

Low Temperature Catalyst for NH₃ Removal

Oscar Monje¹

ESC Team QNA, Kennedy Space Center, FL, 32931

and

Orlando Melendez²

NASA, Kennedy Space Center, FL, 32931

Air revitalization technologies maintain a safe atmosphere inside spacecraft by the removal of CO₂, ammonia (NH₃), and trace contaminants. NH₃ onboard the International Space Station (ISS) is produced by crew metabolism, payloads, or during an accidental release of thermal control refrigerant. Currently, the ISS relies on removing NH₃ via humidity condensate and the crew wears hooded respirators during emergencies. A different approach to cabin NH₃ removal is to use selective catalytic oxidation (SCO), which builds on thermal catalytic oxidation concepts that could be incorporated into the existing TCCS process equipment architecture on ISS. A low temperature platinum-based catalyst (LTP-Catalyst) developed at KSC was used for converting NH₃ to H₂O and N₂ gas by SCO. The challenge of implementing SCO is to reduce formation of undesirable byproducts like NO_x (N₂O and NO). Gas mixture analysis was conducted using FTIR spectrometry in the Regenerable VOC Control System (RVCS) Testbed. The RVCS was modified by adding a 66 L semi-sealed chamber, and a custom NH₃ generator. The effect of temperature on NH₃ removal using the LTP-Catalyst was examined. A suitable temperature was found where NH₃ removal did not produce toxic NO_x (NO, NO₂) and N₂O formation was reduced.

Nomenclature

Cchb	=	concentration in the chamber
Cexterior	=	exterior concentration
LTP	=	Low Temperature Platinum
RVCS	=	Regenerable VOC Control System
SCO	=	Selective Catalytic Oxidation
SCR	=	Selective Catalytic Reduction
TCCS	=	Trace Contaminant Control System

I. Introduction

Ammonia (NH₃) on ISS is produced by crew metabolism, payloads, or from an accidental release of thermal control refrigerant. The Spacecraft Maximum Allowable Concentration for ammonia is 7 ppm. On ISS ammonia (NH₃) is removed in the Trace Contaminant Control system (TCCS) by absorption using Type 3032 activated carbon treated with phosphoric acid (H₃PO₄). Type 3032 activated carbon is no longer commercially available. Ammonia that is not removed or partially oxidized is removed in the downstream high temperature catalytic oxidizer consisting of palladium over alumina pellets. A better approach to cabin ammonia removal is selective catalytic oxidation (SCO) because it builds on an existing thermal catalytic oxidation concepts that have flight experience and could be more readily incorporated into the existing TCCS process equipment architecture on ISS. The selective catalytic oxidation of ammonia produces N₂ and water (a). In addition, nitrogen oxides and nitrous oxide are also formed (b-c). The SMAC for NO and NO₂ are 4.5 and 5 ppm, respectively. The challenge of implementing SCO is to reduce formation of undesirable byproducts (b-c). These products can be further removed by selective catalytic reduction with ammonia (d-f).

¹Senior Research Scientist, ESC Team QNA, Mail Code ESC 53 Kennedy Space Center, FL, 32931

²Senior Chemical Engineer, NASA Surface Systems Division, Mail Code NE-S, Kennedy Space Center, FL, 32931

Selective Catalytic Oxidation (SCO)

- a) $2\text{NH}_3 + 3/2 \text{O}_2 \rightarrow \text{N}_2 + 3\text{H}_2\text{O}$
- b) $2\text{NH}_3 + 2\text{O}_2 \rightarrow \text{N}_2\text{O} + 3\text{H}_2\text{O}$
- c) $2\text{NH}_3 + 5/2 \text{O}_2 \rightarrow 2\text{NO} + 3\text{H}_2\text{O}$

Selective Catalytic Reduction (SCR)

- d) $4\text{NO} + 4\text{NH}_3 + \text{O}_2 \rightarrow 4\text{N}_2 + 6\text{H}_2\text{O}$
- e) $2\text{NO}_2 + 4\text{NH}_3 + \text{O}_2 \rightarrow 3\text{N}_2 + 6\text{H}_2\text{O}$
- f) $\text{NO} + \text{NO}_2 + 2\text{NH}_3 \rightarrow 2\text{N}_2 + 3\text{H}_2\text{O}$

Commercially available sorbent materials were evaluated for NH_3 removal¹⁻². Developmental sorbents, Cu and Co- ion exchange Y-zeolite showed the highest sorption capacity. The sorption capacity is hindered for all zeolites under humid conditions. It was concluded that zeolites providing reversible ammonia removal could be used in a swing bed configuration downstream from a desiccant for short adsorb cycles.

