

Plasma-Catalytic Ammonia Reforming of Methane over Cu-Based Catalysts for the Production of HCN and H₂ at Reduced Temperature

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INTRODUCTION

Hydrocyanic acid (HCN), an important organic chemical featuring the C \equiv N functional group, is widely used in medicine, in metallurgy, and for pesticides, fuels, and polymers.^{1,2} Driven by the demand for plastics and polymers, such as nylon and plexiglass in the 1950s, BASF corporation created the first facility for industrial production of HCN. The annual production of HCN in 1956 was only 2400 tons, but it has increased to more than 100,000 tons/year today,¹ which is mainly achieved by the Andrussow process or the BMA process.

The Andrussow process is an exothermic reaction of CH_4 , NH_3 , and O_2 (eq 1). It is usually realized over a Pt–Rh alloy gauze catalyst at atmospheric pressure and 1300–1400 K. The required energy to maintain the high temperature is mainly supplied by the combustion of H_2 , which leads to a waste of H_2 energy. Alloying of Pt by Rh (10% Rh) to form a Pt–Rh alloy gauze catalyst is necessary to improve the durability of the catalyst, because of the high reaction temperature, which usually results in inactivation of Pt. In addition, the high temperature also results in a long time for feed gas heating and product cooling. Generally, about 60% HCN yield and 60–70% NH_3 utilization can be achieved by the Andrussow process.^{1–4}

$$CH_4 + NH_3 + 1.5O_2 \rightarrow HCN + 3H_2O$$
$$\Delta H^0_{298K} = -483 \text{ kJ/mol}$$
(1)

In contrast, the Blausaure Methane Anlage (BMA) process is a strongly endothermic reaction between CH_4 and NH_3 (eq 2). It is usually operated at atmospheric pressure for HCN synthesis with stoichiometric hydrogen production, which is a significant advantage compared to the Andrussow process.

$$CH_4 + NH_3 \rightarrow HCN + 3H_2$$
 $\Delta H_{298K}^0 = 251 \text{ kJ/mol}$
(2)

This BMA process is also called Degussa process, as it was first exploited by Degussa company in Wesseling.^{3,4} In industrial BMA plants, the Pt mesh catalyst is usually placed in parallel columnar reactors. The equilibrium conversion, selectivity, and yield as a function of temperature, obtained through thermodynamic calculation, are plotted in Figure S1. The BMA process for HCN synthesis is typically operated at a temperature of ~1600 K to balance the HCN yield and cost.

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On the one hand, the HCN yield increases with reaction temperature; on the other hand, the high reaction temperature also causes a higher investment of equipment and energy consumption and waste of feed gas; indeed, a great amount of $\rm NH_3$ and $\rm CH_4$ is decomposed into $\rm N_2$ and coke, respectively.¹⁻⁴

Although the Andrussow process and the BMA process have been used in industrial HCN production for many decades, research is still being conducted on optimizing the reaction conditions^{5,6} and uncovering the mechanism of C–N coupling over Pt and Pt–Rh catalysts.^{7–11} To our knowledge, there are currently no methods available to synthesize HCN at temperatures below 1300–1400 K for the Andrussow process and below 1600 K for the BMA process.

The non-equilibrium character of non-thermal plasma (NTP), that is, ionized gas, consisting of molecules and also electrons, ions, radicals, and excited species, offers a unique approach to enable some thermodynamically unfavorable chemical reactions at low temperature.^{12–14} The gas temperature in such plasma can be maintained even as low as room temperature. The generated electrons, however, are highly energetic with a typical energy of 1–10 eV or 10⁴ to 10⁵ K. Therefore, these energetic electrons can activate reactant molecules (e.g., CH₄ and NH₃) into reactive species, that is, radicals, excited atoms and molecules, and ions, which can easily trigger chemical reactions at room temperature.

Inspired by the catalytic activity of Pt in HCN synthesis (both in the Andrussow process and BMA process), we previously combined supported Pt catalysts with CH₄/NH₃ NTP for HCN synthesis, in the so-called plasma catalysis.¹¹ HCN was produced from a CH₄/NH₃ mixture at 673 K, reaching 26% CH₄ conversion and 81% HCN selectivity when using optimized catalysts, that is, the Pt/TS-1 catalyst (Pt supported on titanium silicalite-1 zeolite). However, this Pt/ TS-1 catalyst is extremely expensive because of the high price of Pt caused by scarcity and the high price of the TS-1 support caused by the long and multistep synthesis process, the expensive titanium precursor (tetraethyl titanate), and organic amine template (tetrapropylammonium hydroxide). Therefore, it is crucial to examine possible lower cost catalysts by only using non-noble metals and low-cost supports for practical application of plasma-catalytic HCN synthesis.

