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Enhanced Transport in Ammonia Slip Catalyst (ASC) Washcoat by using Sacrificial Agents

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Highlights

- ASC: Noted increase in NH_3 conversion while maintaining N_2 selectivity
- SCR: Adequate improvement in NO/NH_3 conversion
- Monolith reactor model predicts and optimizes enhancement

1. Introduction

A dual-layer Ammonia Slip Catalyst (ASC) with base precious group metal (PGM) and top selective catalytic reduction of NOx by NH_3 (NH_3-SCR) layer is commonly used for selective oxidation of NH_3 to N_2. The top SCR (e.g. Cu/Chabazite) layer increases N_2 selectivity at the expense of NH_3 conversion by restricting diffusion of reacting species. To enhance gas transport, the sacrificial agents (including yeast and poly-tert-butyl-acrylate) are used to create calcined holes in SCR layer, increasing the porosity [1]. While keeping a fixed catalyst loading, the dual-layer ASC with modified top SCR layer exhibits a significant increase in NH_3 conversion without affecting the desired product N_2 selectivity. Similar improvements in the NO/NH_3 conversion are achieved with a standalone SCR layer for the standard NH_3+NO reaction.

2. Methods

Catalyst slurry preparation: For the PGM layer, Pt/Al_2O_3 catalyst powder was synthesized using wetness impregnation with Pt precursor hexahydrate chloroplatinic acid. An estimated amount of precursor was added to achieve the target loading of Pt(1.5 g/ft^3) and the corresponding Pt/Al_2O_3 washcoat loading of 1.5 g/in^3. The Pt/Al_2O_3 slurry was prepared by mixing Pt/Al_2O_3, water and boehmite (20 wt% AlOOH) in mass ratio of 4:8:5. For the SCR layer, the powdered catalyst Cu/SSZ-13 used in the experiments was provided by Johnson Matthey Inc. Three different slurries of Cu/SSZ-13 were prepared by mixing powdered Cu/SSZ-13, water and boehmite (20 wt% AlOOH) in mass ratio of 4:8:5. The slurries were then ball milled for 20 h. Out of three Cu/SSZ-13 slurries prepared, one was kept as it is, while active dry yeast was added to second and polymer (poly-tert-butyl acrylate) was added to third slurry.

Monolith coating: For the dual-layer ASC, the base Pt/Al_2O_3 layer was deposited by dipping blank monoliths in Pt/Al_2O_3 slurry, followed by drying at 120 ^oC and calcining at 500 ^oC. For the unmodified dual-layer ASC, the monolith already coated with Pt/Al_2O_3 layer was dipped in Cu/SSZ-13 slurry for 30 s and excess slurry removed by blowing air for 10 s followed by drying in oven at 120 ^oC for 2 h. For the modified dual-layer ASC, the Cu/SSZ-13 slurry with yeast was used to prepare the top layer. Similarly, Cu/SSZ-13 slurry containing polymer was used for making the other modified type of dual-layer samples. The modified dual-layer samples were dried at room temperature for 2 h. The dipping and drying procedure was repeated to achieve required loading. Once the expected loading was met, the normal dual-layer sample was calcined at 500 ^oC for 5 h using temperature ramp up/down of 0.5 ^oC/min. The modified dual-layer samples containing yeast or polymer in the top layer were calcined in flow reactor at 500 ^oC for 2 h using temperature ramp up rate of 3 ^oC/min.

For SCR monolith, the blank monoliths were coated with Cu-SSZ-13 following above procedure.

Samples: aPt(b)Cu(c)y – [here, a is monolith sample length, b is Pt loading in g/ft^3, c is Cu-SSZ-13 loading in g/in^3, y and p for yeast and polymer, no index for conventional dual-layer]

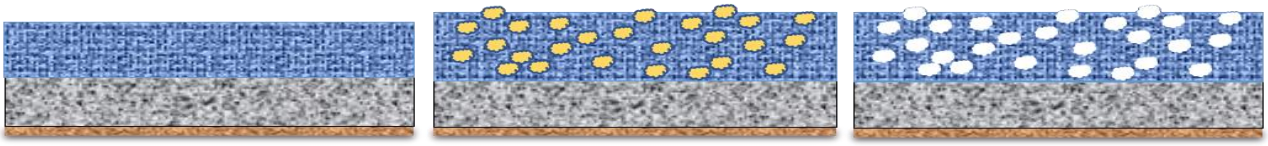

Figure 1. [Left] - Conventional dual-layer ASC (base Pt/Al_2O_3 and top Cu-SSZ-13), [Middle] – Modified dual-layer with yeast/polymer in top layer, [Right] – Modified dual-layer after calcination at 500 °C.

