found to be 4.7731 Å, where Mehl et al. [25] declared the lattice constant of CaO as 4.81 Å in their experimental work. Accordingly, the error between the experimental and theoretical lattice constant was less than 1%, which will make adsorption calculations more reliable in the future steps.

The adsorption of SO_2 on the CaO (001) and hydrated CaO (001) surfaces have been investigated using a periodic structure. A unit cell of the periodic CaO structure including a SO_2 molecule, and replication of this unit cell in x , y , z directions are shown in Figure 3. The binding energies of SO_2 on CaO and hydrated CaO sorbents, represented in Table 4, have been calculated to be -26.35 kcal/mol and -24.07 kcal/mol, respectively. Examination of these strong binding energies indicate chemisorption behavior, which suggests that a reaction might occur between SO_2 and CaO . An experimental study conducted by Lee et al. [10] indicated that sorbents prepared from coal bottom ash, incinerator ash and oil palm ash have good SO_2 adsorption capacity. In addition, these results agree with the theoretical results of Pacchioni et al. [12], who have reported that SO_2 reacts with CaO .

Binding energies of Hg^0 , HgCl_2 and SeO_2 on CaO (001) and hydrated CaO (001) surfaces have also been predicted. It has been found that binding energy of elemental mercury on CaO and hydrated CaO sorbents are -2.89 kcal/mol and -3.59 kcal/mol. As reported in cluster calculations, Hg^0 should be oxidized first in order to be captured. Therefore, this is consistent with the literature, since this small binding energy might decrease when real process conditions considered. Moreover, HgCl_2 and SeO_2 have been found to be captured on the CaO (001) surface. Binding energies have been obtained to be -8.51 kcal/mol and -38.71 kcal/mol, respectively. Investigating the binding energies of HgCl_2 and SeO_2 on hydrated CaO , it has been shown that binding energies of those were changed slightly and found to be -5.32 kcal/mol and -38.4 kcal/mol. According to these results, HgCl_2 does not bond strongly with CaO and the adsorption mechanism of HgCl_2

on the CaO sorbent can be considered as physisorption. An exact comparison with literature cannot be done, but an experimental study conducted by Gullet et al. [6] reported that HgCl_2 can be captured by Ca-based sorbents. Since higher binding energy has been found between SeO_2 and CaO, it is clear that SeO_2 can react with CaO. This result is consistent with experiments of Ghosh-Dastidar et. al. where it has been observed that metal capture occurs between SeO_2 and CaO. It has been concluded that sulfur and selenium bind with oxygen molecule located on CaO surface and adsorbed strongly. However in hydrated CaO, hydroxyl ($-\text{OH}$) groups play a significant role on adsorption. Sulfur and selenium interacts with $-\text{OH}$ groups and captured by CaO surface.

The adsorption of HgCl_2 on HCl added to a CaO unit cell has been considered as well. The binding energy of HgCl_2 on HCl added to the CaO (001) surface has been calculated to be -6.06 kcal/mol. It has been found that HCl decreased the binding energy of HgCl_2 by 2 kcal/mol. As a comparison with the literature, a decrease in the binding energy is consistent with a Hutson et al. [5] study where they have concluded that CaO becomes a Hg-capture inhibitor with the addition of HCl.

Conclusion

The adsorption of SO_2 , Hg^0 , HgCl_2 , and SeO_2 on the CaO (001) and hydrated CaO (001) surfaces have been studied through both cluster and periodic approaches. The effect of HCl on mercury adsorption has been investigated.

Cluster calculations were unable to yield reasonable accuracy for crystal structures while they were useful for predicting trends. It would be better to represent clusters with a larger number of atoms, but in this case it would become computationally expensive. Thus, periodic calculations were more reliable in representing the crystal surface.

It can be concluded that SO_2 and SeO_2 are strongly captured by CaO sorbents and that chemisorption is the likely adsorption mechanism. In addition, elemental mercury was not adsorbed on the CaO surface until it was oxidized. The oxidized form of mercury, HgCl_2 , was captured by CaO sorbents and the mechanism of the adsorption has concluded to be physisorption. In addition, it has been found that HCl has inhibition effects on the adsorption of HgCl_2 on the CaO (001) surface.