In this paper, we report ammonia reforming of methane (ARM) for co-production of HCN and H₂ at 673 K by the combination of CH₄/NH₃ NTP and a Cu/silicalite-1 (Cu/S-1) catalyst (Figure 1), reaching 30% CH₄ conversion with 79%HCN selectivity. The novelty of this work compared to our previous paper is (i) the use of a lower cost Cu catalyst to replace expensive Pt, (ii) the use of a lower cost silicalite-1 zeolite (S-1) support to replace the expensive titanium silicalite-1 zeolite support, and (iii) density functional theory (DFT) calculations to explain the E-R reaction mechanism in plasma catalysis. In general, using lower cost catalysts and milder conditions to realize important reactions for chemical production is one of the major goals in catalysis research. Interestingly, we reduced the cost of the catalyst (Cu/S-1) by 95% compared to the commercial Pt mesh catalyst and by 80% compared to the Pt/TS-1 catalyst. Furthermore, stoichiometric H₂ is produced as well, which can be separated from the mixture and used as green energy. The experimental details are presented in the Supporting Information.



Figure 1. Schematic diagram of the classical methods for HCN synthesis and our novel method presented in this paper.

RESULTS AND DISCUSSION

Figure 2 presents the catalytic performance of the Cu/S-1 catalyst in the ARM reaction. In the absence of plasma, that is,



Figure 2. CH₄ conversion and selectivity toward HCN and CH₃CN at 673 K for (a) catalyst only, plasma only, plasma + S-1 support, and plasma + Cu/S-1 catalyst and (b) for 24 h, to test the stability of the Cu/S-1 catalyst (reaction conditions: 10 wt % Cu loading, CH₄/NH₃ = 1:2, GHSV: 1529 h⁻¹, and discharge length: 5 cm, the error bars are obtained from five repetitions of the experiment).

only using the Cu/S-1 catalyst, the CH₄ conversion is zero, demonstrating that the ARM reaction cannot be triggered at 673 K without the help of plasma. When using a CH₄/NH₃ plasma (673 K), but not using any catalyst, the conversion reaches 11.1%. When we pack the CH₄/NH₃ plasma by S-1 granules, the CH₄ conversion rises to 15.6% (673 K) and it further increases to 30% when using the Cu/S-1 catalyst.

In terms of HCN selectivity, there is little difference between "plasma" and "plasma + S-1", that is, around 60%, while the HCN selectivity rises to 79% in case of "plasma + Cu/S-1". In



Figure 3. Characterization results of the fresh and spent Cu/S-1 catalysts. (a) XRD patterns; (b) XPS spectra; (c) H_2 -TPR profiles; and (d) NH_3 -TPD results.

addition to HCN, the main byproduct was qualitatively analyzed as acetonitrile (CH₃CN); see Figure S2. Furthermore, some other more complex compounds, that is, N,Ndimethyl cyanamide [(CH₃)₂NCN)] and amino acetonitrile (NH₂CH₂CN) were detected as well. The selectivity results shown in Figure 2 were obtained through the C-balance of the total amount of products. Interestingly, no C2 or larger hydrocarbons were detected by gas chromatography (Figure S3), indicating that virtually no C-C coupling to hydrocarbons occurred. The H₂ content in the product was found to be consistent with the stoichiometry of reaction 2. In addition, little N₂ was detected (Figure S3), illustrating that NH₃ was hardly decomposed into N2, attributed to the poor activity of Cu catalysts toward NH₃ decomposition. The above results indicate that plasma catalysis, that is, the combination of the CH₄/NH₃ plasma and Cu/S-1 catalyst, can dramatically improve both CH₄ conversion and HCN selectivity compared to only the Cu/S-1 catalyst or only CH₄/NH₃ plasma. This result implies the possibility to efficiently realize the ARM reaction at low temperature for the production of HCN, CH₃CN, and H₂, without C₂ or larger hydrocarbons or N₂.