3. Results and discussion

The modified dual-layer ASC outperformed conventional dual-layer in NH_3 conversion (Fig. 2, left) for NH_3 oxidation reaction and negligibly affected N_2 selectivity (results not shown for brevity) [2]. The results showed that the more porous and thicker SCR washcoat layer has better transport properties than the thinner and less porous SCR layer. A dual-layer monolith reactor model predicted the noted decline in the ratio τ/ε (tortuosity/porosity) of the modified washcoat. In another experiment, the NH_3 conversion using the modified dual-layer with Pt(1.5) is comparable to the conventional dual-layer with Pt(4.5) at the same GHSV of 332k h^{-1}. The use of the sacrificial agent could reduce the PGM requirements by up to 60%.

Similarly, the SCR reaction results (Fig. 2, right) showed noticeable improvement in temperature regime (250 °C – 400 °C) by using a modified single layer SCR. At temperatures above 250 °C, the NO conversion of the modified sample with 2.1 g/in^3 loading is comparable to conventional SCR sample with 3.2 g/in^3 loading Improvement in gas transport through washcoat can cut the amount of Cu-SSZ-13 by~30%.

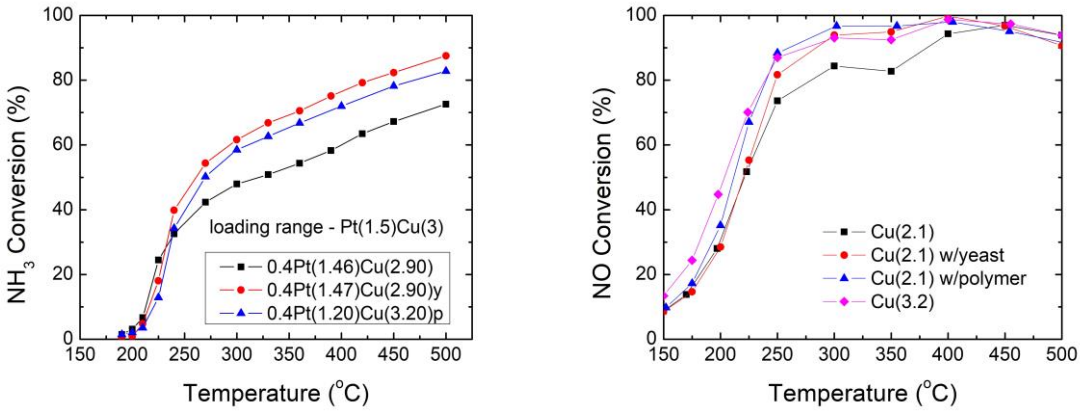

Figure 2. [Left] – NH_3 conversion as a function of temperature (steady state). Reactants: NH_3 = 500 ppm, O_2 = 5% and balance Ar (GHSV = 332 k h^{-1}); [Right] – NO conversion as function of temperature (steady state). Reactants: NO and NH_3 500 ppm each, O_2 = 5% and balance Ar (GHSV: 66kh^{-1})

4. Conclusions

Significant enhancement in NH_3 conversion was achieved for ammonia slip catalysts while maintaining high N_2 selectivity. The improved ASC activity could be explained by the higher porosity generated by sacrificial agents, which was also demonstrated by a mathematical model.

References

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[2] Scheuer, A., Hauptmann, W., Drochner, A., Gieshoff, J., Vogel, H., & Votsmeier, M. (2012). Dual layer automotive ammonia oxidation catalysts: Experiments and computer simulation. *Applied Catalysis B: Environmental*.

Keywords
Ammonia slip catalyst (ASC); selective catalytic reduction (SCR); monolith reactor; vehicle emission control