Enhanced emission of NH\textsubscript{3} and N\textsubscript{2}O from Pd-supported catalysts

Isidro Mejía-Centeno and Gustavo A. Fuentes*

Department of Process Engineering, Universidad A. Metropolitana-Iztapalapa, AP. 53-394; 09340; México, D.F. (México)
*gfuentes@xanum.uam.mx

Introduction
The main technology to remove regulated emissions, i.e. NO\textsubscript{x}, 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\textsubscript{3} and N\textsubscript{2}O 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\textsubscript{2}O at low temperature compared to Pt and Pd, but Pd is the largest producer of N\textsubscript{2}O at temperatures about 350°C [5]. At high temperatures, the selectivity of the catalysts changes to produce NH\textsubscript{3}, which increases along with temperature [5]. The factors involved in the change of selectivity toward N\textsubscript{2}O, NH\textsubscript{3} and N\textsubscript{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\textsubscript{2} with the main components of the TWC might also affect the selectivity toward NH\textsubscript{3} or N\textsubscript{2}O [4].

Materials and Methods
Model catalysts were prepared by wet impregnation with a solution of Pd(NH\textsubscript{3})\textsubscript{2}(NO\textsubscript{3})\textsubscript{2}, Pd / Al\textsubscript{2}O\textsubscript{3} and Pd / CeO\textsubscript{2}-Al\textsubscript{2}O\textsubscript{3} model catalysts containing 2, 4 and 10 wt.% of CeO\textsubscript{2} were used in the catalytic tests. Commercial Al\textsubscript{2}O\textsubscript{3} was crushed/sieved to 120-140 mesh. CeO\textsubscript{2} was formed by thermal decomposition of Ce(NO\textsubscript{3})\textsubscript{3}·6H\textsubscript{2}O at 800°C during 4 h. Before impregnation with Pd, CeO\textsubscript{2}-Al\textsubscript{2}O\textsubscript{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\textsubscript{2} and 6600 ppm of H\textsubscript{2}O was varied from 0 to 20 ppm and N\textsubscript{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\textsuperscript{-1} resolution by averaging 44 scans.

Results and Discussion
Our results from Figure 1 show that NO reduction by CO and H\textsubscript{2} over Pd / 10-CeO\textsubscript{2}-Al\textsubscript{2}O\textsubscript{3} at 500°C follows two reaction pathways to produce NH\textsubscript{3} and N\textsubscript{2}. An important amount of NH\textsubscript{3}, up to 1500 ppm, is produced in absence of SO\textsubscript{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\textsubscript{3} concentration reaches 550 ppm. Besides, the interactions of SO\textsubscript{2} with the support CeO\textsubscript{2}-Al\textsubscript{2}O\textsubscript{3} opens-up a reaction path at 500°C to produce N\textsubscript{2}O. Almost 100 ppm of N\textsubscript{2}O is formed. So, the presence of SO\textsubscript{2} seems to have a dual function. We found that SO\textsubscript{2} suppresses selectively the reaction path leading to NH\textsubscript{3} but N\textsubscript{2}O is promoted at high temperature. When SO\textsubscript{2} is removed, the NO conversion is not recovered completely. Only 80% of NO conversion is reached and 1300 ppm of NH\textsubscript{3} is produced after one hour of reaction. Therefore, N\textsubscript{2}O 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\textsubscript{3} and N\textsubscript{2}O from on-road vehicles is a relevant concern because NH\textsubscript{3} reacts in the atmosphere to produce fine and ultra fines particles while N\textsubscript{2}O is a greenhouse gas. Real-data-time reports of NH\textsubscript{3} and N\textsubscript{2}O 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.

References