Reaction studies on $Pt/BaO/Al_2O_3$ for NO_x storage/reduction catalysts

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Introduction

The control of NO_x (NO and NO_2) emissions from combustion processes, including vehicle engines, remains a challenge particularly for systems operating at high air-to-fuel ratios (so-called 'lean' combustion). The current "3-way", precious metal-based catalytic converters are unable to selectively reduce NO_x with reductants (e.g., CO and residual unburned hydrocarbon) in the presence of excess O_2. In the last few years, worldwide environmental regulations regarding NO_x emissions from diesel engines (inherently operated 'lean') have become significantly more stringent resulting in considerable research efforts to reduce NO_x under the highly oxidizing engine operation conditions. Urea selective catalytic reduction (SCR) and non-thermal plasma assisted NO_x reduction have been explored as possible technologies. In recent years, alkaline and alkaline earth oxide-based NO_x storage/reduction catalysts (especially BaO/Al_2O_3) have been developed, and have shown promising activities for lean-NO_x reduction [1].

The NO_x storage/reduction catalysts have dual catalytic functions. One is the oxidation of NO to NO_2 and its subsequent uptake as nitrate under lean condition, and the other is reduction of the released NO_x under rich condition. Both of these processes are facilitated by a noble metal, in particular Pt. The actual NOx storage material is BaO in most practical applications. Although it is understood that NO_2, formed on Pt, is stored on the BaO phase as $Ba(NO_3)_2$ and the interaction between Pt and BaO is important, the effect of this interaction on the reactivity is not clear [2]. In this presentation, we will elucidate the role of Pt and BaO components, and the interaction between these two constituents during the NOx storage/reduction process by studying $Pt\text{-}BaO/Al_2O_3$ catalysts with varying BaO loadings, and different Pt particle sizes.

Experimental

A series of catalysts with different barium oxide loadings were prepared by conventional impregnation methods. First, $Ba(NO_3)_2$ was loaded by repeated incipient wetness and drying on a high surface area gamma-alumina (Condea, $200m^2/g$), followed by the impregnation of $Pt(NH_3)_4(NO_3)_2$ with the same incipient method and drying. The dried samples were calcined at 500°C for 2 hrs in flowing air, which resulted in 2wt% Pt with 2, 8, and 20wt% BaO supported on Al_2O_3. The reaction studies were carried out in a plug-flow quartz reactor with simulated diesel exhaust. The NO_x levels in the inlet (~200ppm) and outlet gases were measured with a chemiluminescence NO_x analyzer. The NO_x conversion was defined as the ratio of the amount of NO_x stored to the amount of inlet NO_x during lean cycle over different time intervals (typically 4 min and 30 min), prior to the rich cycle for 1 min.

Results and Discussion

Fig.1 shows the TEM image for different BaO samples with variable loading. In spite of the significant difference in BaO loading, all of the samples show highly dispersed Pt clusters of less than 2 nm.

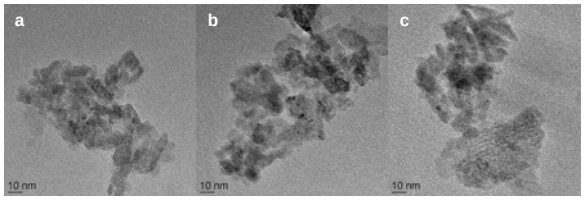

Fig.1 TEM image of $2\%Pt/2\%BaO/Al_2O_3$ (a), $2\%Pt/8\%BaO/Al_2O_3$ (b), and $2\%Pt/20\%BaO/Al_2O_3$ (c).

Fig. 2 shows NO_x conversion at various temperatures, and NO_x uptake profiles at 250°C for these three samples. NO_x conversion increased with BaO loading over the whole temperature range, as did the time for NOx breakthrough. However, NO_x conversion for 30 min was not linearly proportional to the amount of barium oxide; in other words, the BaO portion participating in NO_x storage decreased with barium loading. For the case of $2\%Pt/20\%BaO/Al_2O_3$ catalyst, only 12% of the BaO was converted to barium nitrate, This percentage for the 2 wt% and 8wt% $Pt\text{-}BaO/Al_2O_3$ catalysts was calculated to be 68% and 25%, respectively.

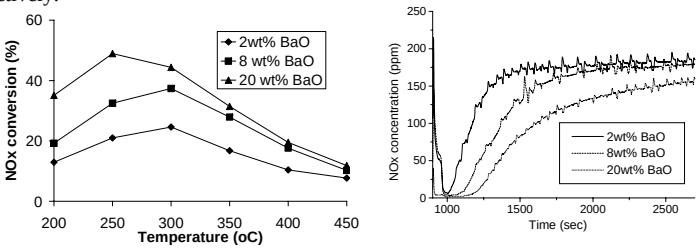

Fig 2 NO_x conversion for 30 min and NO_x uptake profiles (at 250 °C) over $Pt\text{-}BaO/Al_2O_3$.

Low BaO efficiency cannot be explained by the insufficient production of NO_2 arising from the deactivation of Pt because all three samples contain nearly the same size and loading of Pt. However, the fact that NO_x breakthrough increases with BaO loading may imply that the step of transferring NO_2 to the neighboring barium sites determines the NO_x uptake. For example, it has been proposed that an intimate interaction between Pt and BaO is required for facile transfer of NO_2 to BaO, this step perhaps being a key one for obtaining higher NO_x storage.

Significance

Understanding of the key steps, such as NO_2 transfer to barium oxides, will be helpful for the preparation of NO_x storage-reduction catalysts with improved activity**.**

References

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2. Epling, W.S., Parks, J.E., Campbell, G.C. Yezerets, A., Currier, N.W., Campbell, L. E., *Catal. Today* **96** (2004) 21.