

Low Temperature NO_x Removal from Diesel Exhaust by Coupling Ethylene Glycol Reforming with SCR

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Introduction

The main obstacle preventing widespread implementation of diesel-powered engines is the lack of a suitable catalyst/reductant combination for this process. Residual hydrocarbons found in engine exhaust are generally less active and selective compared to NH₃. Although NH₃-SCR is very effective, NH₃ is a corrosive and toxic chemical, making it difficult to handle. Such properties in addition to the requirement of a separate NH₃ source and injection system and issues relating to NH₃ slip, make this approach unappealing. Another effective reductant, urea, also has its shortcomings such as its high freezing point. Even the more aggressively pursued NO_x trap, face serious limitations due to sulfur poisoning and thermal aging which leads to deactivation of the NO_x storage system.

We have investigated a novel strategy to achieve high NO_x removal at low temperatures in an oxygen rich atmosphere, without many of the limitations associated with the technologies mentioned above. This approach involves a coupled system, consisting of an ethylene glycol (EG) reforming unit to convert an EG-H₂O mixture into H₂ and CO followed by a H₂/CO-deNO_x unit. Aqueous phase EG reforming to H₂ with high selectivity has been demonstrated [1], as well as effective H₂ reduction of NO_x over a wide operating window at low temperatures [2]. Ethylene glycol was selected as the hydrocarbon for reforming due to its attractive properties. Unlike alcohols such as methanol and ethanol, it is non-volatile and convenient for transport and storage. Moreover, this chemical has consumer acceptance since it is being used as an antifreeze in automobiles. Here we report the results of the investigation.

Materials and Methods

1 wt% Pt/Al₂O₃ catalyst was prepared by incipient wetness impregnation method using Pt(NH₃)₄(NO₃)₂ as the precursor. Na was added to Pt/Al₂O₃ by incipient wetness using an aqueous solution of Na₂CO₃. It was dried overnight then calcined to 400°C for 3 hours in air. Titania pillared clay catalysts were prepared following the general procedure described by Sterte [3] using bentonite powder (Fisher) as the starting clay. An aqueous solution of Pd(NO₃)₂ was added to the pillared clay support by incipient wetness impregnation. The catalyst was dried overnight then calcined at 500°C for 6 hours in air. Quantification of all reactants and products were made using both gas chromatography and NO_x analyzer. This allows the decoupling of NO_x adsorption from NO reduction at low temperatures over high surface area catalysts.

Results and Discussion

The Na-modified Pt/Al₂O₃ catalyst was found to be effective for gas phase EG reforming at 230°C. At low EG concentrations, near complete conversion of EG to H₂ is achieved, mainly via decomposition (forming 3 moles of H₂ for every mole of EG reacted).

The effect of O₂ in the feed is shown in Fig. 1. A very interesting aspect is the ability of O₂ to prevent deactivation when the reforming reaction was conducted at higher EG concentrations (2.2-4.3%). Not only does O₂ improve the H₂ production, it also allows a facile way to control the ratio of H₂/CO going into the de-NO_x unit. CO can be completely eliminated by operating an O₂/EG ratio of 2 in the reaction feed mixture. This is advantageous when Pd was employed as the deNO_x catalyst since it is more effective when CO content is lower. Addition of Na (equivalent to 12 Na/Pt, mol/mol) increased the EG conversion and led to higher H₂ production.

The output of the EG reforming unit was combined with a simulated exhaust stream and then sent to a deNO_x unit, which consisted of a Pd/TiO₂ catalyst for H₂/CO-SCR at 110°C. Although Pd/TiO₂ has reasonably good activity at 110°C, the presence of CO in the feed had a negative effect on NO conversion over this catalyst. Pd supported on titania pillared clay were synthesized and tested for H₂/CO-SCR and were found to be much more active than Pd/TiO₂ and were able to effectively use CO in the feed. The influence of the preparation method of the Ti-pillared clay support and the Pd loading on the NO reduction activity was examined. Pd particle size was found to have a significant effect on the NO reduction activity (Fig. 2).

Figure 1.

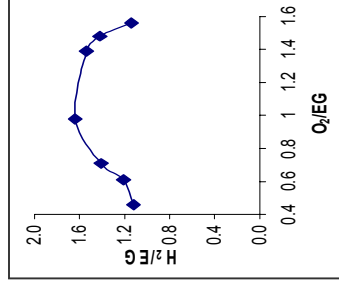


Figure 2.

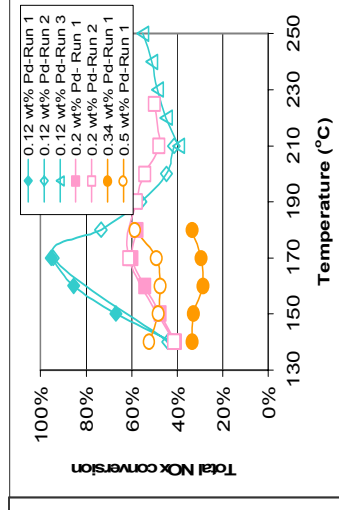


Figure 1. Effect on O₂ on H₂ efficiency over 0.1 g Na/Pt/Al₂O₃

Figure 2. NO conversion vs. temperature. Feed composition of 2000ppm H₂, 1200ppm CO, 500ppm NO, 5% O₂ at a flow rate of 210 ml/min using Pd/Ti-pillared clay catalyst.

Significance

We have demonstrated that a coupled EG reforming and SCR de-NO_x unit can effectively reduce NO_x at temperatures relevant to diesel exhaust treatment.

References

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