Catalysis Today 231 (2014) 105–115

Contents lists available at ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

Selective oxidation of ammonia on mixed and dual-layer Fe-ZSM-5 + Pt/Al_2O_3 monolithic catalysts

Sachi Shrestha[a], Michael P. Harold[a,*], Krishna Kamasamudram[b], Aleksey Yezerets[b]

[a] Dept. of Chemical and Biomolecular Engineering, University of Houston, Houston, TX 77204-4004, USA
[b] Corporate Research and Technology, Cummins Inc., 1900 McKinely Av., Columbus, IN 47201, USA

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_3 oxidation activity and selectivity to N_2. 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_2O_3 catalyst, at the lower space velocity ($66k\,h^{-1}$) light-off was characterized by a sharp increase in NH_3 conversion to >98%, while at high space velocity ($265k\,h^{-1}$) 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_2O_3 catalyst decreased with Pt loading from 0.7 to 10 g Pt/ft^3 monolith and, in general, the selectivity to N_2 decreased while that of N_2O and NO_x increased. A dual-layer ASC comprising a top layer of Fe-ZSM-5 and a bottom layer of Pt/Al_2O_3 resulted in higher selectivity and yield to N_2, due to SCR reactions between the counter diffusing NO_x formed in the Pt/Al_2O_3 and NH_3 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_2O_3 particles were mixed and washcoated as a single layer, this led to an increase in NH_3 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_2 yield was lower due to Pt-catalyzed NH_3 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_x and higher N_2 yields whereas the mixed catalyst out-performed the dual-layer catalyst at low temperature by exhibiting lower N_2O and higher N_2 yield.

1. Introduction

Urea based selective catalytic reduction (SCR) of NO_x is a widely practiced technology for diesel engine vehicles to reduce NO_x ($NO + NO_2$) to N_2 [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_3: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_x emissions, SCR catalysts require occasional over-dosing of NH_3, generated on-board by urea hydrolysis. Furthermore, under the dynamic conditions of vehicle operation, NH_3 is stored on the Lewis and Bronsted acid sites of the Fe- or Cu-exchanged zeolites SCR catalysts [3,4] for NO_x reduction reactions and also to minimize the concentration variations in NH_3 needed for NO_x reduction i.e. adsorption sites acts as NH_3 buffer. However, a sudden increase in the exhaust temperature may lead to NH_3 desorption. SCR catalysts are generally poor NH_3 oxidation catalysts and NH_3 over-dosing and desorption events could potentially lead to NH_3 emissions to the environment, widely referred as NH_3 slip. The “Ammonia Slip Catalyst” (ASC), positioned downstream of the SCR catalyst, is used to oxidize such NH_3 to prevent its emissions in to environment [5,6].

For ASCs, Pt is the catalyst of choice given its high NH_3 oxidation activity; however it also yields undesired products NO_x and N_2O whose selectivity depends on reaction temperature. In fact, Pt is the commercial catalyst for NH_3 oxidation to NO as the first step in nitric acid production [7], albeit at far more strenuous conditions ($T > 1000\,^\circ C$, NH_3 concentrations >10 vol.%) than those encountered in the aftertreatment exhaust gas streams. NO and NO_2 are obviously undesirable products of NH_3 oxidation; their formation in the ASC decreases the overall effectiveness of the aftertreatment

---

* Corresponding author.
E-mail addresses: mharold@uh.edu (M.P. Harold), krishna.kamasamudram@cummins.com (K. Kamasamudram).

0920-5861/$ – see front matter © 2014 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.cattod.2014.01.024

system whose function is to minimize the emission of NO_x from the tail pipe. N_2O 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 NH_3 oxidation catalyst, so that it takes up minimal space in the aftertreatment system, and produces 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 «10 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 NO_x that is produced by NH_3 oxidation on Pt based catalyst is selectively converted to 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 Pt/Al_2O_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. NH_3 in the flowing gas channel diffuses into the layered catalyst, first encountering the top SCR catalyst layer. Some of the NH_3 is stored on this catalyst while the remaining diffuses to the underlying Pt/Al_2O_3 layer. NH_3 that reaches the Pt/Al_2O_3 layer may be oxidized by the excess O_2 present to the various N-containing species through the following global reactions:

$$4NH_3 + 3O_2 \rightarrow 2N_2 + 6H_2O \qquad (R1)$$

$$2NH_3 + 2O_2 \rightarrow N_2O + 3H_2O \qquad (R2)$$

$$4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O \qquad (R3)$$

$$4NH_3 + 7O_2 \rightarrow 4NO_2 + 6H_2O \qquad (R4)$$

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 NH_3:O_2 ratio is a second important parameter with excess NH_3 favoring N_2 and N_2O, and excess O_2 favoring NO and NO_2 [11–13,15,16,20]. The products NO and 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 NH_3 via selective catalytic reduction and oxidation chemistries described below:

$$4NH_3 + 4NO + O_2 \rightarrow 4N_2 + 6H_2O \qquad (R5)$$

$$2NH_3 + NO + NO_2 \rightarrow 2N_2 + 3H_2O \qquad (R6)$$

$$4NH_3 + 3NO_2 \rightarrow 3.5N_2 + 6H_2O \qquad (R7)$$

$$4NH_3 + 3O_2 \rightarrow 2N_2 + 6H_2O \qquad (R8)$$

$$4NH_3 + 4NO + 3O_2 \rightarrow 4N_2O + 6H_2O \qquad (R9)$$

The selective product N_2 formed diffuses back to the flow channel and exits through the tail pipe, thus leading to the overall selective product conversion of NH_3 to N_2. Reactions (R5)–(R7) are called standard, fast and NO_2 SCR, respectively. Several studies have been conducted recently by different groups to understand the effect of feed concentrations of NO and NO_2 on rates of the SCR reactions [4,21–25]. It has been determined that for an equimolar NO and NO_2 R6 is dominant, which is the fastest of all the SCR reactions. Further, for higher NO_2 content in the feed (R7) is dominant, and at lower NO_2 content (R5) is dominant. It has also been determined that at higher temperature the direct NH_3 oxidation, (R8), is also feasible on the SCR catalyst. By-products N_2O 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 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 Pt/Al_2O_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 Pt/Al_2O_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 NH_3 oxidation activity and selectivity to N_2. Another objective of this study is to determine the catalyst composition and architecture that maximizes the selectivity of NH_3 oxidation to N_2 for a wide range of temperatures while minimizing the Pt loading. To this end, the performance of a series of single component Pt/Al_2O_3 catalysts with the same overall washcoat loading but varied Pt loading are reported. These Pt/Al_2O_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 NH_3) and reduction (of NO_x) components. By keeping the loading of zeolitic catalyst and Pt/Al_2O_3 catalyst on both dual and mixed ASC constant, this enables a direct comparison of structural configuration on NH_3 conversion capability and its product selectivity. The findings are interpreted with a phenomenological model.

2. Experimental

2.1. Catalyst synthesis and characterization

Pt/Al_2O_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 γ-Al_2O_3 was prepared by mixing 60 g of γ-Al_2O_3 particles with 60 ml of deionized water. The Al_2O_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 μm [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 Al_2O_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 γ-Al_2O_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 γ-Al_2O_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 Pt/Al_2O_3 catalyst.

The Pt/Al_2O_3 slurry was prepared by mixing the Pt/Al_2O_3 powder, water and boehmite (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,