

Vibrationally Excited Activation of N₂ in Plasma-Enhanced Catalytic Ammonia Synthesis: A Kinetic Analysis

Kevin H. R. Rouwenhorst,*^{,†}[®] Hyun-Ha Kim,[‡] and Leon Lefferts[†][®]

[†]Catalytic Processes and Materials, MESA+ Institute for Nanotechnology, University of Twente, Enschede 7500AE, Netherlands [‡]Institute for Environmental Management Technology, National Institute of Advanced Industrial Science and Technology, Tsukuba, Ibaraki 305-8569, Japan

Supporting Information

ABSTRACT: Plasma-enhanced catalytic ammonia synthesis has been proposed as an alternative pathway for green nitrogen fixation in the case of medium- and small-scale operation. Recently, Mehta et al. [Nat. Catal. 2018, 1 (4), 269-275] postulated that plasma-induced vibrational excitations of N2 decrease the dissociation barrier, without influencing the subsequent hydrogenation reactions and ammonia desorption at atmospheric conditions. In this paper, this postulation is substantiated with experimental data of unpromoted and promoted, alumina-supported ruthenium ammonia synthesis catalysts. Within the temperature regime for plasma-enhanced catalytic ammonia synthesis over ruthenium-based catalysts (>200 °C), synergy is



experimentally observed between the catalyst and the plasma by a lowered apparent activation energy. While the apparent activation energy for thermal-catalytic ammonia synthesis typically ranges from ~60 to ~115 kJ mol⁻¹ depending on the promoters, the apparent activation energy for plasma-enhanced catalytic ammonia synthesis ranges from ~20 to ~40 kJ mol⁻¹, consistent with the hypothesis that ammonia synthesis is enhanced via plasma-induced vibrational excitations of N2. Further support follows from the observation that the effects of promoters and supports on activity are similar for thermal catalysis and plasma-enhanced catalysis. As promoter and support influence activity via enhancing dissociation of N₂, it follows that breaking the N-N bond is still relevant in plasma-enhanced catalytic ammonia synthesis.

KEYWORDS: Plasma-enhanced catalysis, Ammonia, Kinetic analysis, Vibrational excitation, Dielectric barrier discharge

INTRODUCTION

Ammonia is proposed as a hydrogen carrier in the circular economy.²⁻⁴ Various alternative pathways to the Haber-Bosch (HB) process have been proposed for green nitrogen fixation in the form of ammonia, such as electrochemical synthesis, dense metallic membrane reactors, solar thermochemical redox cycles, and plasma-enhanced catalytic synthesis.^{5,6} The Haber-Bosch process typically operates in a centralized and continuous manner, usually at least 2000 tons of NH₃ per day. The efficiency of the Haber-Bosch process decreases upon downsizing and upon intermittent operation,⁶ which is one of the bottlenecks in matching with renewable energy sources. Plasma-enhanced catalytic ammonia synthesis could be a potential technology in combination with intermittent energy sources such as wind and solar, which show fast changes in load.⁷ Nonthermal plasma can be used, in which electrons reach temperatures of a few thousand kelvin, while the heavier radical species remain at a temperature close to the gas temperature.⁸ As the nitrogen and hydrogen are activated by electrons and subsequently have a higher energy, higher equilibrium conversions to ammonia can be attained at low pressure operation due to a change in the Gibb's energy of reaction favoring ammonia formation.⁹ Early developments in plasma-enhanced nitrogen fixation in the form of ammonia date from more than one-and-a-half-centuries ago, when in 1859 Morren and Perrot performed experiments in a dielectric barrier discharge (DBD) reactor.¹⁰

The highest energy yield for plasma-enhanced ammonia synthesis reported so far is 28 kWh kg⁻¹ ammonia (equivalent to 36 g_{NH3} kWh⁻¹).¹¹ Even though various authors have researched ammonia synthesis in the presence of a plasma in various types of plasma reactors, i.e. dielectric barrier discharge, microwave, and radiofrequency reactors,^{12–18} plasma-en-hanced catalysis is poorly understood.^{19,20} The reported energy yields in literature for dielectric barrier discharge, microwave, and radiofrequency reactors are shown in Figure 1. It should be noted that the reported data in Figure 1 is obtained in a wide temperature and pressure range, and at various reactant compositions. It is expected that plasmacatalytic ammonia synthesis may be feasible for small-scale