References

1. 2004 *Coal Combustion Product Survey*. American Coal Ash Association.
<http://www.ACAA-USA.org>
2. Gustin, M. S.; Ladwig, K. Assessment of the Significance of Mercury Release from Coal Fly Ash. *J. Air Waste Manage. Assoc.* **2004**, 54, 320-330.
3. U.S. Environmental Protection Agency. Fact Sheet: EPA's Clean Air Mercury Rule. **2005**.
4. Niksa, S.; Fujiwara, N. The Impact of Wet FGD Scrubbing on Hg Emissions From Coal-Fired Power Stations. Proc. U.S. EPA-DoE-EPRI Combined Power Plant Air Pollutant Control Symp: The MEGA Symp, **2004**, Washington, DC.
5. Hutson, N.; Singer, C.; Richardson, C. Karwowski, J.; Sedman, C.; Practical Applications from Observations of Mercury Oxidation and Binding Mechanism. Proc. U.S. EPA-DoE-EPRI Combined Power Plant Air Pollutant Control Symp: The MEGA Symp, **2004**, Washington, DC.
6. Gullet, B. K.; Ghorishi, B.; Keeney, R.; Huggins, F. E. Mercuric Chloride Capture by Alkaline Sorbents, Proc. Air & Waste Management Association 93rd. Annual Meeting; **2000**, Salt Lake City, UT.
7. Sakai, M.; Su, C.; Sasaoka, E. Simultaneous Removal of SO_x and NO_x Using Slaked Lime at Low Temperature. *Ind. Eng. Chem. Res.* **2002**, 41, 5029-5033.
8. Diaz-Somoano, M.; Martinez-Tarazona, M.R. Retention of Arsenic and Selenium Compounds Using Limestone in a Coal Gasification Flue Gas. *Environ. Sci. Technol.* **2004**, 38, 899-903.

9. Jozewicz, W; Chang, JCS; Brna, T; Sedman, C. Reactivation of Solids from Furnace Injection of Limestone for SO₂ Control. *Environ. Sci. Technol.* **1987**, 21, 664.
10. Lee, K. T.; Bhatia, S.; Mohammed, A. R. Preparation and Characterization of Sorbents Prepared from Ash (Waste Material) for Sulfur Dioxide (SO₂) Removal. *J. Mater Cycles Wate Manag.* **2005**, 7, 16-23.
11. Ghosh-dastidar, A.; Mahuli, S.; Agnihotri, R.; Fan, L.-S. Selenium Capture Using Sorbent Powders; Mechanism of Sorption by Hydrated Lime, *Environ. Sci. Technol.* **1996**, 30, 447-452.
12. Pacchioni, G.; Ricart, J. M.; Illas, F. Ab Initio Cluster Model Calculations on the Chemisorption of CO₂ and SO₂ Probe Molecules on MgO and CaO (100) Surfaces. A Theoretical Measure of Oxide Basicity. *J. Am. Chem. Sci.* **1994**, 116, 10152-10158.
13. Wang, C.; Zhang, S.; Chen, N.-X. Ab initio Interionic Potentials for CaO by Multiple Lattice Inversion, *Journal of Alloys and Compounds* **2005**, 338, 195-207.
14. Malliavin, M.-J.; Coudray, C. Ab Initio Calculations on (MgO)_n, (CaO)_n, and (NaCl)_n Clusters (n=1-6). *J. Chem. Phys.* **1997**, 106, 6.
15. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery Jr., R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, Ö. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K.

- Morokuma, P. Salvador, J. J. Dannenberg, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, A. G. Baboul, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komáromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, J. L. Andres, C. Gonzalez, M. Head-Gordon, E. S. Replogle, and J. A. Pople, Gaussian 98 (Gaussian, Inc., Pittsburgh, PA, **1998**).
16. Kresse, G.; Hafner, J. Ab Initio molecular Dynamics for Open-Shell Transition Metals. *Phys. Rev. B* **1993**, 48, 13 115.
 17. Kresse, G.; Hafner, J. Ab Initio Molecular-Dynamics Simulation of the Liquid-Metal- Amorphous- Semiconductor transition in Germanium. *Phys. Rev. B* **1994**, 49, 14251-69.
 18. Kresse, G.; Furthmuller, J. Efficiency of Ab-Initio Total Energy Calculations for Metals and Semiconductors using a Plane-Wave Basis Set. *Comput. Mater. Sci.* **1996**, 6, 15-50.
 19. Bates, S. P.; Kresse, G.; Gillan, M. J. The adsorption and dissociation of ROH molecules on TiO₂ (110). *Surface Sciences* **1998**, 409, 336-349.
 20. Lindan, P. J. D.; Harrison, N. M.; Gillan M. J. Mixed Dissociative and Molecular Adsorption of Water on the Rutile (110) Surface. *Phy. Rev Lett.* **1998**, 80, 762.
 21. Refson, K.; Wogelius, R. A.; Frase, D. G.; Payne, M. C.; Lee, M. H.; Milman, V. Water chemisorption and reconstruction of the MgO Surface. *Phs. Rev. B* **1995**, 52, 15.

