BaO/Pt(111) Model NOx Strorage/Reduction Catalysts

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Introduction

Studies on model NOx storage/reduction catalysts fall into two major categories depending on whether the active storage component (BaO) is deposited onto (i) a thin oxide film (e.g. Al_2O_3) [1-3], or (ii) a metal substrae (e.g. Pt(111), Cu(100))[4]. The investigations on the model BaO/Al_2O_3 systems provided invaluable insight into the importance of the active oxide-support interaction in the overall NO_x chemistry of the active base metal oxide. On the other hand, studies on the BaO/metal systems may bring us closer to understand the importance of the interaction of the active storage material and the precious metal component. The importance of the intimate contact between BaO and Pt particles in practical catalyst systems have been proposed for the NO_x uptake and reduction processes [2], however have not been studied in great details on model systems where precise control of both the sample and reaction conditions can be achieved.

Materials and Methods

The Pt(111) single crystal (Princeton Scientific) was cleaned by several cycles of Ar^+ sputtering/oxidation/anneal. The cleanliness of the sample was verified by XPS, LEISS, and LEED. BaO films with varying coverages were deposited onto the clean Pt(111) surface by reactive layer assisted deposition (RLAD) of Ba. N_2O_4 ice was deposited onto the cryogenically-cooled sample (~90 K) and then, from a getter source (SEAS), Ba was evaporated. Upon interaction between the N_2O_4 ice and metallic Ba, $BaNO_x$ (mostly nitrate) formed, which then decomposed to BaO at the subsequent annealing step to temperatures higher than 850 K. The thus prepared samples were characterized by XPS, LEISS, and LEED. The NO_2 chemistry on these samples was studied at BaO coverages ranging from multilayer (>10 MLE), to submonolayer equivalent (<1 MLE) using TPD, XPS and IRAS techniques. The role of spillover from the Pt surface onto/into the BaO was also investigated in both the NO and CO oxidation reactions.

Results and Discussion

NO_2 on BaO(>20 MLE)/Pt(111). TPD data obtained after NO_2 adsorption at 300 K with increasing exposures for mass fragments 30, 32, and 46 are shown in Fig. 1. The inset at the top right corner shows the peak deconvolution of the TPD curve, based on the cracking pattern of NO_2 on the mass spectrometer, obtained after maximum NO_2 exposure. In the decomposition process of nitrite–nitrate ion pairs, first nitrites release NO at 583 K. Then nitrates decompose in two steps, at lower temperature as NO_2 only (596 K), and at higher temperature, nitrate dissociates as $NO + O_2$ giving NO and O_2 peaks at 669 K. The N 1s XP spectrum obtained after the adsorption of NO_2 at 300 K on a thick BaO film on Pt(111) shows presence of two different nitrogen containing species. The N 1s peaks at 404.3 and 408.1 eV can be assigned to nitrogen atoms in nitrite and nitrate ions, respectively. The similar

intensities of these two N 1s peaks indicate the presence of equal amounts of nitrites and nitrates, suggesting a cooperative NO_2 adsorption mechanism[16-18]on the thick BaO film.

NO_2 on BaO(~2-3 MLE)/Pt(111). IR spectra collected under UHV conditions (NO_2 pressure - 1.0×10^{-9} Torr), show peaks at 1251, 1412 and 1478 and can be assigned to nitrites (1251 cm^{-1}) and nitrate species, respectively.[12-14] At elevated NO_2 pressures (> 1.0×10^{-6} Torr) the broad IR peaks (1334 and 1487 cm^{-1} in Fig. 2) reveal the presence of amorphous nitrates at 300 K. After annealing this amorphous $Ba(NO_3)_2$ to 500 K (in the absence of NO_2), sharp IR peaks were observed at 1430, 1393 and 1334 cm^{-1}. These changes in the IR spectrum are due to the phase transformation from amorphous to crystalline $Ba(NO_3)_2$.[19]

NO_2 on BaO(< 1 MLE)/Pt(111). The reaction of NO_2 with a sub-monolayer coverage of BaO also leads to the formation of amorphous $Ba(NO_3)_2$ at 300 K. However, after annealing to 500 K, relatively sharp peaks were observed at 1394 and 1430 cm^{-1}, attributed to the transformation of amorphous to crystalline $Ba(NO_3)_2$. In addition to these sharp peaks, a broad peak is present at 1310 cm^{-1}. This peak is most likely due to the remaining amorphous nitrates, which are not converted to crystalline form at 500 K.
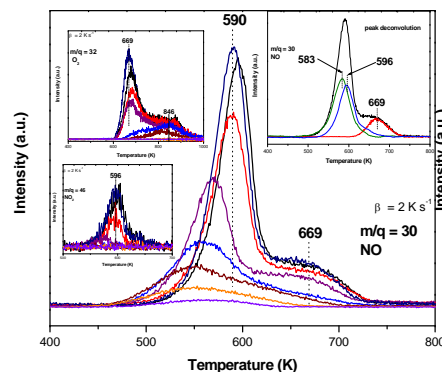

Figure 1. NO_2 adsorption on a thick BaO film at 300 K. (The inset at the top right: peak deconvolution of the TPD curve at maximum NO_2 coverage.)
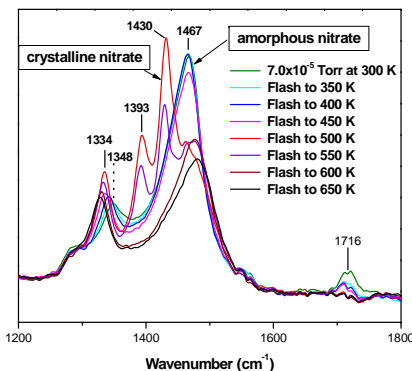
Figure 2. Amorphous to crystalline phase transformation of a NO_2 saturated BaO film

Significance These studies ultimately will lead to the understanding of the role of the interaction between Pt and BaO in the NO_x storage-release processes, as well the influence of other reactions (e.g. CO oxidation) on these processes.

References

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