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Figure 1. Reported energy yields in the literature for dielectric barrier discharge (DBD), microwave (MW), and radiofrequency (RF) reactors. In cases where microwave plasma or radiofrequency plasma was used, the abbreviations "MW" and "RF" are used. Otherwise, the data is reported for dielectric barrier discharge plasma. Pulsed dielectric barrier discharge plasmas are represented by "Pulse". Experimental data is reproduced from the works of Akay et al.,²¹ Barboun et al.,²² Gomez-Ramirez et al.,^{23,24} Hong et al.,²⁵ Iwamoto et al.,²⁶ Kim et al.,¹¹ Mizushima et al.,²⁷ Patil,²⁸ Peng et al.,^{29,30} Shah et al.,³¹ Srinath,³² and Wildfire et al.³³

applications at an energy yield of 150–200 $g_{\rm NH3}\,kWh^{-1}$ and at 1 mol % ammonia. 18

Recent reviews on plasma-enhanced ammonia synthesis by Bogaerts et al.,¹² Hong et al.,¹⁴ Li et al.,¹⁷ and Peng et al.¹ focused mostly on experimental results of plasma-enhanced ammonia synthesis, rather than the underlying catalytic principles. The most recent review of Mehta et al.³⁴ sheds some light on surface processes occurring in plasma-enhanced catalytic ammonia synthesis. Furthermore, the authors discuss how excitation of N₂ can enhance the ammonia synthesis rate over the catalytic surface. Surface processes on catalysts in plasma-enhanced synthesis processes must be understood better for plasma-enhanced catalytic ammonia synthesis to develop further via catalyst material optimization, aiming at energy-efficient plasma-enhanced catalysis.⁷ In the current paper, plasma-enhanced catalytic ammonia synthesis is investigated using heterogeneous catalysis concepts such as the activation barriers for chemical reactions.

Both conventional iron-based ammonia synthesis catalysts^{35–38} and ruthenium-based ammonia synthesis catalysts^{35,37,39,40} were recently reviewed. The thermal-catalytic reaction mechanism for ammonia synthesis is well understood. Aika et al.⁴⁰ found a relation between the electronegativity of both support and promoter and the ammonia synthesis rate over ruthenium-based catalysts for thermal catalysis. The ammonia synthesis rate changes by orders of magnitude among various supports, and the ammonia synthesis rate increases with decreasing electronegativity of the support. Further activity enhancement is observed upon addition of alkali or alkaline earth metals as promoters.

Recently, Mehta et al.¹ developed microkinetic models that incorporate the potential influences of vibrational excitations in N₂, based on density functional theory (DFT) results available in literature. Mehta et al.¹ postulated that plasma-induced vibrational excitation of N₂ enhances N₂ dissociation, the ratedetermining step in thermal-catalytic ammonia synthesis, without influencing the subsequent hydrogenation reactions of NH_x species on the Ru surface and ammonia desorption at atmospheric conditions. The authors claim that the N₂ dissociation can become sufficiently fast, such that the hydrogenation becomes the rate-determining step for plasmaenhanced catalysis. However, limited experimental evidence was provided. Ammonia synthesis rates at a single temperature, flow rate, and plasma power were reported for Fe/ γ -Al₂O₃, Ru/ γ -Al₂O₃, Co/ γ -Al₂O₃, Ni/ γ -Al₂O₃, and Pt/ γ -Al₂O₃. However, apparent activation barriers for plasma-enhanced catalytic ammonia synthesis were not evaluated. Therefore, this postulation is evaluated with additional experimental data in the current paper. Previously reported data of Kim et al.¹¹ as well as new data is used for this analysis.

RESULTS

The experimental setup and catalyst preparation is described in the Supporting Information and was reported previously.¹¹ Various ruthenium-based catalysts were tested for the ammonia synthesis activity ($2Ru/\gamma$ -Al₂O₃, 10K- $2Ru/\gamma$ -Al₂O₃, 5Cs- $2Ru/\gamma$ -Al₂O₃, and 5Mg- $2Ru/\gamma$ -Al₂O₃). Herein, the numbers represent the weight percent loading of the compounds. The same batch of Ru/γ -Al₂O₃ catalysts is used for all experiments (i.e., for the catalysts without promoter, and the catalysts impregnated with Cs, Mg, and K promoters). Thus, the Ru dispersion is the same for all catalysts. Part of the results were previously reported by Kim et al.¹¹ The previously reported results and new results are listed in Table S1 in the Supporting Information.