22. Perdew, J. P.; Wang, Y. Accurate and simple analytic representation of the electron-gas correlation energy. *Phys. Rev. B* **1992**, 45, 13 244.
23. Monkhorst, H.; Pack, J. D. Special points for Brillouin-zone integrations. *Phys. Rev. B* **1976**, 13, 5188.
24. Konigstein, M.; Catlow, C. R. Ab Initio Quantum Mechanical Study of the Structure and Stability of the Alkaline Earth metal Oxides and Peroxides. *Journal of Solid State Chemistry* **1998**, 140, 103-115.
25. Mehl, M. J.; Hemley, R. J.; Boyer, L. L. Potential- Induced Breathing Model for the Elastic Moduli and High-Pressure Behavior of the Cubic Alkaline-Earth Oxides. *Phys. Rev. B* **1986**, 33, 8685.

Table 1. Structure and binding energies of SO₂ adsorbed CaO clusters

	Center & Edge	Two edges	
	Ca ₉ O ₉	Ca ₉ O ₉	Ca ₁₄ O ₁₃
Energy of the structure (Hartree)	-1167.46	-1167.52	-1651.87
Binding Energies (kcal/mol)	-53.94	-89.71	-77.12

Table 2. Bond distances of SO₂ adsorbed on CaO clusters

	Bond Distances (Å)		
	Center & Edge	Two edges	
	Ca ₉ O ₉	Ca ₉ O ₉	Ca ₁₄ O ₉
(O1-Ca)	2.4285	2.4386	2.4771
(O2-Ca)	2.35713	2.4404	2.3616

Table 3. Structure and binding energies of HgCl₂ and SeO₂ adsorbed on CaO clusters

	HgCl ₂	SeO ₂
Energies of the structure (Hartree)	-1079.81	-1166.67
Binding Energies (kcal/mol)	-73.57	-101.39

Table 4. Binding energies of S, Hg, Se Compounds on Calcium Based Sorbents

Sorbent ►	Binding Energies (kcal/mol)	
	CaO	Hydrated CaO
Adsorbate ▼		
SO ₂	-26.34	-24.07
Hg ⁰	-2.89	-3.59
HgCl ₂	-8.5	-5.32
SeO ₂	-39.23	-38.4

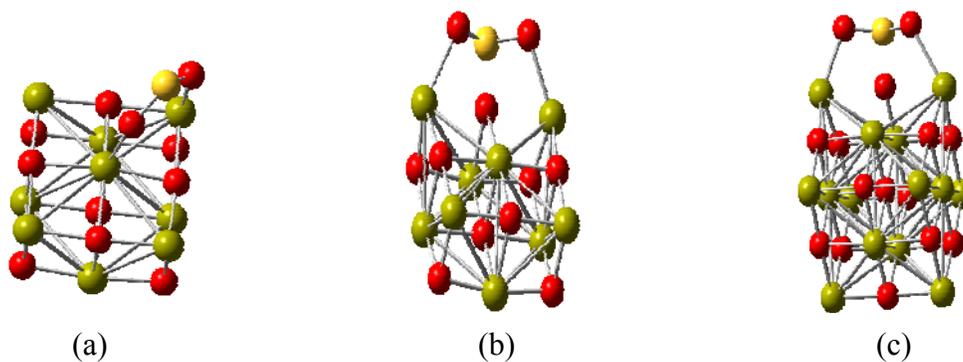


Figure 1. Optimized geometries of CaO clusters with SO₂ (a) Ca₉O₉ bonded edge and center; (b) Ca₉O₉ bonded edges; (c) Ca₁₄O₁₃

