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Understanding the nature of surface nitrates in $BaO/\gamma\text{-}Al_2O_3$ NO_x storage materials: A combined experimental and theoretical study

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ABSTRACT

A combined experimental-theory approach was applied to unambiguously determine the nature of "surface nitrates" in $BaO/\gamma\text{-}Al_2O_3$ NO_x storage materials. High resolution scanning transmission electron microscopy images reveal that at a low BaO coverage of 2 wt% on $\gamma\text{-}Al_2O_3$ monomeric BaO units are present almost exclusively. These molecularly dispersed BaO units are concentrated on the (100) facets of the alumina crystallites, while other facets remain practically BaO-free The results of the density functional theory calculations predicted adsorption geometries for the $(BaO)_x$ ($x = 1$ and 2) units. The energetically most favorable BaO monomer and dimer units anchor to pentacoordinate Al^{3+} sites on the (100) facets of $\gamma\text{-}Al_2O_3$ in such geometries that maximize their interactions with the support surface. The calculated vibrational frequencies of the energetically most favorable nitrate species formed upon the interaction of NO_2 with the monomeric and dimeric BaO units agree remarkably well with those observed experimentally by infrared spectroscopy and identified as "surface nitrates."

1. Introduction

The special role of the interface between the active catalytic phase (metal or metal oxide) and the oxide support in determining the properties of practical catalysts has long been recognized [1]; however, it is still very poorly understood in most systems. The way the active phase is anchored onto the support surface may be especially important when the active phase is very highly dispersed. In such systems, the active oxide is likely anchored to some special sites of the support, and we may expect significant modifications in the chemical properties of these active centers by the underlying oxide support. Investigating the properties of these very highly dispersed active centers, however, is experimentally very difficult, and requires a concerted effort of both experimental and theoretical methods.

In recent years, BaO supported on $\gamma\text{-}Al_2O_3$ has attracted significant attention due to its potential application as a NO_x storage material used to treat exhaust emissions of internal combustion engines operating under lean (oxygen rich) conditions [2]. Numerous studies (both experimental and theoretical) have focused on the elucidation of the interaction of NO_2 with BaO, and the identification and characterization of NO_x species (nitrites and nitrates) formed on the BaO storage material and the $\gamma\text{-}Al_2O_3$ support as well. Density functional theory (DFT) calculations of both Schneider et al. [3–6] and Broqvist et al. [7] pointed to a pairwise, cooperative adsorption mechanism of NO_2 on BaO, resulting in the initial formation of nitrite–nitrate ion pairs. This initial cooperative NO_2 adsorption mechanism on pure BaO has recently been substantiated in an experimental study on model NO_x storage materials [8]. Very recently, we have reported the importance of a strong interaction between the BaO storage and alumina support materials in determining the adsorption mechanism of NO_2 [9]. Furthermore, the existence of two different types of nitrate species on $BaO/\gamma\text{-}Al_2O_3$-based NO_x storage/reduction systems has been evident in TPD, FTIR and ^{15}N solid state NMR studies [10]. Based on the results of these spectroscopic characterizations, we concluded that "surface" and "bulk" Ba-nitrate species formed when $BaO/\gamma\text{-}Al_2O_3$ NO_x storage materials were saturated with NO_2.

The nature of the bulk $Ba(NO_3)_2$ species on the $\gamma\text{-}Al_2O_3$ support is reasonably well understood, and its spectroscopic properties (IR vibrational frequencies of the nitrates) have been accurately predicted by DFT calculations [11,12]. On the other hand, no clear understanding has been developed on the nature of the so-called "surface nitrates."

In this contribution, we report the results of a combined experimental and DFT investigation in which we set out to understand the role of the interaction between BaO and $\gamma\text{-}Al_2O_3$ in the NO_2

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uptake process at low BaO loadings, and the characteristics of the "surface" nitrate species thus formed.

2. Experimental

The BaO/γ-Al_2O_3 NO_x storage materials with varying BaO loadings were prepared by traditional incipient wetness methods using a $Ba(NO_3)_2$ precursor, and a 200 m^2/g γ-Al_2O_3 support material from Condea. After drying the materials in air at 373 K, they were activated by calcination of 773 K in flowing dry air. The details of the IR measurements have been described in detail previously [10]. The HR-STEM images were obtained at the High Temperature Materials Laboratory located at Oak Ridge National Laboratory, using a JEOL 2200 FEF aberration corrected electron microscope.