The energy efficiency for the synthesis of HCN and CH_3CN in the plasma-catalytic ARM reaction is 6.0%, which is much higher than that of plasma only (1.8%) and that of plasma + S-1 (2.3%), as shown in Figure S4. The energy consumption for producing HCN in the plasma-catalytic ARM reaction is 5.2 kJ/mmol, which is much lower than that of plasma only (18.1 kJ/mmol) and that of plasma + S-1 (14.5 kJ/mmol), showing the key role of Cu-based catalysts in improving the reaction performance.

Although the energy consumption in this paper (5.2 kJ/mmol) is higher than that in the BMA process (1.1 kJ/mmol),¹⁶ the use of Cu-based catalysts instead of Pt-based catalysts should also be considered when looking at the overall cost, and the lower temperature allowing safer operation

conditions is an important advantage. The discharge power, needed to calculate the energy efficiency, was obtained by the waveforms of discharge voltage and discharge current (Figure S5).

We also studied the effects of reaction temperature and Cu loading on CH₄ conversion and HCN selectivity, as shown in Figure S6. Our measurements indicate that a relatively high temperature is favorable for the ARM reaction to produce HCN, while higher loadings (15–30%) can slightly further improve the CH₄ conversion and HCN selectivity. In the case of 30 wt % Cu loading, we achieved 32.4% CH₄ conversion with 86.2% HCN selectivity. In addition, the support effect of Cu catalysts has been investigated, as shown in Figure S7, Tables S1 and S2, and S-1 exhibits the best performance. Furthermore, using S-1 as the support, the effect of metal type has also been studied, as shown in Figure S8, and Cu shows the best performance.

The results of the ARM reaction at 673 K for 24 h continuous operation are shown in Figure 2b. Initially, we achieved 30% CH₄ conversion and 79% HCN selectivity. However, these values slightly decreased in the course of the experiment, probably due to carbon deposition, covering Cu active sites. After 24 h of continuous reaction, we still obtain 28% CH₄ conversion and 71% HCN selectivity, indicating a good catalytic stability of the Cu/S-1 catalyst in CH₄/NH₃ NTP for the production of HCN and H₂.

As shown in Figure 3a, the X-ray diffraction (XRD) patterns of S-1, fresh Cu/S-1, and spent Cu/S-1 samples clearly show five peaks at the lower diffraction angles, that is, 7.9, 8.8, 23.1, 24, and 24.4°, which are assigned to the MFI structure of the S-1 zeolite,¹⁷ indicating that the lattice structure of S-1 was not damaged during either catalyst preparation or catalytic tests. In addition, diffraction peaks of CuO (35.6 and 38.7°) and Cu (43.3, 50.4, and 74.1°) can be identified in the XRD patterns of the fresh and spent Cu/S-1 samples, respectively, which



Figure 4. HRTEM patterns of (a) fresh Cu/S-1 catalyst and (b) spent Cu/S-1 catalyst, (c) CuO particle size distribution of the fresh Cu/S-1 catalyst, (d) Cu particle size distribution of the spent Cu/S-1 catalyst, and (e) H_2 -TPR profiles of the spent Cu/S-1 sample after surface passivation by N_2O and after complete oxidation by O_2 (result in e aims to titrate the number of surface Cu atom, so as to calculate the dispersity of Cu).

means that CuO is reduced to metallic Cu during the catalytic test.^{18,19} The X-ray photoelectron spectroscopy (XPS) spectra of fresh and spent Cu/S-1 samples are shown in Figure 3b. For the fresh Cu/S-1 sample, the binding energies of Cu $2p_{3/2}$ and Cu $2p_{1/2}$ are found to be 933.8 eV (with a shake-up satellite at 943 eV) and 953.8 eV (with a shake-up satellite at 963 eV), respectively, which are assigned to Cu²⁺ species. For the spent Cu/S-1 sample, the binding energies of Cu $2p_{3/2}$ and Cu $2p_{1/2}$ decreased to 932.7 eV (without shake-up satellite) and 952.7 eV (without shake-up satellite) and 952.7 eV (without shake-up satellite), respectively, which are attributed to Cu⁰ species.^{20,21} Hence, the XPS results show the transformation of Cu²⁺ to Cu⁰ species during the reaction, which is consistent with the results obtained by XRD (CuO to Cu), even when XPS is a surface sensitive technique, while XRD is a bulk technique.

