Highly Sulfur-Tolerant Al$_2$O$_3$/ZrO$_2$/TiO$_2$-Based LNT Catalysts

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Introduction

Some of the major challenges of NOx Storage Reduction (NSR) or Lean NOx Trap (LNT) catalysts are associated with sulfur poisoning and thermal/stuctural stability [1-6]. On the other hand, improvement of sulfur tolerance of an NSR/LNT system need to be accomplished without compromising the NOx storage capacity. TiO$_2$ which has a moderately high surface acidity is known as a promising oxide support/promoter against sulfur poisoning, providing much lower temperature for sulfur elimination, but leading to a relatively limited NOx storage capacity [7]. In the current contribution, we focus on the surface chemistry of Al$_2$O$_3$/ZrO$_2$/TiO$_2$-based NSR/LNT catalysts. In particular, we elucidate the NOx and SOx adsorption and thermal regeneration performances under reducing conditions at the molecular level by means of in-situ FTIR and TPD techniques. Moreover, NOx uptake capacities of the aforementioned materials are quantitatively investigated in the presence and absence of sulfur poisoning via flow mode performance analysis tests.

Materials and Methods

Detailed description of synthesis of Zr$_2$O$_3$/TiO$_2$ (ZT) binary and Al$_2$O$_3$/ZrO$_2$/TiO$_2$ (AZT) ternary oxide systems via co-precipitation technique has been explained in detail in one of our former reports [24]. The synthesis of the support materials is followed by BaO and Pt addition via incipient wetness impregnation method, forming catalytic materials in the form of Pr/Al$_2$O$_3$/ZrO$_2$/TiO$_2$, Pr/BaO/Al$_2$O$_3$/ZrO$_2$/TiO$_2$, and Pt/BaO/Al$_2$O$_3$. Structural properties of the synthesized catalysts were investigated via XPS, ex-situ Raman spectroscopy, TEM, EDX, XRD and BET while their NOx uptake and release behavior was investigated by employing the flow mode catalytic performance experiments as well as in-situ FTIR and TPD measurements.

Results and Discussion

As illustrated in Figure 1, sulfur regeneration capability of Al$_2$O$_3$/ZrO$_2$/TiO$_2$-supported materials are noticeably higher in the presence of a reducing agent (i.e. H$_2$(g)). While complete SOx regeneration is achieved around 773 K on Pt/AZT, this temperature (c.a. 973 K) is much higher for Pt/Ba/Al. However, NOx sorption ability of Pt/AZT without the basic oxide storage domains (i.e. BaO and K$_2$O) is too low to be considered for LNT applications at the relevant operational temperatures (i.e. 573 K) due to the high surface acidity/low basicity of this support. Therefore, Pt/AZT material are enriched and modified by incorporation of a basic storage domain, namely BaO. While addition of 8wt % BaO has a minor influence on sulfur regeneration temperature, 20wt % BaO loading drastically change the materials characteristics as shown in the in-situ FTIR results. These findings are also supported by the TPD data. SOx uptake capacities of investigated BaO-containing catalysts can be ranked in a decreasing order as Pt/20Ba/Al > Pt/20Ba/AZT > Pt/8Ba/AZT. Finally, Pt/20Ba/AZT catalyst which has 56% greater NOx storage capacity and better sulfur tolerance than the commercial Pt/20Ba/Al benchmark catalyst under realistic flow conditions.

Significance

It is a great challenge to synthesize catalytic materials revealing superior sulfur tolerance and high NOx uptake capacity. In this study, we provide fundamental insight regarding the molecular-level understanding of acidic adsorbates such as NO$_x$ and SO$_x$ species on a novel ternary oxide catalytic support material whose surface properties can be fine-tuned to optimize NSR/LNT performance. This new generation Al$_2$O$_3$/ZrO$_2$/TiO$_2$-support materials offer new opportunities in DeNOx applications.

References


Figure 1: FTIR spectra related to SOx release properties of sulfur-poisoned (a) Pt/AZT, (b) Pt/8Ba/AZT, (c) Pt/20Ba/AZT and (d) Pt/20Ba/Al in the presence of H$_2$(g).

Figure 2: TPD profiles related to SOx desorption from sulfur-poisoned (a) Pt/AZT, (b) Pt/8Ba/AZT, (c) Pt/20Ba/AZT and (d) Pt/20Ba/Al surfaces.