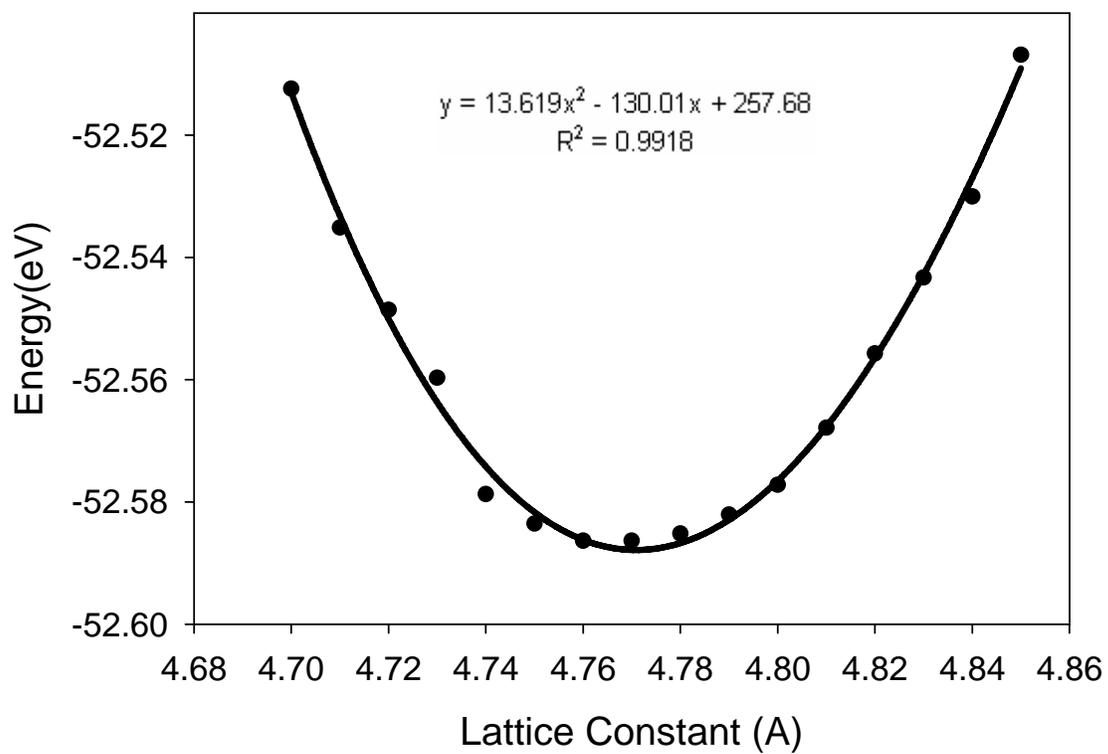


Figure 2. CaO Lattice Constant vs Energetics

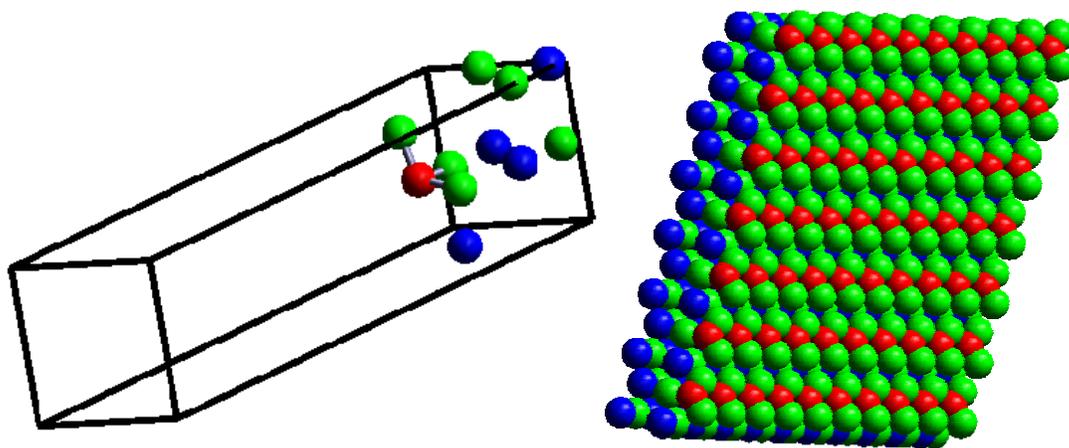


Figure 3. SO₂-CaO periodic slab complex