The H_2 -TPR profiles of the fresh and spent Cu/S-1 samples (Figure 3c) indicate a significant peak (423–573 K) for the fresh Cu/S-1 catalyst, pointing toward the reduction of CuO to

Cu,²² while the spent Cu/S-1 sample exhibits no peaks of H_2 consumption, showing the metallic Cu phase. The H_2 -TPR, along with XRD and XPS, thus proves the transformation of CuO to the metallic Cu phase during the ARM reaction process, implying that metallic Cu is the real active phase for the ARM reaction driven by plasma. The NH₃-TPD experiments were carried out to measure the acidity of S-1, fresh Cu/S-1, and spent Cu/S-1 samples (Figure 3d). No desorption peaks are observed for the S-1 support, mainly because S-1 zeolite has no acid sites. However, desorption peaks of NH₃ are obvious for both fresh and spent Cu/S-1 samples, which means that NH₃ interacts strongly with both CuO and Cu, resulting in chemisorption of NH₃ on both fresh and spent Cu/S-1 catalysts.

Figure 4 shows high-resolution transmission electron microscopy (HRTEM) images of fresh and spent Cu/S-1 samples. Clearly, Cu was highly dispersed on the S-1 support.

The particle-size distribution of CuO, derived from the HRTEM images with 5 and 10 nm scale, is plotted in Figure 4c and shows that the average size of the CuO particles is 2.1-2.2 nm. Figure 4b shows HRTEM images of the spent Cu/S-1 sample, and the particle size distribution of Cu is plotted in Figure 4d. It can be seen that the average size of the CuO particles is 3.3 nm, which is bigger than that of the fresh CuO particles (2.1-2.2 nm) due to aggregation under the reaction conditions.

The dispersity of Cu (proportion of surface Cu atoms in the total Cu atoms) in the spent Cu/S-1 catalyst has been measured by the N₂O chemisorption experiment (N₂O titration), as shown in Figure 4e. The ratio of H_2 consumption after surface passivation by N_2O (reactions 3 and 4) to H_2 consumption after complete oxidation by O_2 (reactions 5 and 6) equals 0.1325, indicating a dispersity of 26.5% (equivalent to 3.77 nm of the Cu particle size under the assumption of spherical particles, similar to that obtained by HRTEM). Based on the Cu dispersity (26.5%) and Cu loading (10.1% detected by XRF), as well as the reaction results (Figure 2), the turnover frequency (TOF) of HCN generation on the Cu/S-1 catalyst is calculated to be 2.54 h^{-1} . As shown in Table S3, the TOF of the Pt/TS-1 catalyst is 17.66 h⁻¹. However, the TOF of Cu increases with Cu loading and it reaches 9.59 h^{-1} at 30 wt % loading. As can be seen from Table S3, the dispersion of Cu dramatically decreases with increasing Cu loading. Note that the dispersion degree of Cu is achieved by N₂O titration experiments, which is the most definitive method for determining the dispersion of Cu. Hence, with increasing Cu loading, the effective number of active sites (surface Cu atoms) decreases, which is caused by a bigger particle size at higher loading. Furthermore, the catalyst granule sizes have no influence on reaction performance (Figure S9), which means that there is no internal diffusion limitation in this reaction. Thus, from the catalytic point of view, the lower the dispersion of Cu, the higher the TOF value, suggesting that the plasmacatalytic CH₄/NH₃ reaction to produce HCN and H₂ is a structure-sensitive reaction. However, to draw firm conclusions on this, we would need to perform a study that involves careful control of the particle size to provide evidence that terrace versus step edge sites promote the reaction. This is however beyond the scope of this paper.

$$2Cu + N_2O \rightarrow Cu_2O + N_2 \tag{3}$$

 $Cu_2O + H_2 \rightarrow 2Cu + H_2O \tag{4}$

$$2Cu + O_2 \rightarrow 2CuO \tag{5}$$

$$CuO + H_2 \rightarrow Cu + H_2O \tag{6}$$

To further demonstrate the active sites for the ARM reaction are in the metallic Cu phase, we detected the species in the product gas in situ by mass spectrometry, as shown in Figure S10, for both the fresh and spent Cu/S-1 samples. When using the fresh Cu/S-1 sample, no HCN was detected in the initial stage, but instead, we can clearly see water droplets on the inner wall of the exhaust pipe, attributed to the reduction of CuO to Cu by NH₃ (eq 7). After the reduction process, the signal of HCN and H₂ dramatically increased and then remained stable (see Figure S10a), indicative for the ARM reaction producing HCN and H₂. When using the spent Cu/S-1 sample, the signal of HCN and H₂ dramatically increased over the first 10 min and then remained stable, implying that the ARM reaction can directly proceed on the spent Cu/S-1 catalysts to produce HCN and H_2 . In other words, the catalytically active sites for the ARM reaction are in the metallic Cu phase.