Thermal Catalysis. The activities for thermal-catalytic ammonia synthesis over $2\text{Ru}/\gamma$ -Al₂O₃, 10K- $2\text{Ru}/\gamma$ -Al₂O₃, 5Cs- $2\text{Ru}/\gamma$ -Al₂O₃, and 5Mg- $2\text{Ru}/\gamma$ -Al₂O₃ in the temperature window between 200 and 330 °C are shown in Arrhenius plots in Figure 2. Herein, the activity for thermal catalysis is



Figure 2. Arrhenius plot of thermal-catalytic ammonia synthesis over various alumina-supported ruthenium-based catalysts. P = 1 bar, $H_2:N_2 = 1:4$, various flow rates (see Table S1): black filled squares (\blacksquare) $2Ru/\gamma-Al_2O_3$; gray filled diamonds (\blacklozenge) $10K-2Ru/\gamma-Al_2O_3$; white filled triangles (\triangle) $5Cs-2Ru/\gamma-Al_2O_3$; and white filled circles (\bigcirc) $5Mg-2Ru/\gamma-Al_2O_3$.

calculated as the ammonia concentration produced, multiplied by the flow rate and divided by the catalyst mass for thermal catalysis. The activity for the unpromoted catalyst is lowest, which is consistent with previous studies in literature.^{41,42} Furthermore, the promotion with Mg appears to be most effective. Due to the limited experimental data available, an apparent activation barrier can only be obtained for 5Mg-2Ru/ γ -Al₂O₃, resulting in 104 kJ mol⁻¹. This is in good agreement with typical values in reported in literature, between 100 and 115 kJ mol $^{-141,42}$ (see Table 1), for promoted aluminasupported ruthenium catalysts.

Table 1. Apparent Activation Energy for Thermal-Catalytic Ammonia Synthesis ($E_{a,app-thermal}$), Apparent Activation Energy for Thermal-Catalytic N₂ Equilibration by Isotope Exchange Reactions with N₁₅ ($E_{a,N2equi}$), and Apparent Activation Energy for Plasma-Enhanced Catalytic Ammonia Synthesis ($E_{a,app-plasma}$)^{*a*}

catalyst	E _{a,app-thermal} (kJ mol ⁻¹)	$\substack{E_{\mathrm{a,N2equi}}\(\mathrm{kJ\ mol}^{-1})}$	E _{a,app-plasma} (kJ mol ⁻¹)
$2Ru/\gamma$ -Al ₂ O ₃	60-70 ^{41,42}	45-60 ^{41,43}	20 ^{<i>a</i>}
10 K-2Ru/ γ -Al $_2$ O $_3$	100–115 ⁴²	95-105 ^{41,43}	41 ^{<i>a</i>}
$5Mg-2Ru/\gamma-Al_2O_3$	104 ^{<i>a</i>}		36 ^a
5 Cs-2Ru/ γ -Al ₂ O ₃	100–115 ^{41,42}		27 ^a
^a The data obtained in this work.			

Plasma-Enhanced Catalysis. The activities for plasma enhanced-catalytic ammonia synthesis over $2Ru/\gamma$ -Al₂O₃, 10K- $2Ru/\gamma - Al_2O_3$, $5Cs - 2Ru/\gamma - Al_2O_3$, and $5Mg - 2Ru/\gamma - Al_2O_3$ in the temperature window between 200 and 330 °C are shown in an Arrhenius plot in Figure 3a. The ammonia synthesis activity for plasma-enhanced catalysis is higher than for thermal catalysis, as can be seen by comparing Figures 2 and 3. The highest concentrations obtained are 0.17 mol % ammonia for 5Mg- $2Ru/\gamma$ -Al₂O₃ at 300 °C, while a concentration of 0.09 mol % ammonia was obtained for $10K-2Ru/\gamma-Al_2O_3$ at 330 °C. The equilibrium concentration of ammonia at 300 and 330 °C is 0.51 and 0.31 mol % at atmospheric pressure and for $H_2:N_2 =$ 1:4, respectively. The concentration of 0.17 mol % ammonia at 300 °C is 33% of the equilibrium concentration, while the concentration of 0.09 mol % ammonia at 330 °C is 29% of the equilibrium concentration. Thus, the measurements are far below the equilibrium concentration, which is required to minimize the effect of the reverse reaction (i.e., the ammonia decomposition reaction). In principle, a catalyst which is active for the ammonia synthesis reaction is also active for the ammonia decomposition reaction.