We performed periodic DFT calculations using the Vienna ab initio simulation package (VASP) [13–16]. The projector augmented wave (PAW) method combined with a plane-wave basis and cutoff energy of 400 eV was used to describe core and valence electrons [17,18]. The Perdew–Burke–Ernzerhof (PBE) form of generalized gradient approximation (GGA) [19] was used in the calculations. The ground-state atomic geometries of NO_x/BaO/γ-Al_2O_3 systems were obtained by minimizing the forces on each atom to below 0.05 eV/Å. Spin-polarization was implemented in all calculations. The γ-Al_2O_3 bulk structure used in this work was taken from Digne et al.'s model [20]. The calculated lattice parameters of bulk γ-Al_2O_3 were $a = 5.58$ Å, $b = 8.41$ Å, $c = 8.07$ Å and $\beta = 90.53°$. These values are in good agreement with previous calculations [20,21]. As indicated in a recent experimental study [22], the Al^{3+}_{penta} sites could be the most active surface sites for anchoring deposited transition metal and metal oxide particles. Consequently, we focused on the γ-$Al_2O_3(100)$ surface in this work because the Al^{3+}_{penta} sites are only available on the γ-$Al_2O_3(100)$ surface.

The γ-$Al_2O_3(100)$ surface was modeled as a 2×1 supercell using four atomic layers (11.16 Å × 8.41 Å × 8.37 Å). As shown in Fig. 2, the γ-$Al_2O_3(100)$-2×1 surface model consists of eight units of Al_2O_3 with only Al^{3+}_{penta} and tri-coordinated O^{2-} on the surface. The surface slab was symmetrical to avoid unphysical dipole–dipole interactions between the neighboring slabs. After testing different k-point grid schedules, a Monkhorst–Pack grid of size of $2 \times 2 \times 1$ was used to sample the surface Brillouin zone. The calculated surface energy is 960.6 mJ/m^2, which is consistent with previously reported values of 958 [21] and 970 [20] mJ/m^2.

Adsorption energies, $E^{ad}_{(BaO)_n}$, of BaO monomer or dimer on the γ-$Al_2O_3(100)$ surface were calculated by Eq. (1)

$$E^{ad}_{(BaO)_n} = E_{(BaO)_n+\gamma\text{-}Al_2O_3(100)} - (E_{\gamma\text{-}Al_2O_3(100)} + E_{(BaO)_n}) \qquad (1)$$

in which $E_{(BaO)_n+\gamma\text{-}Al_2O_3(100)}$ is the total energy of the interacting system of the γ-$Al_2O_3(100)$ surface and $(BaO)_n$ ($n = 1$ or 2); $E_{\gamma\text{-}Al_2O_3(100)}$ is the total energy of the bare γ-$Al_2O_3(100)$ surface; and $E_{(BaO)_n}$ is the energy of the isolated $(BaO)_n$ monomer or dimer in vacuum. Accordingly, the adsorption energies, $E^{ad}_{NO_2+NO_3}$, of co-adsorbed $NO_2 + NO_3$ pair on the γ-$Al_2O_3(100)$ supported BaO monomer and dimer were calculated by Eq. (2)

$$\begin{aligned} E^{ad}_{NO_2+NO_3} &= E_{NO_2+NO_3+(BaO)_n+\gamma\text{-}Al_2O_3} \\ &\quad - (E_{(BaO)_n+\gamma\text{-}Al_2O_3} + E_{NO_2} + E_{NO_3}) \end{aligned} \qquad (2)$$

in which $E_{NO_2+NO_3+(BaO)_n+\gamma\text{-}Al_2O_3}$ is the total energy of co-adsorbed $NO_2 + NO_3$ pair on $(BaO)_n$ over the γ-$Al_2O_3(100)$ surface; E_{NO_2} and E_{NO_3} are the energies of the isolated NO_2 and NO_3 molecules in the vacuum. For comparison, we also calculated the $NO_2 + NO_3$ pair adsorbed on the BaO(001) surface. This model was used to represent the bulk nitrate. The BaO(001) surface slab consists of a 2×2 super cell with three atomic layers. The same PAW-GGA and k-point sampling schedule for NO_x/BaO/γ-Al_2O_3 systems were used in the calculations of NO_x/BaO(001) system. The calculated surface energy of BaO(001) is 0.35 J/m^2. This is in good agreement with previous DFT results of 0.35 J/m^2 [3] with different functionals. In the same way, the adsorption energies, $E^{ad}_{NO_2+NO_3}$, of co-adsorbed $NO_2 + NO_3$ pair on the BaO(001) surface was calculated as follows