$$3CuO + 2NH_3 \rightarrow 3Cu + 3H_2O + N_2 \tag{7}$$

To understand the reaction mechanism of the plasmacatalytic ARM process, we performed in situ optical emission spectroscopy (OES) diagnostics of the CH_4/NH_3 plasma, aiming to identify the reactive species. As shown in Figure 5a,



Figure 5. Optical emission spectra of the CH_4/NH_3 DBD plasma at 673 K, (a) without the catalyst and (b) comparison between plasma-only, plasma + S-1, and the plasma + Cu/S-1 catalyst.

when using plasma without the catalyst, we collected three main molecular spectral bands at 564-567, 610-670, and 720-780 nm. The first band at 564-567 nm belongs to the deexcitation of electronically excited NH₃^{*} (Schuster band),²³ while the latter two bands are attributed to the de-excitation of electronically excited NH₂^{*} radicals (alpha band).²⁴ A partial enlargement of the OES profile for the 320-440 nm range (inset in Figure 5a) shows the emission line at 336 nm, which is assigned to the de-excitation of electronically excited NH* radicals $(A^3\Pi \rightarrow X^3S^-)$ ²⁵ These ammonia-related OES signals demonstrate the presence of NH₂ and NH species in the CH₄/ NH₃ plasma. In addition, the line at 431 nm is assigned to the decay of CH* radicals $(A^2\Sigma \rightarrow X^2\Pi)$,²⁶ demonstrating the presence of CH radicals as well. Generally, in NTP, CH* radicals are produced through cascade dehydrogenation of CH_4 , that is, $CH_4 \rightarrow CH_3 \rightarrow CH_2 \rightarrow CH$, and the probabilities of generating CH₃, CH₂, and CH radicals have been modeled to be 79, 15, and 5%, respectively.²⁷ Although the exact composition will depend on the conditions, we should also expect more CH₃ and CH₂ than CH radicals in our case. Therefore, the OES signal of CH* (431 nm) also indicates the existence of CH₃ and CH₂ radicals in the CH₄/NH₃ plasma. The reason why CH₃ and CH₂ were not detected by OES is

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N + CH → HCN • L-H mechanism: N (s) + CH (s) → HCN (s) • E-R mechanism: N (g) + CH (s) → HCN (s)		→ HCN (g)
• E-R mechanism: N (s) + CH (g) \rightarrow HCN (s)		
NH + CH → HCNH → HCN + H L-H mechanism: NH (s) + CH (s) → HCNH (s) → $ \overrightarrow{HCN}(\overrightarrow{s}) $ + $ \overrightarrow{H}(\overrightarrow{s}) $ E-R mechanism: NH (g) + CH (s) → HCNH (s) → HCN (s) + H (s) E-R mechanism: NH (s) + CH (g) → HCNH (s) → HCN (s) + $ \overrightarrow{H}(\overrightarrow{s}) $		\rightarrow H ₂ (g)
NH ₂ + CH → HCNH ₂ → HCNH + H → HCN + H L-H mechanism: NH ₂ (s) + CH (s) → HCNH ₂ (s) → H (s) + HCNH (s) → \overrightarrow{HC} E-R mechanism: NH ₂ (g) + CH (s) → HCNH ₂ (s) → H (s) + HCNH (s) → HCC E-R mechanism: NH ₂ (s) + CH (g) → HCNH ₂ (s) → H (s) + HCNH (s) → HCC	N (s) + H N (s) + H N (s) + H	(s) (s) (s)

Figure 6. Elementary steps of C–N coupling and formation of hydrogenated intermediates and their dehydrogenation to HCN through ER and LH mechanisms, considered in our calculations.

