SURFACE SCIENCE

Surface Science Letters

Effect of γ-Al$_2$O$_3$ substrate on NO$_2$ interaction with supported BaO clusters

Lei Cheng, Qingfeng Ge *

Department of Chemistry and Biochemistry, Southern Illinois University, 142D Nickers Hall, Carbondale, IL 62901, United States

Abstract

BaO oxide is the main storage component of the NO$_x$ storage and reduction catalysts. Herein, the interactions between the NO$_2$ molecule and the unsupported as well as γ-Al$_2$O$_3$ supported BaO clusters have been studied using the first principle density functional theory calculation. Our results indicated that there is a strong synergetic effect involving both the BaO clusters and the surface of the γ-Al$_2$O$_3$ substrate toward NO$_2$ adsorption. The interfacial region between the monodispersed BaO cluster and the substrate surface that allows NO$_2$ to bond with the cluster and the surface simultaneously was shown to be optimal for NO$_2$ adsorption.
© 2007 Elsevier B.V. All rights reserved.

Keywords: Density functional theory calculations; NO$_x$ storage and reduction; Substrate effect; Barium oxide; γ-Al$_2$O$_3$

The introduction of "lean-burn" engine technology, i.e. operating an engine at a higher than stoichiometric air-to-fuel ratio, improves fuel efficiency but makes NO$_x$ removal extremely difficult. This is due to the fact that the conventional three-way catalyst has been optimized for engines operating at a stoichiometric ratio [1]. Meanwhile, the NO$_x$ emission standards are becoming more stringent worldwide. These trends have stimulated extensive research on the development of new catalysts to reduce NO$_x$ under lean-burn conditions. NO$_x$ storage-reduction (NSR) catalysis is one of the leading technologies that has been developed since early 1980s [2]. NSR is based on the cyclic operation of an engine between rich and lean conditions. During the lean cycle, excessive O$_2$ entering the exhaust pipe oxidizes NO$_x$ to NO$_2$, which is stored in the catalytic converter. The stored NO$_x$ is then released and reduced to N$_2$ during the rich cycle, before being emitted to the air. Typically, a NSR catalyst consists of Pt and BaO supported on γ-alumina, in which Pt acts as a redox catalyst and BaO as a storage component. BaO was shown to have

the best NO$_x$ storage capability among the alkaline earth metal oxides tested for NO$_x$ storage [3]. Many important fundamental and technological aspects in catalytic deNOx processes, including NSR, were summarized in two recent reviews [4,5].

Among all the steps involved in the cycle of NSR catalysis, the NO$_x$ storage step has attracted much attention. Many experimental studies on supported high surface area catalysts showed that NO$_x$ was stored in BaO mainly as a surface nitrate species, with the oxidation of NO to NO$_2$ over Pt sites preceding the storage step [6,7]. On the other hand, theoretical studies revealed a strong cooperative effect between adsorbed NO$_2$ pairs, i.e., the average adsorption energy for each NO$_2$ is greater than that of any isolated single NO$_2$ molecule when two NO$_2$ molecules were placed on neighboring Ba and O sites [8]. This effect was attributed to the charge transfer between two adsorbed NO$_2$ molecules. A similar cooperative effect was also found on the decarbonated BaCO$_3$ surface [9] – adsorption of a NO$_2$ pair causing desorption of one CO$_2$ molecule with an energy gain of 1.5 eV and complete decarbonation of the BaCO$_3$ surface (adsorption of two NO$_2$ pairs and desorption of two CO$_2$ molecules) resulted in an energy gain of 2.2 eV.

---

* Corresponding author. Tel.: +1 618 4536406; fax: +1 618 4536408.
E-mail address: qge@chem.siu.edu (Q. Ge).

Although most experimental studies focused on BaO supported on various oxide substrates and demonstrated that the nature of the support materials has strong influence on the sorption property of BaO toward NO_x [10,11], previous theoretical studies utilizing either periodic supercells or molecular clusters of BaO were almost exclusively focused on the bulk BaO surface or unsupported BaO clusters [12–15]. In the present letter, we report our results of the density functional theory (DFT) study on the substrate effect of γ-Al_2O_3 on BaO clusters towards NO_2 adsorption. We demonstrated that supporting BaO clusters on γ-Al_2O_3 greatly enhances the adsorption of NO_2 over the BaO clusters.

All the calculations were carried out using the DFT with a plane-wave basis set as implemented in the VASP code [16]. The interaction between ions and electrons is described with the projector augmented wave method [17,18], and a plane-wave cutoff energy of 400 eV was used to expand the valence electrons. The nonlocal exchange-correlation energy was evaluated by the PBE form of generalized gradient approximation (GGA) [19]. Calculations including spin-polarization have been performed for all isolated clusters and molecules and for selected slab geometries. The atomic structures were relaxed until the forces on unconstrained atoms were less than 0.05 eV/Å.