When the data for plasma-enhanced catalysis is plotted in an Arrhenius plot in a similar manner as for thermal catalysis (Figure 3a), no linear correlation is obtained (R^2 0.65–0.93),

which is probably caused by variation in the specific input energy (SIE). The SIE is defined as the energy input per amount of volumetric gas flow. Kim et al.¹¹ reported that the ammonia synthesis rate increases linearly with plasma power at various temperatures, which can be rationalized with the fact that more N_2 molecules can be activated when increasing the SIE due to the increased electron density. Therefore, we propose a new parameter to analyze the kinetics of plasmaenhanced catalysis, namely the activity divided by the SIE, allowing for kinetic analysis of experiments with various SIEs. To avoid significant heating of the gas by the plasma, the SIE was limited in this study to relatively low values in the range between 83 and 367 J L⁻¹.

Figure 3b indeed shows linear correlations in an Arrhenius plot based on activity divided with the SIE, proofing a powerful tool to analyze the kinetics of plasma-enhanced catalysis. This results in apparent activation energies for plasma-enhanced catalytic ammonia synthesis over $2\text{Ru}/\gamma$ -Al₂O₃, $5\text{Mg}-2\text{Ru}/\gamma$ -Al₂O₃, $10\text{K}-2\text{Ru}/\gamma$ -Al₂O₃, and $5\text{Cs}-2\text{Ru}/\gamma$ -Al₂O₃ (Figure 3b), resulting in 20 kJ mol⁻¹ ($R^2 = 0.99$), 36 kJ mol⁻¹ ($R^2 = 0.99$), 41 kJ mol⁻¹ ($R^2 = 0.99$), and 27 kJ mol⁻¹ ($R^2 = 0.91$), respectively. This is significantly lower than the apparent activation energy for thermal-catalytic ammonia synthesis over both unpromoted and promoted ruthenium-based catalysts (typically 60–70 and 100–115 kJ mol⁻¹, respectively).

DISCUSSION

The apparent activation energies for thermal operation of alumina-supported ruthenium-based catalysts are mostly due to N_2 dissociation, as discussed by Aika et al.⁴³ and Muhler et al.⁴¹ It is well established that the rate-determining step for thermal catalysis over conventional ruthenium-based catalysts is the dissociation of nitrogen.^{35,44,45}

The catalytic activity is enhanced by plasma via promoting N₂ dissociation, as is apparent from the differences between thermal catalysis and plasma-enhanced catalysis in both the apparent activation energies as well as the absolute activities (Figures 2 and 3 and Table 1). Table 1 also presents the activation energy for N₂ dissociation over ruthenium-based catalysts ($E_{a,N2equi}$) based on isotope-exchange experiments with ¹⁵N₂.^{41,43} The difference between the apparent activation



Figure 3. Arrhenius plot of plasma-enhanced catalytic ammonia synthesis over various alumina-supported ruthenium-based catalysts. P = 1 bar, $H_2:N_2 = 1:4$, various flow rates (see Table S1). (a) Activity defined in same manner as for thermal catalysis (i.e., not divided by the SIE). (b) Activity divided by the SIE: black filled squares (\blacksquare) $2Ru/\gamma-Al_2O_3$; gray filled diamonds (\blacklozenge) $10K-2Ru/\gamma-Al_2O_3$; white filled triangles (\triangle) $5Cs-2Ru/\gamma-Al_2O_3$; and white filled circles (\bigcirc) $5Mg-2Ru/\gamma-Al_2O_3$.

