



## Selective oxidation of ammonia on mixed and dual-layer Fe-ZSM-5 + Pt/Al<sub>2</sub>O<sub>3</sub> monolithic catalysts



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### ARTICLE INFO

#### Article history:

Received 17 October 2013

Received in revised form 6 January 2014

Accepted 7 January 2014

Available online 11 March 2014

#### Keywords:

Ammonia oxidation

AMOX

Ammonia slip catalyst

ASC

Platinum catalyst

Zeolite

Selective catalytic reduction ;

### ABSTRACT

The development of improved Ammonia Slip Catalysts (ASCs) was pursued by changing the composition and architecture of the critical functions, Selective Catalytic Reduction (SCR) and oxidation, needed in the catalyst for high NH<sub>3</sub> oxidation activity and selectivity to N<sub>2</sub>. Selected space velocities and reactant compositions were used to probe chemical and physical processes that limit the performance of ASCs. On a single component Pt/Al<sub>2</sub>O<sub>3</sub> catalyst, at the lower space velocity (66k h<sup>-1</sup>) light-off was characterized by a sharp increase in NH<sub>3</sub> conversion to >98%, while at high space velocity (265k h<sup>-1</sup>) the transition in conversion was more gradual and the limiting conversion was below 98%, indicative of transverse transport limitations. The light-off temperature of ammonia oxidation on Pt/Al<sub>2</sub>O<sub>3</sub> catalyst decreased with Pt loading from 0.7 to 10 g Pt/ft<sup>3</sup> monolith and, in general, the selectivity to N<sub>2</sub> decreased while that of N<sub>2</sub>O and NO<sub>x</sub> increased. A dual-layer ASC comprising a top layer of Fe-ZSM-5 and a bottom layer of Pt/Al<sub>2</sub>O<sub>3</sub> resulted in higher selectivity and yield to N<sub>2</sub>, due to SCR reactions between the counter diffusing NO<sub>x</sub> formed in the Pt/Al<sub>2</sub>O<sub>3</sub> and NH<sub>3</sub> reactant in the Fe-zeolite layer. However, the diffusion resistance provided by the Fe-ZSM-5 layer inhibited the overall ammonia conversion at high space velocity. When Fe-zeolite and Pt/Al<sub>2</sub>O<sub>3</sub> particles were mixed and washcoated as a single layer, this led to an increase in NH<sub>3</sub> conversion at high space velocity due to a decrease in the diffusion barrier that was observed with the dual-layer structure. When SCR and oxidation catalyst particles were contiguous in the washcoat structure as in single-layer mixed catalysts, the N<sub>2</sub> yield was lower due to Pt-catalyzed NH<sub>3</sub> oxidation, compared to the dual-layer ASC, which was especially apparent at low space velocity. The dual-layer catalyst was superior to the mixed layer catalyst at high temperatures, exhibiting lower NO<sub>x</sub> and higher N<sub>2</sub> yields whereas the mixed catalyst out-performed the dual-layer catalyst at low temperature by exhibiting lower N<sub>2</sub>O and higher N<sub>2</sub> yield.

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### 1. Introduction

Urea based selective catalytic reduction (SCR) of NO<sub>x</sub> is a widely practiced technology for diesel engine vehicles to reduce NO<sub>x</sub> (NO + NO<sub>2</sub>) to N<sub>2</sub> [1,2]. Urea is injected at a rate dictated by the NO emission rate, which itself is a function of the engine operating conditions, so that a nominal NH<sub>3</sub>:NO feed ratio of unity is achieved as required by the SCR stoichiometry. In order to meet the stringent EPA and European standards for NO<sub>x</sub> emissions, SCR catalysts require occasional over-dosing of NH<sub>3</sub>, generated on-board by urea hydrolysis. Furthermore, under the dynamic conditions of vehicle operation, NH<sub>3</sub> is stored on the Lewis and Bronsted acid sites of the Fe- or Cu-exchanged zeolites SCR catalysts [3,4] for NO<sub>x</sub> reduction

reactions and also to minimize the concentration variations in NH<sub>3</sub> needed for NO<sub>x</sub> reduction i.e. adsorption sites acts as NH<sub>3</sub> buffer. However, a sudden increase in the exhaust temperature may lead to NH<sub>3</sub> desorption. SCR catalysts are generally poor NH<sub>3</sub> oxidation catalysts and NH<sub>3</sub> over-dosing and desorption events could potentially lead to NH<sub>3</sub> emissions to the environment, widely referred as NH<sub>3</sub> slip. The “Ammonia Slip Catalyst” (ASC), positioned downstream of the SCR catalyst, is used to oxidize such NH<sub>3</sub> to prevent its emissions in to environment [5,6].

