Enhanced emission of NH_3 and N_2O from Pd-supported catalysts

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Introduction

The main technology to remove regulated emissions, i.e. NOx, CO and HC's, from gasoline cars was the introduction of the Three-Way Catalytic Converter (TWC) [1]. In vehicles, the commercial converters containing Rh and Pt are still the most widely used, but the number of vehicles equipped with Pd-only converters will increase as a consequence of the world trend to produce and use gasoline with low sulfur content [1]. The use of low sulfur gasoline improves the performance of the TWC to remove regulated emissions [2], but the level of sulfur in gasoline affects the NH_3 and N_2O emissions from the TWC [3,4]. This is a problem that has not received much attention in the literature.

Rh produces the largest amount of N_2O at low temperature compared to Pt and Pd, but Pd is the largest producer of N_2O at temperatures about 350°C [5]. At high temperatures, the selectivity of the catalysts changes to produce NH_3, which increases along with temperature [5]. The factors involved in the change of selectivity toward N_2O, NH_3 and N_2 are unclear, but the components of the catalysts and the temperature can play a major role [5]. As a result, the interaction of SO_2 with the main components of the TWC might also affect the selectivity toward NH_3 or N_2O [4].

Materials and Methods

Model catalysts were prepared by wet impregnation with a solution of $Pd(NH_3)_4(NO_3)_2$. Pd / Al_2O and Pd / CeO_2-Al_2O_3 model catalysts containing 2, 4 and 10 wt.% of CeO_2 were used in the catalytic tests. Commercial Al_2O_3 was crushed/sieved to 120-140 mesh. CeO_2 was formed by thermal decomposition of $Ce(NO_3)_3 \cdot 6H_2O$ at 800°C during 4 h. Before impregnation with Pd, CeO_2-Al_2O_3 was dried at 115°C during 4 h and calcined at 800°C during 8 h. The catalysts were dried at 120°C by 4 h and calcined during 12 h after wet impregnation with Pd. Samples of 100 mg of catalyst were tested in a tubular quartz reactor mounted in an electric furnace. The feed stream composition was 2100 ppm of NO, 2200 ppm of H_2 and 6600 ppm of H_2. SO_2 was varied from 0 to 20 ppm and N_2 was the gas balance. The analysis of reactants and products was made by GC (HP6890 and Shimadzu GC-12A) in line with an FTIR Spectrophotometer (Bruker Tensor 27) equipped with a 0.75 cm path length infra red gas cell. Spectra were acquired at 4 cm^{-1} resolution by averaging 44 scans.

Results and Discussion

Our results from Figure 1 show that NO reduction by CO and H_2 over Pd / 10-CeO_2-Al_2O_3 at 500°C follows two reaction pathways to produce NH_3 and N_2. An important amount of NH_3, up to 1500 ppm, is produced in absence of SO_2 in the feed stream. The NO conversion reaches 100%. The presence of 20 ppm in the feed stream modifies the selectivity and the conversion of the model catalysts. After one hour of reaction, the conversion of NO is almost 45% and the NH_3 concentration reaches 550 ppm. Besides, the interactions of SO_2 with the support CeO_2-Al_2O_3 opens-up a reaction path at 500°C to produce N_2O. Almost 100 ppm of N_2O is formed. So, the presence of SO_2 seems to have a dual function. We found that SO_2 suppresses selectively the reaction path leading to NH_3 but N_2O is promoted at high temperature. When SO_2 is removed, the NO conversion is not recovered completely. Only 80% of NO conversion is reached and 1300 ppm of NH_3 is produced after one hour of reaction. Therefore, N_2O formation is blocked.

Significance

The massive introduction of Pd-only TWC and the use of low sulfur gasoline by cars can be important factors that affect the air quality in urban settings. The emission of NH_3 and N_2O from on-road vehicles is a relevant concern because NH_3 reacts in the atmosphere to produce fine and ultra fines particles while N_2O is a greenhouse gas. Real-data-time reports of NH_3 and N_2O emission from vehicles agree with our experimental results. The survey of the phenomena involved could be useful to improve the global performance of the next generation of TWC.

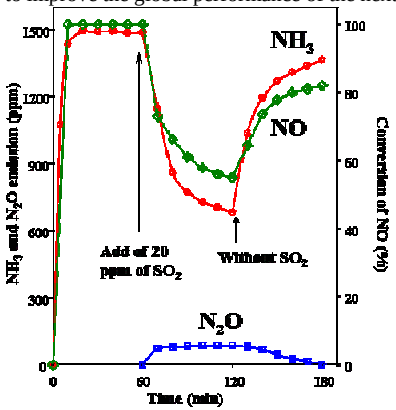

Figure 1. Effect of SO_2 upon NH_3 and N_2O formation over Pd /10CeO_2-Al_2O_3 model catalyst at 500°C.

Acknowledgements

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