energy for thermal catalysis and plasma-enhanced catalysis is in the range of the activation energy for N₂ dissociation for the unpromoted as well as K promoted catalysts (Table 1). This is in line with the hypothesis that the activity enhancement is due to N₂ excitation in the plasma before adsorption. It cannot be excluded that the hydrogenation reactions on the surface become rate limiting,¹ which is also the case for the most active Ru catalysts reported recently.^{46–48}

Activity Trends in Plasma-Enhanced Catalysis. As follows from Figures 2 and 3, the absolute ammonia synthesis activity differs among the catalysts. However, the activity trends among various ruthenium-based catalysts are similar, both for thermal catalysis and plasma-enhanced catalysis. The unpromoted catalyst $(2Ru/\gamma - Al_2O_3)$ is least active. Among the promoted catalysts, 5Cs-2Ru/γ-Al₂O₃ and 10K-2Ru/γ-Al₂O₃ show similar activity, while $5Mg-2Ru/\gamma-Al_2O_3$ is most active for both thermal catalysis and plasma-enhanced catalysis. This indicates that the reaction mechanisms for thermal catalysis and plasma-enhanced catalysis are similar. As the physical packing structure is the same for the different catalysts, the difference in activity is attributed to a catalytic enhancement of the promoters rather than a plasma modification. Thus, the promoters retain their function, i.e. electronic promotion of N₂ dissociation,^{35,40} for plasma-enhanced catalysis like for thermal catalysis. The nitrogen adsorption rate is higher for promoted catalysts, as follows from IR spectroscopy.⁴⁹ This gives a different sticking probability, which means more of the activated N₂ is adsorbed on promoted catalysts.

As reported by Aika et al.,⁴⁰ the ammonia synthesis rate over ruthenium-based catalysts is influenced by the electronegativity of both the support and the promoter, where a lower electronegativity leads to a higher ammonia synthesis rate. As shown Figure 4, similar trends are observed for thermal



Figure 4. (a) Activity for ammonia synthesis (ammonia synthesis rate expressed as turnover number per active Ru site) as a function of electronegativity for thermal-catalytic ammonia synthesis. Experimental data reported in ref 50. (b) Activity for ammonia synthesis (ammonia concentration for the same catalyst mass, temperature and flow rate) as a function of electronegativity for plasma-enhanced catalytic ammonia synthesis. Experimental data reported in ref 51.

catalysis (Figure 4a) and for plasma-enhanced catalysis (Figure 4b). This again indicates that plasma-enhanced catalysis proceeds via a mechanism similar to thermal catalysis, but with plasma-activation of the reactants.

Heating Effects and Power Effects. In principle, heating effects by the DBD plasma influence the experimental reaction rates.⁵² Kim et al.⁵³ and Jidenko et al.⁵⁴ reported an increase in temperature with increasing SIE (range $0-400 \text{ J L}^{-1}$) in a DBD reactor. These reactors operate at an ambient surrounding temperature and the temperature increase was

reported to be maximum 100 $^{\circ}$ C at a SIE of 400 J L⁻¹. However, when the temperature of the reactor is controlled with an oven, this heating effect of the plasma is expected to be smaller, as the temperature control loop corrects at least partly for the heating effect of the plasma.

Arrhenius-type kinetics show exponential increase in activity with absolute temperature. In the Supporting Information, experimental data with a constant SIE was used to estimate the effect of a temperature offset. From this analysis it follows that the apparent activation energy for plasma-enhanced catalysis increases hardly, remaining substantially lower than for thermal catalysis. From this, it follows that the decrease in apparent activation barrier is caused by a plasma-activation effect of the reactants.

Kim et al.¹¹ reported an apparent linear relation between the activity and the SIE for a fixed oven temperature for the same reactor configuration as reported in this paper. Using a linear relation between the activity and the SIE appears to be a valid descriptor to analyze the kinetics of plasma-enhanced catalytic ammonia synthesis (Figure 3b), allowing consideration of experiments performed with different SIEs. The measurements of SIE and activity are experimentally relatively simple, in contrast to measurement of the temperature inside the plasma reactor, requiring complex *in situ* techniques.^{53,55}

Plasma-Induced Excitations in N₂. Mehta et al.¹ postulated that plasma-induced vibrational excitation of N₂ decreases the dissociation barrier, without influencing the subsequent hydrogenation reactions and ammonia desorption. The experimental results in this paper substantiate these claims with the change in apparent activation barrier upon plasma-illumination. Furthermore, for ruthenium-based catalysts, the light-off temperature for thermal catalysis (200 °C) is the same as the temperature at which the activity for ammonia synthesis in the presence of a plasma is enhanced.¹⁸ This indicates that the desorption step of ammonia is probably not influenced by plasma-induced changes in the electronic structure of the transition metal catalyst.