$$E^{ad}_{NO_2+NO_3} = E_{NO_2+NO_3+BaO(001)} - (E_{BaO(001)} + E_{NO_2} + E_{NO_3}) \qquad (3)$$

in which $E_{NO_2+NO_3+BaO(001)}$ and $E_{BaO(001)}$ are the total energies of the $NO_2 + NO_3$ pair interacting with BaO(001) surface and the clean BaO(001) surface respectively. Based on above definitions, a negative $E^{ad}_{(BaO)_n}$ or $E^{ad}_{NO_2+NO_3}$ indicates a favorable (exothermic) adsorption.

3. Results and discussion

Fig. 1 shows a high resolution STEM image of a 2 wt% BaO/γ-Al_2O_3 sample. The image clearly shows that single BaO molecules (bright spots) are dispersed on the surface of γ-Al_2O_3. This high resolution TEM image allows us to differentiate regions on the γ-Al_2O_3 support that have significantly different BaO populations. In region A no BaO units are seen, in accord with the prediction of DFT calculations [20,21] that suggests the complete absence of pentacoordinate Al^{3+} (Al^{3+}_{penta}) sites on other facets that would serve as anchoring points for BaO. In regions B and C of the TEM image the BaO units are fairly uniformly dispersed, and as line sections 1 and 2 show they consist of single BaO units. The decoration of facet boundaries by BaO monomers seems to be also evident, for example in regions D of the HR-TEM image. These observations are all consistent with the results of our recent high resolution ^{27}Al solid state NMR study that showed the preferential anchoring of BaO monomers onto Al^{3+}_{penta} sites formed by the dehydroxylation of the γ-$Al_2O_3(100)$ surface [22]. We have also shown that, in order to saturate all the Al^{3+}_{penta} sites on the γ-Al_2O_3 surface (with specific surface area of ~200 m^2/g) upon calcination at 773 K for 2 h, approximately 4 wt% BaO loading was required. This result suggests that at 2 wt% BaO loading about 50% of the Al^{3+}_{penta} sites are occupied by BaO monomers. When the BaO loading is increased to 8 wt%, the number of BaO molecules is twice that of the Al^{3+}_{penta} sites. Therefore, if we assume an even distribution of BaO on the γ-Al_2O_3 support surface, and that BaO only anchored to the γ-Al_2O_3 surface through Al^{3+}_{penta} sites, we may expect to observe two BaO molecules occupying each Al^{3+}_{penta} site. And, indeed, $(BaO)_2$ dimers dispersed on the γ-Al_2O_3 surface are the primary Ba-containing phase in the 8 wt% BaO/γ-Al_2O_3 sample, however, $(BaO)_x$ units with $x > 2$ present as well (TEM image not shown).

In order to characterize these $(BaO)_x$ ($x \leqslant 2$) units anchored to the Al^{3+}_{penta} sites on the γ-Al_2O_3 surface, and then their interactions with NO_2, we performed DFT calculations on these systems. As a model for the support material we have chosen a (2×1) unit cell of the γ-$Al_2O_3(100)$ surface. Previous DFT calculations [23] have shown that this surface was completely dehydroxylated at 600 K; therefore, the effect of OH groups on the anchoring of $(BaO)_x$ units as well as on the NO_2 chemistry was not considered here. Fig. 2a shows the most stable structure of a BaO monomer anchored to a Al^{3+}_{penta} site on the γ-$Al_2O_3(100)$ surface with an adsorption energy of −4.08 eV. The energetically most favorable configuration of the $(BaO)_2$ dimer on the dehydrated γ-$Al_2O_3(100)$ surface is displayed in Fig. 2b. The adsorption energy of this $(BaO)_2$ dimer is −3.82 eV, slightly lower than that found for the BaO monomer. These model calculations show that both the BaO monomer and the $(BaO)_2$ dimer assume configurations on the γ-$Al_2O_3(100)$ surface that maximize their interactions with the support material; i.e. the Ba–O bond is almost parallel with the support surface.