Density Functional Theory Study of Surface and Bulk Nitrates of γ-Al_2O_3 Supported Alkaline Earth Oxides

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Introduction

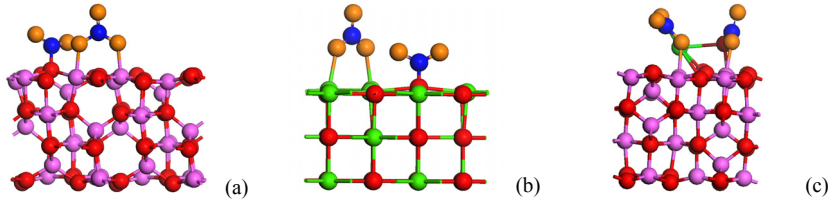
Alkaline earth oxides (AEOs) such as BaO have received considerable attention for their application in the lean-burn engine NO_x storage/reduction (NSR) technology [1]. Previous experimental investigations have indicated that barium nitrate is the most stable form of the stored NO_x in Ba-containing NSR catalysts. Two distinctive types of barium nitrates, $Ba(NO_3)_2$, i.e. "surface" and "bulk" nitrate species, have been postulated on the basis of infrared and NMR spectroscopic and TPD measurements [2]. However, the specific identities and the structures of these two types of nitrate species on BaO/γ-Al_2O_3 materials, and the nature of the interactions between NO_x, BaO and the γ-Al_2O_3 substrate are still not well understood. Furthermore, other γ-Al_2O_3-supported AEO (MgO, CaO and SrO) materials are also potentially useful for the storage and release of NO_x yet are much less well studied [2]. A systematic study of NO_x interacting with a series of AEO/γ-Al_2O_3 surfaces at the atomic level will provide important details of this particular catalytic process for the further development of more effective NSR catalysts.

Computational Method

Periodic DFT slab calculations were performed using the Vienna ab-initio simulation package (VASP). The core and valence electrons were represented by the projector augmented wave method and plane wave functions with a kinetic energy cutoff of 400 eV. The generalized gradient approximation (GGA) combined with the Perdew-Burke-Ernzerhof functional describing the exchange correlation functional was used. The ground-state atomic geometries were obtained by minimizing the forces on each atom to below 0.05 eV/Å. A 15 Å thick vacuum layer was inserted between two surface slabs, and a (3×3×1) k-point sampling scheme was implemented. Spin-polarization was applied to all calculations.

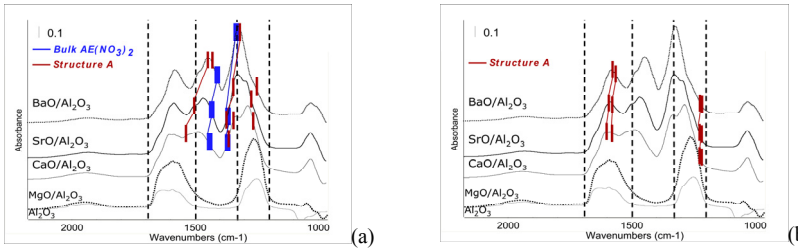
Results and Discussion

We use two molecular models to represent the experimentally identified "surface" and "bulk" nitrates on the γ-Al_2O_3-supported AEOs. In particular, "surface" nitrates were modeled by the adsorption of NO_2+NO_3 pairs on γ-Al_2O_3-supported monomeric AEOs, while "bulk" nitrates were modeled by the adsorption of NO_2+NO_3 pairs on the AEO(001) surfaces. Figure 1 shows the optimized structures of different nitrate species over three model surfaces. We found that the calculated vibrational frequencies based on the proposed molecular structure models were in good agreement with experimental FTIR measurements of AEOs/γ-Al_2O_3 catalysts after prolonged NO_2 exposure (Figure 2). We also found that the adsorption strengths of NO_2+NO_3 pairs on the AEO(001) surfaces increase in the order of MgO < CaO < SrO ~ BaO. In contrast, the adsorption strengths of NO_2+NO_3 pairs on the monomeric AEO/γ-Al_2O_3(100) surfaces were essentially identical. NO_2+NO_3 pairs interacting both monomeric AEO structures and the γ-Al_2O_3 support surface are about 0.5 eV more stable than when directly interacting with only the monomeric AEOs.



(a) (b) (c)

Figure 1. The optimized structures of adsorbed NO_2+NO_3 pair on the (a) γ-Al_2O_3(100) surface; (b) BaO(001) surface and (c) γ-Al_2O_3(100) supported monomeric BaO.



(a) (b)

Figure 2. Comparison of calculated and experimental vibrational frequencies for "bulk" and "surface" nitrates. Experimental vibration frequencies were taken from reference [2]. (a) "bulk" nitrate, and (b) "surface" nitrate.

Significance

The "surface" and "bulk" nitrates formed on AEO/γ-Al_2O_3 catalysts from NO_2 exposures were elucidated at the atomic level for the first time. We confirm that the "surface" nitrates are a consequence of NO_x adsorption on 'submonolayer'AEO structures on the γ-Al_2O_3 surface whereas the "bulk" nitrates formed by NO_x adsorption on supported AEO particles.

References

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