Electronic excitations and ionic states of N2 may also be of importance.¹⁴ Based on observed ammonia synthesis rates, it is difficult to discriminate between vibrational excitations and electronic excitations of N₂. However, as follows from kinetic studies by Hong et al.⁵⁶ and DFT calculations by Mehta et al.¹ the rate of vibrational excitation of N₂ is about $\sim 10^6 - 10^7$ times larger than the rate of electronic excitation of N2 for atmospheric pressure plasmas in a DBD reactor. Furthermore, ionic states have very short lifetime at atmospheric pressure and are probably not relevant in DBD plasma reactors.¹⁹ Metastable electronically excited N₂ molecules with an energy level of 6.2 eV have a relatively long lifetime in the range 10⁻⁵-10⁰ s.⁵⁷⁻⁶⁰ However, according to Fridman and Rusanov,⁶¹ most of the plasma energy (\sim 97%) is going to vibrational excitation for electrons of 1–3 eV. Ohmori et al.⁶² indicated that the vibrational cross section q_v (~10⁻¹⁶ cm⁻²) dominates over ionization (q_i) and dissociation (q_d) cross sections for low energy electrons (<4 eV) in nitrogen. Thus, vibrational excitations of N2 are probably the dominant species for excitation of N_2 in atmospheric pressure.

An alternative pathway is the dissociation of N_2 in the plasma with subsequent adsorption of N* radicals on Ru. However, this cannot be the dominant mechanism for plasmaenhanced catalytic ammonia synthesis, as it would fail to explain the fact that the trends in activity with electronegativity of the support and promoters are very similar for plasma-



Figure 5. Reaction mechanisms of plasma-phase ammonia synthesis (a), surface-enhanced plasma-driven ammonia synthesis (b), plasma-enhanced semicatalytic ammonia synthesis (c), and plasma-enhanced catalytic ammonia synthesis (d). Reactions relevant for mechanism are depicted with full arrows, while the subsequent reaction to ammonia is depicted with a dashed arrow. For details, see text.

enhanced catalysis and thermal catalysis (Figure 4). As these effects are caused by enhancement of N₂ dissociation on the catalyst surface, it follows that the plasma enhances N₂ dissociation on the surface via excitation vibration, instead of N₂ dissociation in the plasma. The low cross section of q_d (~10⁻¹⁸ cm⁻²) for N₂ also provides a rationale for this interpretation. Thus, the postulate of Mehta et al.¹ concerning the plasma-induced vibrational excitations of N₂ without influencing subsequent reaction steps is experimentally substantiated. The important role of vibrationally excited N₂ agrees with the optimum N₂:H₂ ratio in plasma-enhanced catalysis, which shifts to the N₂-rich range as compared to thermal catalysis.¹¹ N₂-rich conditions provide higher probability for collisions of electrons and N₂ molecules and thus N₂ excitation.

Conditions for Plasma-Enhanced Catalytic Ammonia Synthesis. Inspired by the discussion so far, we categorize various reaction pathways possible when combining plasma with catalysts. We propose nomenclatures for those pathways, as we are not aware of a general agreement on the definitions of specific plasma-catalyst reaction pathways.