The structure of γ-Al_2O_3 has been described as a defective spinel with vacancies being created from a perfect spinel structure in order to maintain stoichiometry. In the present study, the spinel γ-Al_2O_3 model with a unit cell of 16 Al and 24 O atoms as described by Pinto et al. [20] was re-optimized using the VASP code with our chosen parameters. However, we note that the nature and distribution of the vacancies in the spinel structure have been debated, and even the validity of the spinel model has been questioned [21–24]. The γ-Al_2O_3(1 1 1) surface with low surface energies of 1.51 and 0.98 J/m^2 before and after relaxation was chosen as the substrate for supported BaO clusters. The supercell size in the z direction was set to 27.32 Å to minimize any spurious interaction originating from the periodicity. Among nine atomic layers, the atoms in the bottom four layers were frozen at their corresponding bulk positions and those in the top five layers of alumina, along with the supported BaO clusters and adsorbed NO_2 molecules when present, were allowed to relax.

For comparison, the interactions between NO_2 and unsupported BaO, $(BaO)_2$ and $(BaO)_4$, were also investigated. In these calculations, the supercell size was set to be $15 \times 15 \times 20$ Å and all the atoms in the cell were allowed to relax until the maximum force is less than 0.05 eV/Å.

We first calculated the BaO cluster structures as well as their interaction with NO_2 molecule. We examined clusters up to $(BaO)_{32}$ but only report BaO, $(BaO)_2$, and $(BaO)_4$ in the present letter. These results serve as references for NO_2 interaction with the supported BaO clusters. The average Ba-O bond lengths were calculated to be 2.02 Å, 2.30 Å, and 2.45 Å for BaO, $(BaO)_2$, and $(BaO)_4$, respec-

tively. These bond lengths are significantly shorter than the Ba-O bond length of 2.79 Å in the bulk BaO. The short Ba–O bond length in the clusters can be attributed to the significantly more covalent Ba–O interaction in the clusters than in the bulk oxide. Results from the Bader charge analysis performed using the program developed by Henkelman et al. [25] support this conclusion: the negative charges localized on the O atoms are 0.62, 1.31 and 1.36 electrons for BaO, $(BaO)_2$, $(BaO)_4$, respectively. In contrast, the corresponding value in the bulk BaO is 1.46 electrons. Clearly, the ionic nature of Ba–O bond in the clusters quickly approaches that of the bulk structure as the size of the cluster is increased.

The adsorption energies of NO_2 on unsupported clusters were calculated as the difference between total energy of the cluster plus adsorbed NO_2 molecule and the sum of the bare cluster and free NO_2 molecule. Initial structures were chosen based on chemical intuition and then allowed to optimize. The most stable structure was determined from the relaxed stable structures for each cluster size. The most stable NO_2 adsorption geometries on the three clusters are shown in Fig. 1 and the corresponding adsorption energies are listed in Table 1. In all these structures, the O atoms of NO_2 point to the cluster Ba sites. The structures and energies of $NO_2/(BaO)_n$ are generally in agreement with the previous report [12]. We note that the NO_2 adsorption energy decreases as the size of the BaO cluster increases.

We then examined the interaction of BaO clusters with the γ-Al_2O_3 support. A c(2×1) unit cell of the γ-Al_2O_3(1 1 1) slab consisting of 32 Al and 48 O atoms was used as the substrate in the calculations of supported BaO clusters. There might be low energy structures in which the cluster is partially or completely dissociated with BaO fragments or individual Ba and O atoms bound to the
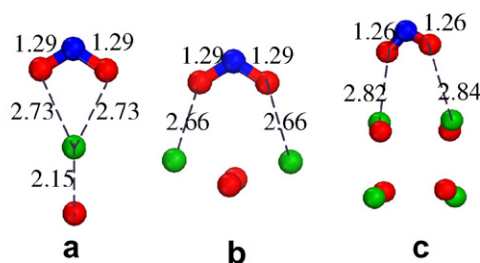

Fig. 1. The most favorable adsorption geometries of NO_2 over the unsupported (a) BaO, (b) $(BaO)_2$, and (c) $(BaO)_4$ clusters. Blue: N; Red: O; Green: Ba. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Table 1
GGA adsorption energies, E_a, of NO_2 over the unsupported and γ-Al_2O_3 supported $(BaO)_n$ clusters in the most stable configuration

	Unsupported clusters			Supported clusters		
	BaO	$(BaO)_2$	$(BaO)_4$	BaO	$(BaO)_2$	$(BaO)_4$
E_a (eV)	1.68	1.56	0.88	0.85	3.10	2.23