Table 1. Calculated Activation Energy of the Elementary Steps of C–N Coupling, Formation of Hydrogenated Intermediates and Their Dehydrogenation to HCN Through ER and LH Mechanisms, and for the Desorption of HCN and H₂, on Cu(111), (200), and (220) Crystal Planes^{*a*}

	no	reaction	Cu(111)	Cu(200)	Cu(220)			
	8	$N(s) + CH(s) \rightarrow HCN(s)$ (8)	0.78	0.75	0.62			
	9	$N(g) + CH(s) \rightarrow HCN(s)$ (9)	0.00	0.00	0.00			
	10	$N(s) + CH(g) \rightarrow HCN(s)$ (10)	0.00	0.00	0.00			
	11	$HCN(s) \rightarrow HCN(g)$ (11)	(0.83)	(0.70)	(0.88)			
	12	$NH(s) + CH(s) \rightarrow HCNH(s)$ (12)	0.45	0.50	0.72			
	13	$NH(g) + CH(s) \rightarrow HCNH(s)$ (13)	0.00	0.00	0.00			
	14	$NH(s) + CH(g) \rightarrow HCNH(s)$ (14)	0.00	0.00	0.00			
	15	$HCNH(s) \rightarrow HCN(s) + H(s)$ (15)	1.38	1.32	1.48			
	16	$NH_2(s) + CH(s) \rightarrow HCNH_2(s)$ (16)	1.20	1.60	1.54			
	17	$NH_2(g) + CH(s) \rightarrow HCNH_2(s)$ (17)	0.00	0.00	0.00			
	18	$NH_2(s) + CH(g) \rightarrow HCNH_2(s)$ (18)	0.00	0.00	0.00			
	19	$\text{HCNH}_2(s) \rightarrow \text{HCNH}(s) + \text{H}(s)$ (19)	1.27	1.25	1.30			
	20	$H(s) + H(s) \rightarrow H_2(g) (20)$	1.01	0.91	0.89			
The values in parentheses are reaction energies instead of activation energies. All values are in eV								

because their emission lines appear in the infrared region, which is out of the wavelength range of our OES measurements. Finally, the line at 388 nm corresponds to the decay of CN*, that is, $B^2\Sigma \rightarrow X^2\Sigma$,²⁸ which indicates the presence of CN radicals in the plasma, produced by the reaction between CH_x and NH_x radicals. In summary, CH_x (CH₃, CH₂, and CH), NH_x (NH₂ and NH), and CN radicals are present in our CH₄/NH₃ plasma without the catalyst.

As shown in Figure 5b, when the CH_4/NH_3 plasma was packed by S-1 zeolite (plasma + S-1), the OES intensities reduced a lot, which is caused by optical shielding due to the granules. Interestingly, when packing with the Cu/S-1 catalyst, the OES bands and lines nearly disappeared, implying that the excited species are adsorbed by the metallic Cu active sites.

In order to understand how the plasma-induced radicals detected by OES contribute to the plasma-catalytic conversion process and thus to understand why the catalytic process is activated by the plasma, we performed dispersion-corrected DFT calculations to find the minimum energy path (MEP) for the reactions of N, NH, CH, and NH_2 to produce HCN on various Cu surfaces. Based on the surface morphology seen in the XRD patterns (Figure 3a), we employed Cu(111), Cu(200), and Cu(220) slabs for the calculations. In contrast to thermal catalysis, where the reactions normally occur via the

Langmuir–Hinshelwood (LH) mechanism,²⁹ in plasma catalysis, both Eley–Rideal (ER) and LH mechanisms can occur,³⁰ and depending on the mechanism to proceed, the reaction barrier will be different. In Figure 6, we summarize the elementary steps of C–N coupling and the formation of hydrogenated intermediates and their dehydrogenation to HCN, considered in our calculations, occurring through both ER and LH mechanisms.

The activation energies calculated for these reactions are listed in Table 1. The values in parentheses represent the reaction barriers for these endothermic reactions, in which no saddle point is detected along the path. The equilibrium bond lengths calculated for HCN in the gas phase (C–N: 1.158 Å and C–H: 1.074 Å) are in good agreement with experimental and theoretical data.^{31,32}

For direct C–N coupling as one of the most critical steps in HCN synthesis, we can see that the reactions happening via the ER mechanism are barrierless, thanks to the high reactivity of the plasma radicals. For instance, Figure 7 shows the interaction of N and CH to form HCN via both LH and ER mechanisms (reactions 8-10) on the Cu(111) surface (corresponding to the highest intensity in the XRD patterns of Figure 3a). The LH interaction of pre-adsorbed N(s) and



Figure 7. MEP (black curve, left *y*-axis) and C–N distance (red curve, right *y*-axis) for (a) the interaction of pre-adsorbed N and CH, (b) gas phase N with pre-adsorbed CH, and (c) gas phase CH with pre-adsorbed N to form HCN(s) on the Cu(111) surface. All energies are with respect to that of the pre-adsorbed N and CH on Cu(111). The insets illustrate the configurations of the initial state, transition state, and final state, where brown, black, blue, and yellow colors correspond to Cu, C, N, and H atoms, respectively.

