Plasma-enhanced ammonia synthesis: from plasma-phase ammonia synthesis towards plasma-enhanced catalytic ammonia synthesis

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Abstract: Recently, Mehta et al. [1] postulated that plasma-induced vibrational excitations in N₂ decrease the dissociation barrier for plasma-enhanced catalytic ammonia synthesis, without influencing the subsequent hydrogenation reactions and ammonia desorption. The postulate is experimentally substantiated with unpromoted and promoted, γ -Al₂O₃-supported ruthenium-based ammonia synthesis catalysts. The apparent activation barrier decreases from 60-115 kJ mol⁻¹ for thermal catalysis to 20-40 kJ mol⁻¹ for plasma-enhanced catalysis.

Keywords: plasma-enhanced catalysis, ammonia, vibrational excitation, DBD.

1. Background

Ammonia is proposed as a hydrogen carrier in the circular economy. Various alternative pathways to the Haber-Bosch process have been proposed for green nitrogen fixation in the form of ammonia. One of the alternatives for renewable ammonia synthesis is plasma-enhanced ammonia synthesis.

So far, the highest energy yield for plasma-enhanced ammonia synthesis reported so far is 20-35 g_{NH3} kWh⁻¹ [2]-[4]. Even though various authors have researched ammonia synthesis in the presence of a plasma [4]-[10], plasmaenhanced catalysis is not fully understood and the dominant reaction mechanisms are currently unknown [11], [12]. Recent reviews on plasma-enhanced ammonia synthesis by Hong et al. [7], Li et al. [10] and Peng et al. [6] focused mostly on experimental results of plasmaenhanced catalysis, rather than the underlying catalytic principles. Surface processes must be understood better for plasma-enhanced catalytic ammonia synthesis to develop further [13]. In the current work, plasma-enhanced catalytic ammonia synthesis is investigated using catalysis concepts such as the activation barriers for chemical reactions.

Recently, Mehta et al. [1] performed density function theory (DFT) calculations on plasma-enhanced catalytic ammonia synthesis, based on scaling relations. Mehta et al. [1] postulated that plasma-induced vibrational excitation in N_2 enhances the catalytic ammonia synthesis rate, without influencing the subsequent hydrogenation reactions and ammonia desorption at atmospheric conditions. However, limited experimental evidence was provided. Therefore, this postulation is evaluated with experimental data in the current paper. Previously reported data of Kim et al. [2] as well as new data is used for this analysis. The proposed mechanism is evaluated with the experimental data for thermal catalysis and plasma-enhanced catalysis over promoted and unpromoted ruthenium-based catalysts.

2. Conditions for plasma-enhanced catalysis

Before evaluating experimental data for plasma-enhanced catalytic ammonia synthesis, a framework is set up for the conditions for plasma-enhanced catalytic ammonia synthesis. The definition of plasma-enhanced catalysis is not generally accepted.

Ammonia synthesis in the presence and absence of a plasma was reported below and above the light-off temperature by Kim et al. [4]. As shown in Figure 1, no ammonia is thermally synthesized below 200°C, while some ammonia is formed in the presence of a plasma. At temperatures below the light-off temperature (200°C for ruthenium-based catalysts), ammonia is not desorbed from the metal surface [4], [14]. This suggests that ammonia formation below 200°C is due to plasma alone rather than any synergistic interaction of the plasma and the catalyst at low temperatures.



Figure 1. Ammonia synthesis with and without plasma. Reproduced from [4].

When the temperature is increased, ammonia is synthesized catalytically both thermally (plasma off) and in the presence of a plasma (plasma on), as shown in Figure 1. At temperatures above the light-off temperature, the ammonia synthesized in the presence of a plasma is plasma-enhanced catalytic ammonia synthesis. The ammonia concentration achieved with plasma-enhanced catalysis is higher than the sum of the concentrations in plasma-phase ammonia synthesis (i.e., the activity when the plasma is on at temperatures below the light-off temperature) and thermal-catalytic ammonia synthesis, indicating a synergistic activating effect of the catalyst.

3.Experimental

A dielectric barrier discharge reactor, consisting of catalyst pellets, quartz tube, stainless steel tube, and power supply was used for the experiments performed, as previously reported in [2]. Pellet-shaped Ru/ γ -Al₂O₃ catalysts (diameter, 3.2 mm; length, 3.6 mm; surface area, 98.6 m²/g; 2 wt.% Ru) were used as the reference catalyst in this study. Cesium (Cs), magnesium (Mg), and potassium (K) were loaded as a promoter. The promoter loading was 5 wt.% or 10 wt.%. The catalyst amount packed in the plasma reactor was approx. 13.5 g. The reactant gas consisted of 80% N₂ and 20% H₂. The total flow rate was 4 L min⁻¹. The ammonia concentration was determined using an on-line Fourier transform infrared spectrometer. For a detailed description of the reactor setup and the analysis techniques used, see ref. [2].

4. Results & Discussion

The apparent activation barriers for thermal catalysis and plasma-enhanced catalysis are obtained from Figure 2 and from Table 1. The Arrhenius plot for thermal catalysis is not shown here.