Other studies have evaluated commercial catalysts for ammonia removal. A proposed advanced water processor system for ISS includes a vapor phase catalytic ammonia reduction (VPCAR) subsystem using new catalysts developed by TDA and HSSSI for vapor phase ammonia oxidation³⁻⁴. These new catalysts were studied and compared to commercially available catalysts. Most commercial catalysts showed some activity for ammonia in the presence of oxygen at temperatures from 150 to 250 °C. However, NO_x formation increased rapidly above 200 °C. The TDA catalysts demonstrated high activity above 200 °C with low NO formation (1 mg/hr). The HSSSI catalysts demonstrated activity below 200 °C but produced 1.7 mg/hr of NO .

A low temperature platinum-catalyst (LTP-Catalyst) was developed at KSC in FY12 for converting NH_3 to H_2O and N_2 gas by SCO. This SCO catalyst could significantly reduce the upstream sorbent bed size of TCCS to address only organo-silicone compounds, which currently also adsorbs NH_3 .

II. Experimental Method and Results

A. LTP Synthesis and Ammonia Generation

The LTP-Catalyst was synthesized and dried at 120 °C overnight and calcined at 500 °C for six hour. The Regenerable VOC Control System (RVCS) Testbed was modified by adding a 66 L semi-sealed chamber and an NH_3 generator. NH_3 was generated by supplying NH_4Cl solutions of known molarity onto excess NaOH pellets. NH_3 is released into a 2L NH_3 generator as an NH_4Cl solution is delivered to NaOH pellets via syringe. NO_2 was found to be generated via this procedure. The NH_3 generated in the NH_3 Generator can be swept into the 66L chamber as needed to bring the NH_3 concentration in the chamber to the same initial concentration. A pump recirculates chamber air among the chamber, an FTIR and the catalyst bed. The FTIR measures NH_3 , NO , N_2O , and NO_2 production during SCO.

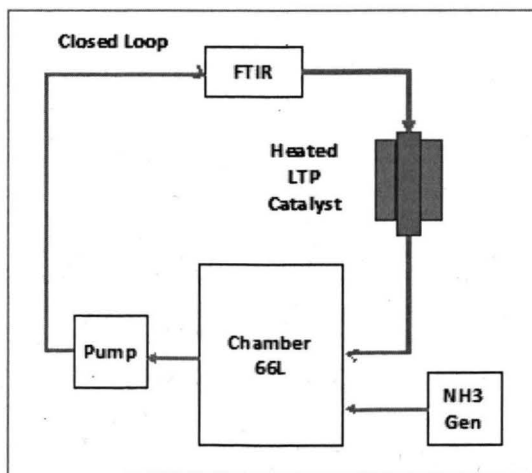
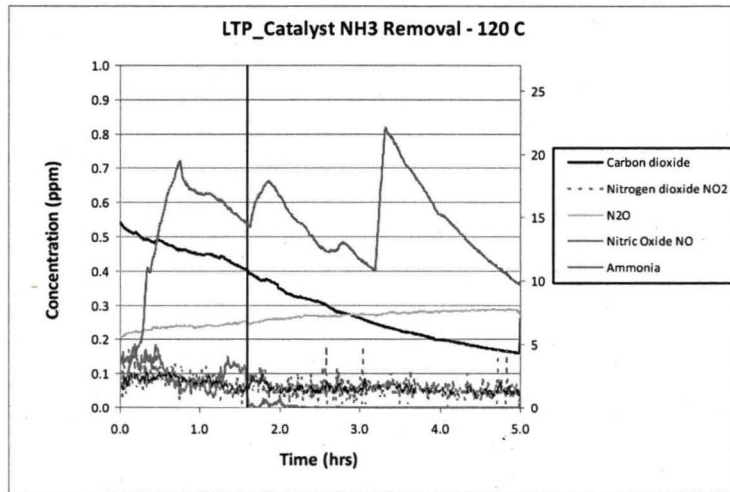


Figure 1. The RVCS was reconfigured in a closed-loop mode to test the SCO NH₃ removal rate using the LTP-Catalyst. An NH₃ generator was devised to supply NH₃ concentrations ranging from 1 to 700 ppm to a 66L chamber. A pump recirculates chamber air among the chamber, an FTIR and the catalyst bed. The FTIR measures NH₃, NO, N₂O, and NO₂ production during SCO.

