Specific role of alumina surfaces for BaO anchoring and nitrate formations in BaO/γ-Al$_2$O$_3$ NO$_x$ Storage Materials

Ja Hun Kwak[1]*, Donghai Mei[1],Cheol-Woo Yi[3], Do Heui Kim[1], Charles H.F. Peden[1], Lawrence F. Allard[2], and János Szanyi[1]*

[1]Institute for Interfacial Catalysis, Pacific Northwest National Laboratory, Richland, WA 99352 (USA), [2]*High Temperature Materials Laboratory, Oak Ridge National Laboratory*
*Kwak@pnl.gov, and janos.szanyi@pnl.gov

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.

However, investigating the properties of these very highly dispersed active centers, is experimentally very difficult, and requires a concerted effort of both experimental and theoretical methods. Recently, our group demonstrated the specific role of penta-coordinated aluminum formed on the γ-alumina surfaces as a anchoring sites of BaO which is active phase of NOx storage/reduction catalysts by using ultrahigh field solid state ^{27}Al-NMR study[2]. These results strongly suggested that the monomeric or dimeric BaO formation on (100) facet of γ-Al$_2$O$_3$. And also we reported that two different types of nitrates, surface and ionic nirtates, from IR studies. However, the origin of surface nitrates were still not clearly understood.

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 γ Al$_2$O$_3$ in the NO$_2$ uptake process at low BaO loadings, and the characteristics of the "surface" nitrate species thus formed..

Materials and Methods

The BaO/γ-Al$_2$O$_3$ NO$_x$ storage materials with varying BaO loadings were prepared by traditional incipient wetness methods using a Ba(NO3)2 precursor, and a 200 m2/g γ Al2O3 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 [3]. 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). The details of simulation methods have been described in our previous reports [4]

Results and Discussions

STEM image for 2%BaO/Al2O3 samples after calcined at 773K, clearly demonstrate the monomeric BaO formed on the alumina surface which is exactly consistent resutls what we expected from solid state ^{27}Al-NMR[2]. Interestingly, BaO distributed heterogenously and molecularly dispersed 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 γ-Al$_2$O$_3$ 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".

Significance

Combined spectroscopic and theoretical studies allow us to unambiguously understand the nature of both surface and bulk types of nitrates on BaO/γ-Al$_2$O$_3$ NO$_x$ storage systems, a subject actively debated
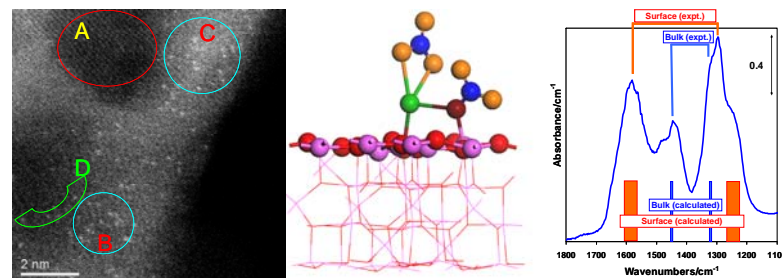

Figure 1. High resolution STEM image for 2%BaO/Al$_2$O$_3$, optimized structure of adsorbed NO$_2$ on BaO monomer on alumina and IR spectrum of 8%BaO/Al$_2$O$_3$ after NO$_2$ saturation at 300 K

References
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