Plasma-Assisted Catalysis NH_3 Generation in a Hybrid ns Pulse / RF Discharge

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Abstract: Plasma-assisted catalysis generation of ammonia in a repetitively pulsed "hybrid" ns pulse / sub-breakdown RF discharge is studied by Fourier Transform Infrared (FTIR) absorption spectroscopy. The plasma is sustained in an H_2-N_2 mixture in a heated flow reactor, with different catalyst samples placed in the flow channel. The ammonia product is measured in the reactor exhaust. The addition of sub-breakdown RF waveform to a ns pulse train increases yield by up to 25%. The mechanism of the yield enhancement is discussed.

1. Introduction

Kinetic mechanism of ammonia generation by plasma-assisted catalysis has been the focus of experimental and modeling studies over the last few years [1,2]. Kinetic modeling indicates that NH_3 production in the plasma is dominated by reactions of N and H atoms on the catalyst surface [3]. It was also suggested that vibrational excitation of N_2 in the plasma may increase the rate of its dissociation on the catalyst and enhance the ammonia yield [4].

2. Methods

To isolate the effect of vibrational excitation of N_2 on ammonia yield, the vibrational temperature must be varied independently of other plasma parameters. Previously, the addition of a sub-breakdown RF voltage waveform to a ns pulse discharge was demonstrated to increase the N_2 vibrational temperature [5], compared to the ns pulse train alone. In this work, 1 kV peak voltage, 13.56 MHz, 70 μs duration RF waveforms are generated between 15 kV peak voltage, 100 ns pulses repeated every 100 μs, with 100-300 pulses per burst. The pulse bursts are repeated at 10 Hz. The plasma is operated in a heated H_2-N_2 flow without a catalyst, and over "blank" γ-Al_2O_3, Ni/γ-Al_2O_3, and Ru/γ-Al_2O_3 catalyst samples. No optical emission is detected during the RF waveforms. Tunable Diode Laser Absorption Spectroscopy (TDLAS) is used to measure $N_2(A^3\Sigma)$ metastables with and without RF voltage, to monitor electronic excitation and generation of N and H atoms. FTIR absorption spectroscopy is used to measure NH_3 yield in the reactor exhaust.

3. Results and Discussion

Fig. 1 illustrates the ammonia yield increase in 10% H_2-N_2 due to the addition of sub-breakdown RF excitation to 100-, 200-, and 300-pulse bursts. Adding the RF excitation results in the transient yield increase by up to 25% (blue boxes in Fig. 1), and scales with the number of ns discharge pulses. The transient rise and decay of the yield (~ 5 min) occur faster than the long-term increase caused by the N atom accumulation on the catalyst (~ 1 hr). This indicates that the RF plasma-enhanced reactive species that control the yield become available rapidly, and do not accumulate on the surface. This effect is demonstrated on Ni and Ru catalysts, as well as on blank Al_2O_3. Significantly lower yield enhancement was observed without the sample present in the reactor. No evidence of $N_2(A^3\Sigma)$ populations increase, or its accelerated quenching by N or H atoms

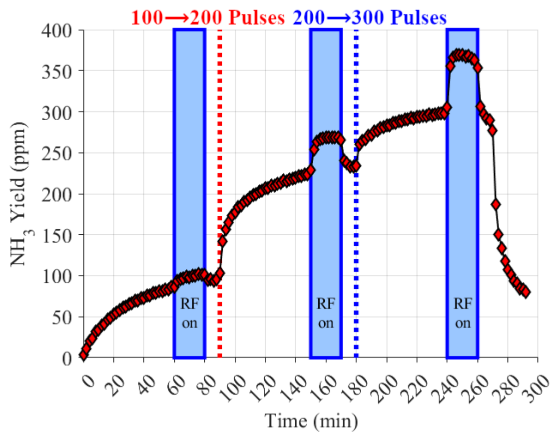

Fig. 1. Time-resolved NH_3 yield in ns pulse and hybrid ns / RF) discharges, for 100, 200, and 300 pulses per burst. 10% H_2-N_2 over Ru catalyst. P=190 Torr, T=573 K. Blue bars indicate RF excitation on.

during the RF excitation was detected. This indicates no additional molecular dissociation or electronic excitation by sub-breakdown RF excitation. The results suggest that NH_3 yield increase is due to either $N_2(v)$ excitation or accelerated N, H atom transport to the catalyst surface by the RF waveform. Indirect evidence of the former mechanism is the enhanced NO generation in the hybrid ns / RF discharge in N_2-O_2 mixtures at the same conditions, up to 150% compared to ns pulse discharge alone.

4. Summary

The addition of sub-breakdown RF waveform to a ns pulse discharge increases the ammonia yield, measured over blank alumina, as well as Ni and Ru catalysts, by up to 25% compared to the ns pulse discharge operating alone.

Acknowledgement

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References

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