For ASCs, Pt is the catalyst of choice given its high NH<sub>3</sub> oxidation activity; however it also yields undesired products NO<sub>x</sub> and N<sub>2</sub>O whose selectivity depends on reaction temperature. In fact, Pt is the commercial catalyst for NH<sub>3</sub> oxidation to NO as the first step in nitric acid production [7], albeit at far more strenuous conditions (T > 1000 °C, NH<sub>3</sub> concentrations > 10 vol.%) than those encountered in the aftertreatment exhaust gas streams. NO and NO<sub>2</sub> are obviously undesirable products of NH<sub>3</sub> oxidation; their formation in the ASC decreases the overall effectiveness of the aftertreatment

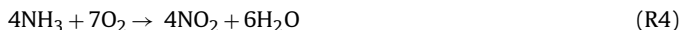
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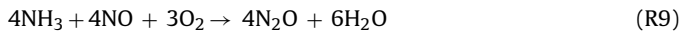
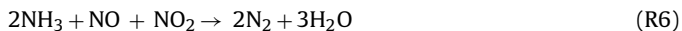
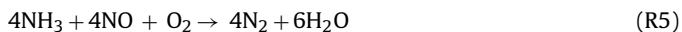
system whose function is to minimize the emission of  $\text{NO}_x$  from the tail pipe.  $\text{N}_2\text{O}$  is a greenhouse gas (GHG) and its emission is subject to emerging GHG regulations.

There is therefore a need to develop a very active, selective and compact  $\text{NH}_3$  oxidation catalyst, so that it takes up minimal space in the aftertreatment system, and produces  $\text{N}_2$  as the main product. Moreover, this must be accomplished while reducing the cost of the ASC by limiting the precious metal loading to  $\ll 10 \text{ g/ft}^3$  [8]. Several approaches have been taken by the exhaust aftertreatment community to achieve the goals mentioned above. One such approach involves the use of a bi-functional catalyst in which  $\text{NO}_x$  that is produced by  $\text{NH}_3$  oxidation on Pt based catalyst is selectively converted to  $\text{N}_2$  with a second reduction catalyst component such as metal exchanged zeolite (SCR) catalysts. The bi-functional ASC can have a variety of architectures defined by the specific proximity of the Pt (oxidative function) and SCR (reductive function) components. An architecture that has been described in the recent literature is a dual-layer ASC comprising a  $\text{Pt/Al}_2\text{O}_3$  washcoat, itself coated with a Fe- or Cu-exchanged zeolitic catalyst [9,10].

The basic working principle of the dual-layer ASC is described as follows.  $\text{NH}_3$  in the flowing gas channel diffuses into the layered catalyst, first encountering the top SCR catalyst layer. Some of the  $\text{NH}_3$  is stored on this catalyst while the remaining diffuses to the underlying  $\text{Pt/Al}_2\text{O}_3$  layer.  $\text{NH}_3$  that reaches the  $\text{Pt/Al}_2\text{O}_3$  layer may be oxidized by the excess  $\text{O}_2$  present to the various N-containing species through the following global reactions:



Many studies have shown that at lower temperatures (R1) and (R2) are dominant, while at higher temperature (R3) and (R4) are dominant [11–19]. The  $\text{NH}_3:\text{O}_2$  ratio is a second important parameter with excess  $\text{NH}_3$  favoring  $\text{N}_2$  and  $\text{N}_2\text{O}$ , and excess  $\text{O}_2$  favoring  $\text{NO}$  and  $\text{NO}_2$  [11–13,15,16,20]. The products  $\text{NO}$  and  $\text{NO}_2$  that are formed in the bottom oxidation catalyst layer then diffuse through the top SCR catalyst layer where they may react with stored and counter-diffusing  $\text{NH}_3$  via selective catalytic reduction and oxidation chemistries described below:



The selective product  $\text{N}_2$  formed diffuses back to the flow channel and exits through the tail pipe, thus leading to the overall selective product conversion of  $\text{NH}_3$  to  $\text{N}_2$ . Reactions (R5)–(R7) are called standard, fast and  $\text{NO}_2$  SCR, respectively. Several studies have been conducted recently by different groups to understand the effect of feed concentrations of  $\text{NO}$  and  $\text{NO}_2$  on rates of the SCR reactions [4,21–25]. It has been determined that for an equimolar  $\text{NO}$  and  $\text{NO}_2$  R6 is dominant, which is the fastest of all the SCR reactions. Further, for higher  $\text{NO}_2$  content in the feed (R7) is dominant, and at lower  $\text{NO}_2$  content (R5) is dominant. It has also been determined that at higher temperature the direct  $\text{NH}_3$  oxidation, (R8), is also feasible on the SCR catalyst. By-products  $\text{N}_2\text{O}$  may be formed by reaction (R9).

