Model NO_x storage materials: NO_2 and H_2O chemistry on $BaO/Al_2O_3/NiAl(110)$ and (100)

Cheol-Woo Yi, Emrah Özensoy, Charles H.F Peden, and János Szanyi*
Institute for Interfacial Catalysis, Pacific Northwest National Laboratory
Richland, WA 99352 (USA)
*janos.szanyi@pnl.gov

Introduction

Lean NOx traps or NOx storage/reduction materials is one of the leading technologies being developed for diesel engine emission control [1]. Studies on high surface area supported catalysts are abundant, however, only a very few investigations have been reported on model, single-crystal-based materials [1-3]. NiAl single crystals, in particular the (110) and (100) faces, have been widely used for over a decade for the preparation of well ordered crystalline alumina films. These films have been used as supports for metal particles in model catalytic systems fabrications [4]. These substrates afford the use of an array of UHV surface analysis tools, which are instrumental to understand the catalytic systems on the atomic scale. Alkali or alkaline earth oxides (mostly K_2O or BaO) are the most widely used NO_x storage components of fully formulated systems, and here we report on studies of BaO. The focus of our study was to understand the interactions of molecules present in the exaust (specifically H_2O and NO_2) with both the alumina support (θ-, and γ-alumina thin films) and the active storage component of BaO.

Materials and Methods

Model NO_x storage systems have been prepared on well ordered, clean NiAl(110) and (100) metal alloy substrates following well established protocols [5]. BaO films/particles were deposited onto the thin alumina films from a getter source, and were subsequently oxidized to obtain the model BaO/Al_2O_3 NO_x storage systems. The sequence of preparation steps is displayed in Figure 1 for the $BaO/\theta\text{-}Al_2O_3$ system. The preparation of these systems was followed by, and the film characterization was accomplished by the use of an array of surface analysis tools (AES, XPS, LEISS, and RAIRS). The interactions of H_2O and NO_2 were studied by TPD, RAIRS, and XPS.

Results and Discussion

The thin films of θ-, and $\gamma\text{-}Al_2O_3$ exhibit very different surface structures, that may lend them vastly different properties toward the adsorption and reaction of probe molecules, in this case H_2O and NO_2. Well-ordered $\theta\text{-}Al_2O_3$ films have an open surface structure, terminating with parallel running oxygen and aluminum rows [6]. The plane of the oxygen rows lies somewhat higher, than the aluminum rows. $\gamma\text{-}Al_2O_3$ films, on the other hand, represent a fully oxygen terminated surface [7]. These differences in surface structure manifest in their H_2O and NO_2 adsorption properties. Water initially binds to the Al^{3+} ions in the aluminum rows, giving a perturbed first order desorption behavior. After the saturation of the aluminum sites water clusters grow, which exhibit a zero order desorption kinetics [8]. On the $\gamma\text{-}Al_2O_3$ film the interaction of the first layer of water with the film is very weak, showing only ~5K temperature difference between the maximum desorption rate from the first and multilayer. Above 250 K no water desorption is seen from either of these two surfaces, suggesting only molecular adsorption. Very similar trends are seen for the adsorption of NO_2 on these two surfaces. However, in contrast to water adsorption, NO_2 adsorption also results in the formation of ionic NO_x species on both alumina surfaces. These ionic species desorb from the surfaces at temperatures higher than 300 K. The deposition of BaO results in the stabilization of adsorbed water, and formation of ionic Ba-related NO_x species (nitrites and nitratres). The presentation will focus on the formation mechanism and the chemical nature of these different NO_x species on the two alumina surfaces, and the BaO films/clusters. Results of TPD, XPS, LEISS and RAIRS studies will be presented to develop an understanding for the formation of NO_x species in these systems.

Significance

The results of this multi-spectroscopy study on the BaO/alumina model NO_x storage systems brings us closer to understand the formation mechanisms and the chemical nature of ionic NO_x species.

Figure 1.

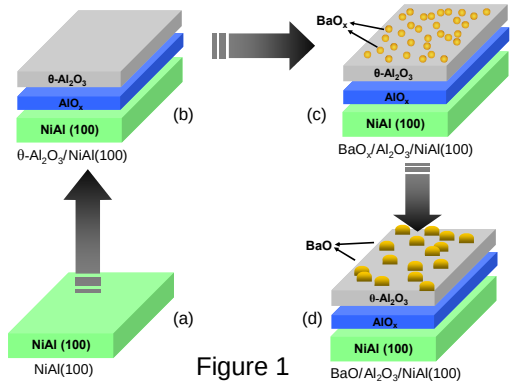

Figure 1

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