Effect H_2O on the NO_x Adsorption on BaO - functionalized $Al_2O_3/ZrO_2/TiO_2$ $DeNO_x$ Catalysis

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Introduction

Surface chemistry of NSR/LNT catalysts can be fine-tuned by promoting them with different reducible metal oxides (i.e CeO_2 and TiO_2) which have direct influence on their NO_x storage capacity and sulfur regeneration performance [1-9]. In one of our recent studies, a novel family of AZT ($Al_2O_3/ZrO_2/TiO_2$) based catalysts were found to have up to 40 % higher NO_x trapping ability along with a superior NO_x regeneration performance as compared to that of a conventional $Pt/20BaO/Al_2O_3$ catalyst [8]. In the current study, we focus on the molecular level understanding of the effect of BaO loading on water-induced NO_x trapping chemistry. Along these lines, we systematically investigate the effect of H_2O exposure on the adsorption geometry of stored NO_x species and NH_4NO_3 formation by means of in-situ spectroscopic techniques.

Materials and Methods

Detailed description of the synthesis of AZT - based ternary oxide systems via precipitation technique can be found elsewhere [3,8,9].In-situ FTIR spectroscopy and Temperature Programed Desorption (TPD)results were collected via a custom-designed in-situ batch reactor.

Results and Discussion

NO_2-TPD experiments were carried out on dry and pre-H_2O-exposed Pt/20BaO/AZT surfaces as shown in Figures 1a and 1b, respectively. Comparison of these results reveal the presence of an additional m/z=44 (N_2O) desorption peak at 593K (T1) in the presence of water (Figure 1b). Furthermore, this particular desorption peak is concomitant to a complex desorption signal at m/z=30 originating from NO and N_2Oas well as a minor contribution from NO_2. Simultaneous desorption of N_2O and H_2O is a well-known signature for the decomposition of NH_4NO_3 from Cu-exchanged zeolites [10]. However, these results can lead us to conclude an overall NH_4NO_3 decomposition route from Pt/20BaO/AZT surface through following equation:

$$4NH_4NO_3 \rightarrow 3N_2O + 8H_2O + 2NO$$

NO (m/z=30) desorption features at 665 K (T2) and 785 K (T3) in Figure 1, appearing without a significant amount of N_2O and H_2Odesorption also deserve attention. These desorption signals can be attributed to surface nitrates and bulk like nitrates on BaO, respectively. It is apparent that presence of excess H_2O and formation of NH_4NO_3 (Figure 1b) significantly suppresses the surface nitrate population with respect to that of Figure 1a, suggesting that the surface nitrates are responsible for the formation of NH_4NO_3.

Results of the TPD experiments were further supported by *in-situ* FTIR spectroscopic studies as shown in Figure 2. As can be seen in Figure 2, gradual introduction H_2O on an NO_2-saturated Pt/20BaO/AZT surface leads to a monotonic decrease in the vibrational intensities of the surface nitrate features along with a continuous growth in NH_4NO_3 IR bands.

Significance

Ammonium nitrate is an important intermediate/byproduct in $DeNO_x$ catalysis. Studying the fundamental molecular-level mechanism of ammonium nitrate formation is crucial for shedding light on NO_x abatement. *Via in-situ* spectroscopy, current study reveals valuable insight regarding the formation pathways of NH_4NO_3 through the reaction of surface nitrate species and adsorbed water on sulfur-resistant $Pt/BaO/Al_2O_3/ZrO_2/TiO_2$ NSR/LNT catalysts.

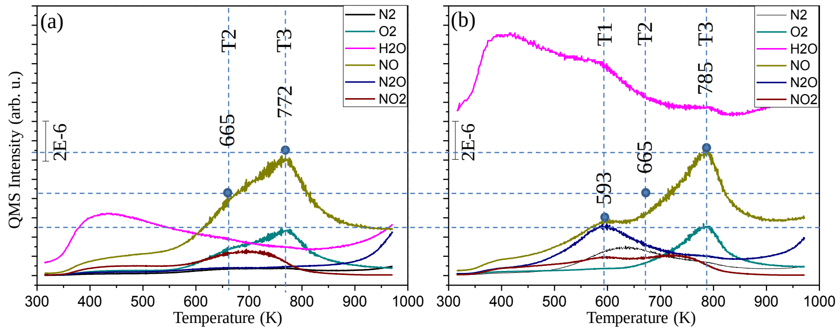

Figure 1: TPD Analysis of NO_2(g) saturated (a) dry and (b) water exposed Pt/20BaO/AZT

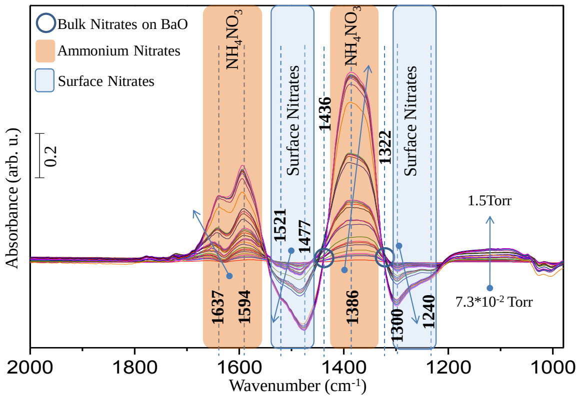

Figure 2: *In-situ* FTIR spectra presenting the changes in the surface functional groups upon increasing H_2Oexposureson NO_2(g)-saturated Pt/20BaO/AZT at 323K.

References

[1]Say, Z., Vovk, E.I., Bukhtiyarov, V.I., Ozensoy, E.Topics in Catalysis 56, 950 (2013).
[2]Say, Z., Vovk, E.I., Bukhtiyarov, V.I., Ozensoy, E. Applied Catalysis B: Environmental 142-143, 89 (2013).
[3]Say, Z., Tohumeken M., Ozensoy, E. Catalysis Today 231, 135 (2014).
[4]Say, Z., Dogac, M., Vovk, E.I., Kalay, Y.E., Kim, C.H., Li, W., Ozensoy, E., Applied Catalysis B: Environmental 154-155, 51 (2014)
[5]Dogac, M., Say, Z., Vovk, E.I., Kim, C.H., E. Ozensoy, Accepted in Topics in Catalysis (2016)
[6]Senturk, G.S., Vovk, E.I., Zaikovskii, V.I., Say, Z., Soylu, A.M., Bukhtiyarov, V.I., Ozensoy, E. Catalysis Today 184, 54 (2012).
[7]Matsumoto, S., Ikeda, Y., Suzuki, H., Ogai, M., Miyoshi, N. Applied Catalysis B: Environmental 25, 115 (2000).
[8]Say, Z., Mihai, O., Tohumeken, M., Ercan, KE., Olsson, L., Ozensoy, E. Accepted in Catalysis Science and Technology (2016)
[9] Say, Z., Tohumeken M., Ozensoy, E. Catalysis Today 167, 267 (2016).
[10] Mihai, O.,Widyastuti, CR., Andonova, S., Kamasamudram, K., Li J., Joshi, SY., Currier, NW., Yezerets, A., Olsson, L., Journal of Catalysis 170, 311 (2014).