Ammonia can be synthesized via gas-phase radical chemistry, in which N* radicals and H* radicals recombine in the plasmaenvironment to form ammonia. This is coined plasma-phase ammonia synthesis (Figure 5a). The second pathway is surfaceenhanced plasma-driven ammonia synthesis (Figure 5b), in which N* radicals and H* radicals adsorb on a surface. The surface has a quenching effect, as the electrons on the surface may interact with the electrophilic radicals.^{14,18} Subsequent hydrogenation of NH_x species and ammonia formation may occur over the surface or in the plasma-environment.⁵⁶ Both plasma-phase ammonia synthesis and surface-enhanced plasma-driven ammonia synthesis are essentially diffusion limited, nonselective processes. These regimes can be identified based on low apparent activation energies smaller than typically 5 kJ mol⁻¹, due to changes in diffusivity of the reactants and changes in the electronic properties of the electrode with increasing temperature (such as the conductivity and resistivity).³⁴ Yin et al.⁶³ and Iwamoto et al.²⁶ showed that the electrode properties have an influence on the

ammonia synthesis rate. The orders in H_2 and N_2 are both 1, indicating that both N* and H* radicals are required for the diffusion-limited recombination reaction.^{14,22} Both pathways have a theoretical minimum energy consumption of 18.4 kWh kg⁻¹ ammonia, which is the energy required to break the bonds in both N_2 and H_2 molecules. The lowest energy consumption obtained so far is 48.8 kWh kg⁻¹ ammonia, as reported by Peng et al.³⁰

The third pathway is plasma-enhanced semicatalytic ammonia synthesis (Figure 5c), in which N* radicals adsorb on a surface, while H₂ is dissociated over a catalyst. The term semicatalytic is used, as the rate limiting step is not catalyzed, i.e. N2 dissociation. Thus, the catalyst has an activating role for H₂ dissociation, while the catalyst is not able to dissociate N2 at sufficient rates due to inhibition by adsorbed species (atomic hydrogen or NH_X species). Temperature effects on the ammonia synthesis rate are minor²² and apparent activation energies lower than 10 kJ mol⁻¹ are obtained. The orders in H₂ and N_2 are are 0 and 1, respectively,²² typically for this regime. This is possibly due to full coverage of the transition metal with H atoms, i.e., the so-called hydrogen inhibition effect as reported for ruthenium-based catalysts at low temperatures.³⁵ On the other hand, the orders in N₂ are similar in case of plasma-phase ammonia synthesis and in case of surfaceenhanced plasma-driven ammonia synthesis. Possibly, the experimental data of Barboun et al.²² for Ru/γ -Al₂O₃, Co/ γ -Al₂O₃, and Ni/ γ -Al₂O₃ represents this regime, as for all catalysts the orders in H₂ and N₂ are 0 and 1. However, for thermal-catalytic ammonia synthesis, implying N₂ dissociation on the catalyst surface, the order in H₂ varies widely among transition metal catalysts, ranging from -1.2 to 2.3 for the catalysts in ref 64. Subsequent reactions between hydrogen atoms and nitrogen atoms may occur over the catalyst, as proposed by Mizushima et al. 65 The theoretical minimum energy consumption is 7.7 kWh kg⁻¹ ammonia, which is required for the rupture of the triple nitrogen bond.

Plasma-phase ammonia synthesis, surface-enhanced plasmadriven ammonia synthesis, and plasma-enhanced semicatalytic ammonia synthesis have a minimum energy consumption which is above the required benchmark for small-scale applications (5–7 kWh kg^{-1,18}). Thus, these pathways cannot provide sufficiently energy efficient ammonia synthesis, even at 100% efficiency. However, lower energy input is feasible if N_2 is only partially activated by the plasma in combination with subsequent dissociation of excited N_2 molecules over a catalyst.

The fourth pathway is plasma-enhanced catalytic ammonia synthesis (Figure 5d), in which both H_2 and N_2 adsorb dissociatively on the catalyst surface. This is the pathway described by the postulate of Mehta et al.¹ The nitrogen is vibrationally excited in the plasma, while the catalyst surface (a transition metal) performs the final rupture of the bond between the two nitrogen atoms as well as dissociation of H₂. Subsequent hydrogenation of NH_x surface species and ammonia desorption occur over a transition metal, unaffected by the plasma.¹ As discussed by Kim et al.,¹⁸ the light-off temperature for thermal catalysis is the same as the temperature at which the activity for ammonia synthesis in the presence of a plasma is enhanced, indicating that ammonia desorption is probably not influenced by the plasma. This reaction pathway obeys classical thermodynamics, albeit with a change in the equilibrium constant due to the excitation of the reactants by the plasma.9 A clear Arrhenius-type temperature dependence is obtained and apparent activation energies are significantly larger than 5 kJ mol⁻¹ and depend on the catalyst formulation. The orders in H₂ and N₂ also vary depending on the catalyst formulation. In this case, a general theoretical minimum for energy consumption cannot be defined, as the required preactivation in the plasma to facilitate N_2 dissociation at sufficient rates depends on the transition metal used for plasma-enhanced catalysis. The lowest energy consumption reported so far is 27.8 kWh kg^{-1.1}

