Surface Science 605 (2011) 818–823

Contents lists available at ScienceDirect

Surface Science

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

Surface reactions of AsH_3, H_2Se, and H_2S on the $Zn_2TiO_4(010)$ surface

Shiqiang Hao [a], Rees B. Rankin [b,c,1], J. Karl Johnson [b,c], David S. Sholl [a,*]

[a] School of Chemical & Biomolecular Engineering, Georgia Institute of Technology, Atlanta, GA 30332, USA
[b] Department of Chemical and Petroleum Engineering, University of Pittsburgh, Pittsburgh, PA 15261, USA
[c] The National Energy Technology Laboratory, Pittsburgh, PA 15236, USA

ARTICLE INFO

Article history:
Received 22 December 2009
Accepted 20 January 2011
Available online 27 January 2011

Keywords:
Density functional calculations
Hydrogen sulfide
Surface chemical reaction

ABSTRACT

Removal of toxic species such as As, Se, and S is critical to the successful implementation of high efficiency Integrated Gasification Combined Cycle (IGCC) processes for coal utilization. In this work we study the initial low-coverage surface reactions of AsH_3, H_2Se and H_2S with a regenerable sorbent, zinc orthotitanate (Zn_2TiO_4), using first principles density functional theory. AsH_3 adsorbs more preferentially on oxygen-rich (010) surfaces, while H_2Se and H_2S are more favorably bound to metal-rich (010) surfaces. We calculated the dissociation pathways and rates for each adsorbed species, finding that dehydrogenation of AsH_3, H_2Se, and H_2S should be facile on these surfaces at the high temperatures relevant for IGCC processes.

1. Introduction

The Integrated Gasification Combined Cycle (IGCC) process is a promising approach for utilization of coal for energy production with high efficiency and greatly reduced environmental impact compared to traditional pulverized coal power plants [1–3]. In the IGCC process, the cleaning of coal fuel gas prior to further processing of this gas is a crucial step. Among other contaminants, As, Se and S form volatile toxic compounds during coal gasification that remain in the gas phase at high temperature [4,5]. Although hot gas desulfurization has received extensive attention, removal of other corrosive or toxic species such as As and Se is also of great interest. Currently, multiple sorbents with different operating conditions are required to remove the various contaminant species present after coal gasification, a situation with severe implications for the complexity and cost of gas cleaning process. If a single unit operation was available for simultaneously removing multiple contaminants from coal gasification products, it could have a significant positive impact on this gas cleaning process in the overall IGCC process.

One material that has been suggested as a candidate sorbent for removal of multiple contaminants from hot gas streams is zinc orthotitanate, Zn_2TiO_4 (ZTO) [6]. ZTO is regenerable with minimal performance loss between cycles [7] and has been characterized as having higher adsorption capacity and thermal stability than single-metal oxides [7]. In describing the behavior of ZTO in reactive environments and in considering whether related materials with higher performance can be developed, it would be helpful to understand the energies and reactivities of relevant molecules on the surfaces of ZTO.

We have recently reported a series of density functional theory (DFT) calculations that make it possible to consider the reactivities of ZTO surfaces with gas phase molecules. ZTO has an inverse spinel structure, and prior to our work the ordering of Zn and Ti cations within the bulk structure was not known. We used a combination of DFT calculations and extended X-ray absorption fine structure (EXAFS) observations to determine how these cations are ordered [8]. We then used DFT to examine a large number of surface terminations of this bulk structure in order to assess which surfaces might be most relevant in applications of ZTO as a sorbent [9]. These calculations showed that the (010) surface is likely to represent a large fraction of the total surface area of ZTO crystals, and that this surface has two distinct terminations, one that is oxygen rich and the other that is metal rich. We have also reported on the adsorption properties of the atomic species H, As, S, and Se on these (010) surfaces [10].

In this paper, we examine the adsorption and decomposition of AsH_3, H_2Se, and H_2S on ZTO(010) surfaces. These species were selected to represent the gas phase species most relevant to decontamination of gas streams from coal gasification. AsH_3 has been reported to be the most common species among As-containing compounds in coal gasification product streams at temperatures of 300–500 °C [4]. The same study concluded that H_2Se is the dominant chemical form of Se in the gas phase over the temperatures range of 0–1600 °C [4]. In both cases, other chemical compounds containing As and Se may be present at lower levels in practical applications. Characterizing the surface chemistry of AsH_3 and H_2Se, however, is a reasonable initial step towards characterizing the uptake of As and Se by ZTO.

---

[*] Corresponding author.
E-mail address: david.sholl@chbe.gatech.edu (D.S. Sholl).

[1] Current address: Center for Nanoscale Materials, Argonne National Laboratory, Argonne, Illinois, 60439.

0039-6028/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.susc.2011.01.025

Achieving a full description of the uptake of trace gases from realistic gasifier mixtures is a formidable task because of the enormous number of surface (and bulk) species that would have to be considered. It is not our aim in this paper to give a comprehensive description of the adsorption of AsH_3 and H_2Se in the presence of large concentrations of CO, CO_2, H_2O and other syngas species. Rather, our more modest goal is to give fundamental information on the adsorption of AsH_3 and H_2Se under much simpler conditions that may in the long term be useful for moving towards an atomically-detailed description of the properties of ZTO in realistic settings.