Most of the published studies reported to date on the ASC have been modeling-focused [9,26–29], with a few notable exceptions. Colombo et al. [27,30] reported experimental findings involving

powder catalysts in different configurations including the “Double Bed” and “Mechanical Mixture”. These respectively mimicked dual-layer and mixed-catalyst configurations. Kamasamudram et al. [31] studied the behavior and the functionality of ASC by direct comparison of ASC with diesel oxidation catalyst and SCR catalyst by the means of accelerated progressive catalyst aging. Scheuer et al. [9] studied the effect of catalyst size and the thickness of the SCR layer on  $\text{NH}_3$  oxidation through an experimentally-validated 2-D model. In a recent study, our group reported data for the dual-layer ASC comprising a bottom  $\text{Pt/Al}_2\text{O}_3$  and Cu-ZSM-5 top layer supported on a cordierite monolith [10]. That study provided for the first time experimental verification of the workings of the dual-layer architecture through the systematic variation of the SCR layer loading.

In this work we advance the understanding of the chemical and physical processes occurring during ammonia oxidation on a series of synthesized ASCs of different catalyst architectures containing  $\text{Pt/Al}_2\text{O}_3$  and Fe-ZSM-5. Our objective is to examine the effect of the composition and architecture of the two critical ASC functions, SCR and oxidation, to achieve high  $\text{NH}_3$  oxidation activity and selectivity to  $\text{N}_2$ . Another objective of this study is to determine the catalyst composition and architecture that maximizes the selectivity of  $\text{NH}_3$  oxidation to  $\text{N}_2$  for a wide range of temperatures while minimizing the Pt loading. To this end, the performance of a series of single component  $\text{Pt/Al}_2\text{O}_3$  catalysts with the same overall washcoat loading but varied Pt loading are reported. These  $\text{Pt/Al}_2\text{O}_3$  catalysts were then modified with Fe-ZSM-5 catalyst. Two different structures, dual-layer and mixed, are compared to better understand the effect of proximity of the oxidation (of  $\text{NH}_3$ ) and reduction (of  $\text{NO}_x$ ) components. By keeping the loading of zeolitic catalyst and  $\text{Pt/Al}_2\text{O}_3$  catalyst on both dual and mixed ASC constant, this enables a direct comparison of structural configuration on  $\text{NH}_3$  conversion capability and its product selectivity. The findings are interpreted with a phenomenological model.

## 2. Experimental

### 2.1. Catalyst synthesis and characterization

$\text{Pt/Al}_2\text{O}_3$  catalysts with 0.03, 0.14 and 0.46% Pt loadings (mass basis) were prepared via the incipient wetness impregnation method. Aqueous slurry of  $\gamma\text{-Al}_2\text{O}_3$  was prepared by mixing 60 g of  $\gamma\text{-Al}_2\text{O}_3$  particles with 60 ml of deionized water. The  $\text{Al}_2\text{O}_3$  slurry was ball milled for approximately 20 h using an alumina ball milling machine. The pH of the slurry was adjusted to 3.5 using acetic acid or ammonium hydroxide, which upon milling gave a particle size in the range 3–10  $\mu\text{m}$  [32,33]. The slurry was dried overnight at 120 °C, followed by calcination at 500 °C for 5 h with a temperature ramp rate of 0.5 °C/min to yield  $\text{Al}_2\text{O}_3$  support. Pt precursor solution was prepared by mixing the appropriate amount of chloroplatinic acid hexahydrate into deionized water, whose volume was equal to the manufacturer-provided pore volume of the  $\gamma\text{-Al}_2\text{O}_3$ . The impregnation was carried out by drop-wise addition of Pt containing aqueous solution while constantly stirring the powder to obtain a uniform impregnation of Pt into  $\gamma\text{-Al}_2\text{O}_3$  particles. The resulting powder was dried overnight in an oven at 120 °C, followed by calcination at 500 °C for 5 h with the temperature ramp rate of 0.5 °C/min to yield  $\text{Pt/Al}_2\text{O}_3$  catalyst.

The  $\text{Pt/Al}_2\text{O}_3$  slurry was prepared by mixing the  $\text{Pt/Al}_2\text{O}_3$  powder, water and boehmite ( $\text{AlOOH}$ ; 20 wt%) solution at a mass ratio of 8:15:2. The pH of the slurry was adjusted to about 4 using acetic acid or ammonium hydroxide, and then ball milled for approximately 20 h. Cordierite monolith cores of 400 cpsi provided by BASF (Iselin, NJ) were cut into 2 or 0.5 cm long and 0.8 cm diameter samples,

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