The absolute activity of promoted and unpromoted catalysts varies by an order of magnitude in case of plasmaenhanced catalysis, while the apparent activation barrier remains nearly constant (see Figure 2). This is similar to trends observed in thermal catalysis, as reported by Aika et al. [15]. Thus, the function of the promoter is probably similar for thermal catalysis and for plasma-enhanced catalysis.



Figure 2. Arrhenius plot of plasma-enhanced catalytic ammonia synthesis over various alumina supported ruthenium-based catalysts.

As follows from Table 1, the apparent activation barrier for plasma-enhanced catalysis is lower than for thermal catalysis. Various mechanisms have been proposed to be responsible for plasma-enhanced catalysis, such as (1) plasma-induced surface charging [16], and (2) plasmainduced electronic or vibrational excitations in N_2 [1], [7].

Table 1. Apparent activation energy for thermal-catalytic ammonia synthesis ($E_{a,app-thermal}$) and for plasma-enhanced catalytic ammonia synthesis ($E_{a,app-plasma}$).

Catalyst	E _{a,app} -thermal (kJ mol ⁻¹)	Ea,app-plasma (kJ mol ⁻¹)
2Ru/γ-Al ₂ O ₃	60-70 [17], [18]	20
10K-2Ru/y-Al ₂ O ₃	100-115 [17]	41
5Mg-2Ru/γ-Al ₂ O ₃	104	36
5Cs-2Ru/γ-Al ₂ O ₃	100-115 [17], [18]	27

Plasma-induced surface charging

Bal et al. [16] postulated that plasma-induced surface charging may be significant for plasma-enhanced catalytic processes, by altering the electronic nature of the catalytic surface.

For thermal ruthenium-based catalysts it is well known that supports have a profound influence the catalytic performance due to their electronegativity [17]-[19], and possibly an electron donation ability [20]. This changes the activity of the ruthenium-based catalysts by orders of magnitude, while the apparent activation energy remains within the same range (70-120 kJ mol⁻¹) [18], [19], [21]. Furthermore, the apparent activation energy does not change to activation barriers as low as 20-40 kJ mol⁻¹ among oxide-supported transition metals, because of scaling relations. When moving along the periodic table (from Fe to Ru and Co), the activation barrier remains more or less constant (in the range 70-110 kJ mol⁻¹) [21]. Thus, surface-induced surface charging is not the dominant mechanism for plasma-enhanced catalytic ammonia synthesis.

<u>Plasma-induced vibrational or electronic excitations in N₂</u> The mechanism of the catalytic activity enhancement for ammonia synthesis is related N₂ activation by the plasma, as follows from the apparent activation energies for thermal catalysis and plasma-enhanced catalysis (see Table 1). The difference between the apparent activation energy for thermal catalysis and plasma-enhanced catalysis is in the range of the activation energy for dissociative N₂ adsorption (45-60 kJ mol⁻¹ [18], [22] for the unpromoted ruthenium catalyst and 95-105 kJ mol⁻¹ [18], [22] for the promoted ruthenium catalysts).

Mehta et al. [1] postulated that plasma-induced vibrational excitations in N_2 decrease the dissociation barrier, without influencing the subsequent hydrogenation reactions and ammonia desorption. In case N_2 activation is the major mechanism for plasma-enhanced catalytic ammonia synthesis, the rate of adsorption of excited N_2 can be high. The dissociative sticking probability increases when the internal energy of N_2 increases [23]–[25] by up to a few orders of magnitude as compared to the ground state [24].

As discussed by Kim et al. [4], the light-off temperature for thermal-catalytic and plasma-enhanced catalytic ammonia synthesis is the same. This indicates that the ammonia desorption is indeed not directly influenced by the plasma.

Electronic excitations in N₂ (i.e., N₂*) may also be of importance [7]. Based on observed ammonia synthesis rates, it is difficult to discriminate between vibrational excitations and electronic excitations in N₂. However, as follows from kinetic studies by Hong et al. [26] and DFT calculations by Mehta et al. [1], the rate of vibrational excitations in N₂ is about ~10⁶-10⁷ times larger than the rate of electronic excitations in N₂ for atmospheric pressure plasmas. Thus, vibrational excitations in N₂ are the dominant species for excitations in N₂ in atmospheric pressure.

5. Conclusion

The conditions for plasma-enhanced catalysis have been identified. Furthermore, the non-zero apparent activation energies at elevated temperatures (200-330°C) indicate that the ammonia synthesis must be plasma-enhanced catalytic ammonia synthesis over alumina-supported ruthenium-based catalysts instead of plasma-phase ammonia synthesis.

The mechanism for activity enhancement in plasmaenhanced catalytic ammonia synthesis is due to plasmainduced vibrational excitations in N_2 without affecting the subsequent hydrogenation steps and ammonia desorption, as was previously postulated by Mehta et al. [1]. This was substantiated with the activation barriers for thermal catalysis and plasma-enhanced catalysis over various ruthenium-based catalysts. Promoter effects were found to be similar for thermal catalysis and plasma-enhanced catalysis.

6. References

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