2. Methods

We used density functional theory (DFT), within the generalized gradient approximation using the PW91 functional [11] with periodic boundary conditions and a plane wave basis set as implemented in the Vienna *ab initio* simulation package [12]. The all-electron projector augmented-wave (PAW) potentials [13,14] were used for all species. The Brillouin zone in reciprocal space was sampled using a Monkhorst–Pack grid with $3\times3\times1$ *k*-points. The cutoff energy for all calculations was 460 eV. Energy minima were located via geometry optimization in which the atomic positions of all unconstrained atoms were relaxed until the forces exerted on these atoms were smaller than 0.03 eV/Å. Transition states for reactive events connecting local minima on the potential energy surface were located using the nudged elastic band (NEB) method [15,16]. The vibrational frequencies of all energy minima (transition states) were calculated to verify that these states had only real frequencies (one imaginary frequency) using finite difference approximations to the Hessian matrix from displacements of each atom in the adsorbed species by 0.02 Å.

All of the surface calculations reported below are for the (010) surfaces of ZTO described in detail in our earlier work [8–10]. The slab used in these calculations contains 56 atoms with a vacuum spacing of 8.5 Å. The dimensions of the supercell in the plane of the surface were fixed by the DFT-optimized lattice constant of ZTO. The atoms in the center of the slab relative to the surface normal were constrained in their bulk-optimized positions, but all other atoms were unconstrained. As mentioned above, the (010) surface of ZTO exposes two distinct surface terminations, one rich in oxygen atoms and the other rich in metal atoms. These two surfaces are shown in Fig. 1. It is of course possible that ZTO(010) surfaces in reactive environments could contain mixtures of these two terminations. By examining the two surfaces separately in our calculations, our results give insight into the reactivity that would be possible on the full range of mixed terminations that are possible.

Because the structure of the ZTO(010) surfaces is relatively complex, searching for adsorption sites based on symmetry considerations alone, an approach that is often feasible on simpler surfaces, may be unreliable. For this reason, we followed the approach taken in our earlier calculations for atomic adsorbates [10] in which adsorbing species are initially placed in positions defined by uniform 5×5 grids on the surface unit cell. Energy minimization from each of these initial configurations was then used to construct a list of distinct energy minima for adsorption of each species. For each minimum, the molecular adsorption energy was defined by

$$E_{ads} = E_{tot} - E_{slab} - E_g, \qquad (1)$$

where E_{tot} and E_{slab} are the total energies of slabs with and without the adsorbed species present, and E_g is the total energy of molecular species in the gas phase. With this convention, negative adsorption energies define states that are energetically favorable relative to the gas phase molecule and the clean surface. This definition does not include zero point energy contributions to the molecular adsorption energies.

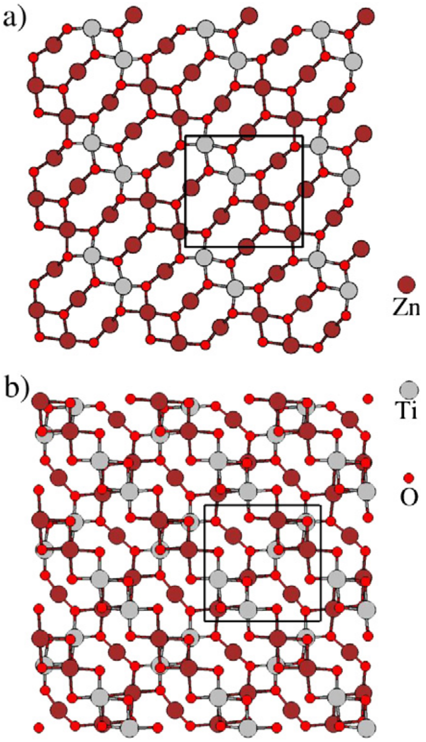

Fig. 1. Top views of the surface configuration of the (a) metal-rich and (b) oxygen-rich ZTO(010) surface. Solid lines indicate the surface unit cell.

3. AsH_3 adsorption and decomposition

The adsorption sites for AsH_3 on the two terminations of ZTO(010) were examined using 25 initial configurations on each surface as described in Section 2. This procedure identified 8 distinct adsorption minima on the metal-rich surface and 7 distinct minima on the oxygen-rich metal surfaces. The adsorption energies of these minima are listed in Table 1, and the locations of the As atom for each configuration within the surface unit cell are shown in Fig. 2. In each case, the molecule adsorbed with the As atom closest to the surface and the H atoms pointing away from the surface. The vibrational frequencies of the adsorbed states with positive adsorption energies were found to be real, indicating that an energy barrier exists to desorption from these states, even though they are energetically unfavorable relative to gaseous AsH_3.

The most favorable adsorption site for AsH_3 is on the oxygen-rich surface (site O1 in Fig. 2), where As bonds to three O atoms on the surface with one H pointing away from surface and the other two H atoms buckling towards the surface. The surface adsorption

Table 1
Calculated adsorption energies of AsH_3 on Zn_2TiO_4(010). M- and O-sites are on the upper (metal-rich) and lower (oxygen-rich) side of the surface, respectively. The positions of As in each site are illustrated in Fig. 2. The most favored site is shown in bold.

Metal-rich surface	E_{ad} (eV)	Oxygen-rich surface	E_{ad} (eV)
M1	−0.28	O1	**−0.58**
M2	−0.16	O2	0.31
M3	−0.05	O3	0.33
M4	0.33	O4	0.36
M5	0.42	O5	0.39
M6	0.44	O6	0.47
M7	0.47	O7	0.48
M8	0.48		