CH(s) (reaction 8) exhibits a reaction barrier of 0.78 eV toward the formation of HCN (Figure 7a).

Figure 7b,c shows the same reaction via both ER mechanisms (reactions 9 and 10). In this case, the energy of the initial gas phase radicals is much higher, so the whole configuration is highly unstable, representing the nonequilibrium status of the plasma-catalytic system. As displayed in Figure 7b, N is initially in the gas phase and approaches the pre-adsorbed CH(s). At the C-N distance around 3.47 Å, N(g) enters the reaction channel and the energy of the system decreases steeply. The same happens to the alternative ER pathway, starting with the gas phase CH interacting directly with pre-adsorbed N(s) (Figure 7c). CH(g) experiences the van der Waals attraction at a C-N distance around 3.02 Å, and the gas phase radical falls into the lower energy levels toward coupling with N. We observed the same pattern for all the reactions occurring through the ER mechanism and on all three Cu surfaces, which emphasizes that the C-N coupling reactions containing gas-phase radicals can easily happen via this mechanism, without the need to overcome any reaction barrier (see Figures S11 and S12).

These results are consistent with our OES spectra, showing the disappearance of the excited species with the Cu/S-1 catalyst packing (Figure 5). The highly reactive N, NH, NH₂, and CH radicals created in the plasma either interact directly with pre-adsorbed species or get adsorbed on the Cu surface, to be involved in LH reactions. The barrierless C–N coupling via the ER mechanism can explain why HCN formation can proceed in plasma catalysis at 673 K, with high conversion, while this is not possible in thermal catalysis at such low temperature, due to the relatively large activation barriers for CH₄ dissociation and C–N bond formation, as the most critical steps in HCN synthesis.

For the dehydrogenation step of the hydrogenated intermediates, that is, HCNH and HCNH_2 , Table 1 suggests that the activation barriers for the reactions taking place on the rougher Cu(220) are slightly higher than for the same reactions occurring on the flatter Cu(111) and Cu(200) surfaces. This suggests that the dehydrogenation steps are more likely to happen on Cu(111) and Cu(200) surfaces. However, a more detailed study considering the highly complex network of possible reaction pathways and coverage effects is needed to determine the surface sensitivity of the plasma-assisted HCN synthesis from ammonia and methane.

CONCLUSIONS

In conclusion, we demonstrated plasma-catalytic ARM at 673 K for the production of HCN and H_2 using the CH_4/NH_3 plasma with the Cu/S-1 catalyst, reaching 30% CH₄ conversion with 79% HCN selectivity and stoichiometric H₂. Catalyst characterization results clearly illustrate that highly dispersed metallic Cu particles (2-3 nm) are the catalytically active centers in the plasma-catalytic ARM. By combined experimental and DFT calculation results, we can conclude that HCN production in plasma catalysis is mainly attributed to the barrierless ER reactions between radicals generated in plasma and adsorbed species over the Cu surface, as shown in Scheme 1. Note that the obtained energy consumption may not yet be the best achievable number. It may be possible to further optimize the plasma-driven process to close the gap of energy consumption by optimizing reaction conditions (flow rate, residence time, etc.), catalysts (local environment of Cu particles, etc.), and plasma state (spark discharge, arc discharge, pulse discharge, etc.).

Scheme 1. Schematic Diagram of the Reaction Mechanism in Plasma-Catalytic ARM for HCN Synthesis. (Left) Reaction between the Gas-Phase CH and Pre-adsorbed NH_x ; (Right) Reaction between the Pre-adsorbed CH and Gas-Phase NH_x



ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acscatal.0c04940.

More experiment details, characterizations, and catalytic results (PDF)

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Notes

The authors declare no competing financial interest.

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