In terms of the energy efficiency, plasma-enhanced catalytic ammonia synthesis is the preferred pathway for ammonia synthesis in the presence of a plasma and a catalyst (see Figure 6). Prerequisites for plasma-enhanced catalytic ammonia



Figure 6. Energy consumption of plasma-phase ammonia synthesis (PPAS), surface-enhanced plasma-driven ammonia synthesis (SEP-DAS), plasma-enhanced semicatalytic ammonia synthesis (PEQCAS), and plasma-enhanced catalytic ammonia synthesis (PECAS). The gray bars represent the theoretical minimum, while the black bars represent the best reported result so far. For details, see text.

synthesis are (1) a sufficiently low plasma power such that vibrationally excited N_2 are the dominant plasma-excited species, (2) sufficient number of empty sites for N_2 dissociation, i.e. other surface species do not compete too strongly for the same sites, and (3) operation at temperatures sufficient for desorption of ammonia from the transition metal.

Ammonia cannot desorb from the metal surface at temperatures below the light-off temperature for thermal catalysis, e.g. about 200 °C for ruthenium-based catalysts.⁶⁶ For rutheniumbased catalysts, the desorption of ammonia is increasingly inhibited with increasing electronegativity of the support and modifiers.⁶⁷ When these prerequisites are not satisfied, plasmaenhanced catalytic ammonia synthesis over a transition metal is not possible (at measurable rates).

CONCLUSION

Ammonia synthesis by plasma-enhanced catalysis at temperatures between 200 and 330 $^{\circ}$ C is discussed based on kinetic data. The activation energies deduced from the Arrhenius plot have been compared between thermal catalysis and plasmaenhanced catalysis. Furthermore, apparent activation energies at elevated temperatures (200–330 $^{\circ}$ C) indicate that the ammonia synthesis proceeds via plasma-enhanced catalytic ammonia synthesis instead of plasma-phase ammonia synthesis over alumina-supported ruthenium-based catalysts.

The activity divided by the specific input energy (SIE) was introduced as a new descriptor to analyze the kinetics of plasma-enhanced catalytic ammonia synthesis, allowing considering experiments performed with different SIEs.

The mechanism of plasma-enhanced catalytic ammonia synthesis involves plasma-induced vibrational excitation of N₂ at the catalyst surface, without affecting the subsequent hydrogenation steps of NH_x species on the surface as well as ammonia desorption, as previously postulated by Mehta et al.¹ This postulation was substantiated with the fact that the apparent activation barriers for plasma-enhanced catalysis over various ruthenium-based catalysts is significantly smaller than for thermal catalysis, the decrease being in the order of the activation energy of N-N dissociation. The observed barriers vary between 20 and 40 kJ mol⁻¹, significantly higher than in the case of diffusion control in plasma-phase ammonia synthesis. The effects of promoters and supports on the activity effects are similar for thermal catalysis and plasmaenhanced catalysis, indicating that the properties of the catalyst to dissociate N₂ are still relevant, also when N₂ is vibrationally excited.

Four different types of pathways for ammonia synthesis in the presence of a plasma are defined and described, namely (1) plasma-phase ammonia synthesis, (2) surface-enhanced plasma-driven ammonia synthesis, (3) plasma-enhanced semicatalytic ammonia synthesis, and (4) plasma-enhanced catalytic ammonia synthesis.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acssuschemeng.9b04997.

Experimental setup and analysis techniques, experimental data, and analysis of relative contributions of heating and plasma-activation of N_2 with figures and calculations (PDF)

AUTHOR INFORMATION

Corresponding Author

*Email: k.h.r.rouwenhorst@utwente.nl. ORCID ©

Kevin H. R. Rouwenhorst: 0000-0002-2794-199X

Leon Lefferts: 0000-0003-2377-5282

Notes

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