B. Ammonia Removal Experiment

The 66L chamber was filled with lab air, which contains atmospheric NO, and with water vapor. Initially, the gas was recirculated bypassing the catalyst bed. Then, the gas was mixed with NH₃ generated in the NH₃ Generator (Figure 2) and NH₃ concentration (right axis) rose up to 18 ppm after 1 hour. The Gas Generator introduced up to 0.1 ppm of NO and NO₂. The chamber was then recirculated bypassing the bed and the concentration of most gases (NH₃, CO₂, NO, and NO₂) decreased at the chamber leak rate. At 1.8 the Gas Generator increased the NH₃ concentration and the air was circulated through the LTP-Catalyst bed. At 3.2 h the NH₃ was increased again and allowed to flow through the bed.

Figure 2. NH₃ was added to the 66L chamber with the NH₃ Generator and leak rate measured in the 1st 1.7 h. NH₃ removal by the LTP-Catalyst was measured after 1.7 hours.



1. Chamber Leak Rates

The 66L chamber was found to be leaky, thus its leak rate had to be determined in order to accurately determine NH₃ removal rates. NH₃ concentration in the chamber (C_{chb}) will decrease due to a concentration gradient to a lower C_{exterior} concentration. The chamber leak rate was determined by fitting NH₃ concentration data to Equation 1.

$$\text{Leak (\%/hr)} = (100 / \text{dTime}) * \text{LN}([C_{chb_1}] - [C_{exterior_1}] / ([C_{chb_2}] - [C_{exterior_2}])) \quad (1)$$

The chamber leak rate was found to be 30-33 %/hr and it was sensitive to the recirculating flow rate of the closed-loop system. The chamber leak rate was also confirmed by using changes in chamber CO₂ concentration.

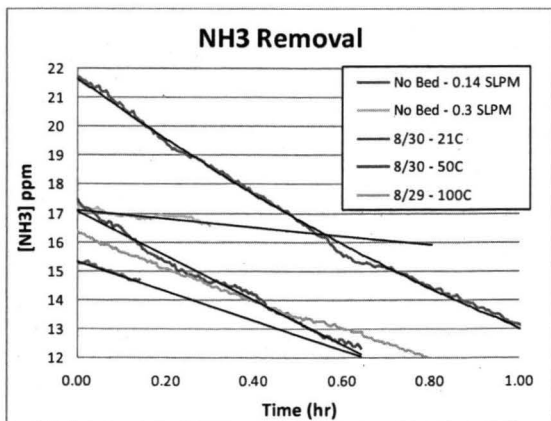


Figure 3. NH₃ concentration in the 66L chamber decreased when the LTP-Catalyst bed was not present due to the chamber leak rate. The NH₃ removal was not obtained from changes in chamber concentration must be corrected for the leak rate.

2. NH_3 Removal vs. NH_3 Concentration

The NH_3 removal rate corrected for chamber leak rate, rNH_3 , was determined at 150 °C and 1.4% water vapor using two NH_3 concentrations (Table 1). rNH_3 was 3.3 mg/g-h at 17 ppm and rose to 53 mg/g-h. The NH_3 removal rates for a 500 g bed of LTP-Catalyst at 150 °C were 1.7 and 27 g/h at 17 and 420 ppm, respectively.

Table 1. Leak Rate Corrected NH_3 Removal rates at 150 °C and 1.4% water vapor.

NH_3 ppm	rNH_3 mg/gh	550 g Bed g/h
17	3.3	1.7
420	53	27

3. Temperature Effects

The N_2O concentration in the 66L chamber was 0.35 ppm from a catalyst bed temperature of 20 to 150 °C. It rose to 0.47 ppm at 170 °C, and was 1.8 ppm at 200 °C. NO and NO_2 formation was not detected during NH_3 removal via SCO with the LTP-Catalyst.

