Identification of surface nitridation during plasma catalytic ammonia synthesis in N_2/H_2 mixtures

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Abstract: We aim to understand the formation of nickel nitride on nickel catalyst surfaces in plasma-assisted catalytic ammonia synthesis. Nitrogen-based species on the Ni catalyst were detected after AC dielectric barrier discharge (DBD) plasma in N_2/H_2 mixtures. Effects of nickel nitride formation and gas-phase N and H radicals on NH_3 synthesis is reported.

1. Introduction

Understanding the role of excited and ionized species produced in non-thermal plasma and their interaction on catalyst surfaces remains a challenge for plasma-assisted catalysis. Plasma can activate N_2, enabling NH_3 formation at lower temperatures and pressures, and this is often attributed to different mechanisms and rate-determining steps from thermal catalysis, e.g., Eley- Rideal reactions. However catalyst surface modification may also play a role, such as in the formation of metal nitrides. Here, we identify the formation of nickel nitride and discuss the role of a Mars-van Krevelen (MvK) mechanism.

2. Methods

An 18 kV, AC-powered DBD plasma was struck within a quartz parallel plate reactor containing a 99.9% Ni foil catalyst. The N_2/H_2 ratio was varied with the reactor held at a pressure of 100 Torr and ambient temperature. High resolution X-ray photoelectron spectroscopy (HR-XPS) was used to obtain the elemental composition and chemical states at the surface. Concentrations of gas phase N and H radicals were measured via operando femtosecond two-photon absorption laser induced fluorescence (fs-TALIF) [1]. Reaction performance was studied using both gas chromatography (GC) for NH_3 detection and in-situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) to probe N-H surface-bound intermediates.

3. Results and Discussion

Figure 1 displays the N 1s HR-XPS spectra from Ni after different exposures. Treating a Ni surface under N_2 plasma yielded three peaks, with the two peaks at 407 and 403 eV assigned to $Ni(NO_3)_2$ and NO_x species [2]. When H_2 was added into the N_2 feed, those two peaks disappeared, leaving one large broad peak at 398.0 eV assigned to nickel nitride(s). Peaks from surface NH_x species were found on the high binding energy tail at 398.5–402.0 eV. The N_2/H_2 plasma-treated samples had similar spectra to those after thermal NH_3 treatment, which produces Ni_3N at the surface. XPS depth profiling showed that the nitride extended beyond a nm into the Ni surface, Ni_xN_y nitride species are consistent with other surface characterization techniques, such as Raman spectroscopy.

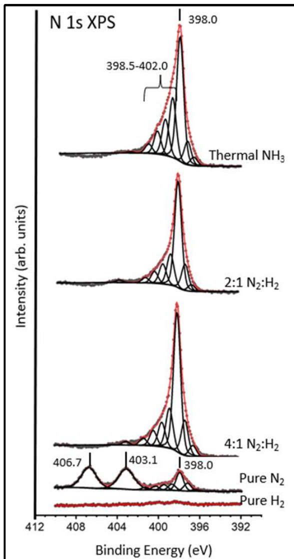

Fig. 1. Comparison of N 1s XPS spectra for Ni after different exposures.

The increase in nitride concentration in plasma likely plays a role in both the total NH_3 production and the reaction pathways at low temperatures. Using DRIFTS, NH_2, NH_3 and NNH_2 are found at the catalyst surface, with larger peaks for a pre-nitrided catalyst. Surface NNH_2 species disappear at high temperatures. Presence of these N-H species implies that N-N activation may not be the rate determining step at low temperatures but instead may be NH_3 formation from reaction of adsorbed NH_2 ($NH_2^* + H^* = NH_3^*$). As the catalyst temperature increases, the rate-determining step may revert to N_2 activation or NH formation.

4. Conclusion

Understanding the formation of nickel nitride in plasma and its role in NH_3 synthesis mechanisms will lead to optimizing the synergy between plasma and catalyst in plasma assisted ammonia synthesis. The formation of nitrides on the catalyst surface opens the door to exploring the possibility of a MvK mechanism playing a role in in NH_3 synthesis under these conditions.

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References

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