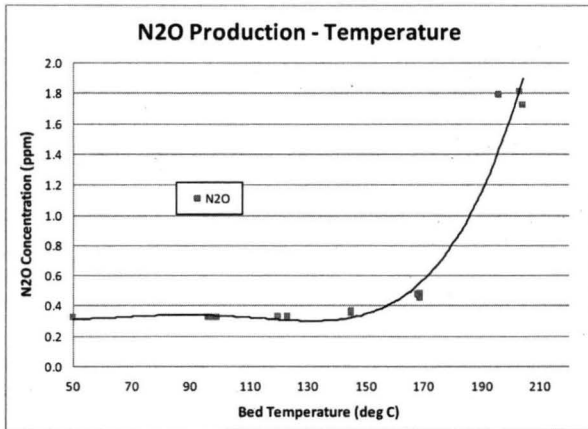
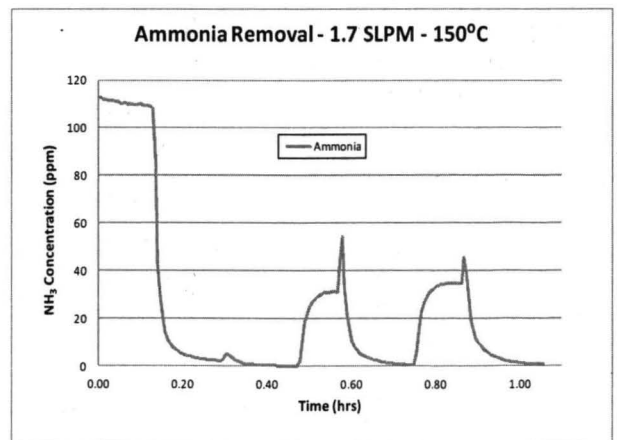


Figure 4. N_2O concentration in the 66L chamber increased dramatically as the LTP-Catalyst bed temperature exceeded 170 °C

Figure 5 shows the ammonia concentration versus time at a constant temperature of 150 °C. The initial ammonia concentration of 110 ppm decreases rapidly when ammonia goes through the catalyst in the bed. After ammonia removal the bed is closed at times 0.4 and 0.7 hours. At times 0.5 and 0.8 hours the bed is open to 50 ppm of ammonia followed by rapid ammonia removal by the LTP catalyst. The ammonia spikes seen in the graph at 0.6 and 0.9 hours correspond to ammonia left in the bed after closing of the bed.

Figure 5. NH_3 concentration in the effluent concentration leaving the LTP-Catalyst bed held at a Temperature of 150 °C



4. Pressure drop

The bed containing 3g of LTP-Catalyst decreased the flow rate through it by 50%. The talcum powder consistency of the LTP-Catalyst resulted in a large pressure drop. It was also hard to contain with 100-mesh screens. The powder was found outside the bed on several occasions.

C. Future Development of LTP-Catalyst

The LTP-Catalyst is a fine powder, which leads to high pressure drop and poor containment. Future work should aim to reduce pressure drop and improve reliability. Precision Combustion, Inc was contacted for exploring the possibility of coating the LTP-Catalyst onto Microlith® metal mesh elements.

References

¹ Luna, B., Podolske, J., Ehresmann, D., Howard, J., "Evaluation of Commercial Off-the-Shelf Ammonia Sorbents and Carbon Monoxide Oxidation Catalysts," SAE Technical Paper 2008-01-2097, 2008, doi:10.4271/2008-01-2097

² Luna, B., Somi, G., Winchester, J.P., Mulloth, L. and Perry, J L., "Evaluation of Commercial Off-the-Shelf Sorbents and Catalysts for Control of Ammonia and Carbon Monoxide" Presented at the 40th International Conference on Environmental Systems; 11-15 Jul. 2010; Barcelona, Spain.

³ Flynn, M., Tleimat, M., Nalette, T., and Quinn, G., "Performance Testing of the Vapor Phase Catalytic Ammonia Removal Engineering Development Unit," SAE Technical Paper 2005-01-3033, 2005, doi:10.4271/2005-01-3033.

⁴ Wickham, D., Engel, J., Yu, J., Nalette, T. et al., "Results of VPCAR Pilot Scale and System Level Tests for the Selective Oxidation of Ammonia to Nitrogen and Water," SAE Technical Paper 2005-01-3034, 2005, doi:10.4271/2005-01-3034.