Supporting information

Plasma-catalytic Ammonia Reforming of Methane over Cu-based Catalysts for

the Production of HCN and H₂ at Reduced Temperature

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1 Thermodynamic equilibrium calculations



Figure S1. Thermodynamic equilibrium of the BMA process for HCN synthesis at atmospheric pressure. (a) equilibrium conversion; (b) equilibrium selectivity; (c) HCN equilibrium yield.

2 Catalyst and plasma characterization

High angle annular dark field scanning transmission electron microscopy (HADDF-STEM) was performed by Titan^{3TM} G2 60-300 with Cs-corrector configuration and high-resolution transmission electron microscopy images were obtained with Tecnai G2 F30 S-Twin. The powdered catalyst was dispersed in ethanol, and the mixture was sonicated to obtain a monodisperse catalyst solution, then, dropping the solution on TEM grid (ultrathin carbon membrane coated, 300 mesh). After dried, the sample were imaged.

X-ray diffraction (XRD) patterns were recorded on a SmartLab 9KW X-ray diffractometer using Cu K_{α} radiation (λ =0.15406 nm). The X-ray tube was operated at 240 kV and 50 mA. The data was recorded at 5°-80°. The scanning speed was 10 °/min with a step size of 0.02°.

X-ray photoelectron spectroscopy (XPS) was conducted by Thermo Fisher ESCALAB XI+ with Al Kα X-ray source. The BE values were calibrated using the C 1s line at 284.8 eV as internal reference.

The redox behavior of the catalyst was studied by Quantachrome ChemBET Pulsar Chemisorption using temperature programmed reduction (H_2 -TPR) technology. The sample was pretreated with helium flow from ambient temperature to 423 K and kept 1 hour before the analysis. After that, the sample was cooled to 323 K in helium. Finally, temperature programmed reduction (TPR) studies were done in a reducing gas of 10 % H_2 in Ar (120 mL/min). The temperature was increased at 10 K/min from 373 K to 1,073 K.

The number of surface metallic Cu atoms and the dispersion were determined by N₂O dissociative adsorption at 363 K and followed by H₂ titration using the procedure described by Van Der Grift et al.¹ Briefly, 0.15 g spent Cu/S-1 catalysts were reduced by H₂ plasma at 673 K with a flow rate of 60 mL/min, and then purged by He at 363 K. After that, a flow of N₂O/N₂ mixture (5% N₂O, 50 mL/min) was used to oxidize surface metallic Cu atoms to Cu₂O at 363 K for 30 minutes, and then flushed by He to remove the physically adsorbed oxidant. Finally, the sample was reduced through the H₂-TPR procedure in a 10% H₂/Ar mixture until 723 K (50 mL/min). The amount of hydrogen consumption was denoted as X. The reduced catalyst was heated from ambient temperature to 673 K, and was

calcined at 673 K for 3 hours in O₂ atmosphere, aiming to completely oxidize Cu to CuO. After calcination, the sample was flushed with He to remove gaseous O₂ and physically adsorbed O₂. Finally, another TPR experiment was performed under the same conditions as above, and the hydrogen consumption of the second TPR was expressed as Y. The dispersity of Cu is calculated by the formula D = (2*X/Y)*100%.

The ammonia temperature-programmed desorption (NH₃-TPD) was performed on a Quantachrome Chembet 3000 chemisorb instrument. Sample pellets (0.15 g, 380-830 μ m) were loaded into a quartz U reactor and pretreated under helium flow at 873 K for 1 hour. Subsequently, the temperature was lowered to 373 K in order to absorb ammonia for 30 minutes with a mixture of 5 % NH₃ in He. After adsorption, the samples were cleaned for 30 minutes with 50 ml/min helium flow to remove physically adsorbed NH₃. Meanwhile, the desorption curve was recorded from 373 to 873 K. The temperature was increased at a rate of 16 K/min.

The electrical signals (discharge voltage and current) were analyzed by a digital phosphor oscilloscope (Tektronix, DPO 3012) with a high voltage probe (Tektronix P6015A) and a current probe (Pearson 6585).

The CH₄/NH₃ plasma (in the presence and absence of the catalysts) was diagnosed using optical emission spectra (OES). The OES were collected by an ICCD spectrometer (Princeton Instruments SP 2758) in the range of 300-900 nm, using a 300 G/mm grating in the monochromator. The light emitted by the CH₄/NH₃ plasma was first collected by a lens, and then directed to the monochromator by an optical fiber cable (2 meter long). In order to eliminate the effect of gas composition on the OES results, the lens was installed in the DBD reactor from the inlet direction of the feed gas, since the light emitted from the other regions in the plasma was influenced by the conversion (i.e., a different gas composition yields different OES intensities). The distance between the head of the lens and the upper edge of the CH₄/NH₃ plasma was fixed at ca. 4 cm. During the OES analysis, a 50 μ m slit width of the spectrometer and 5 s exposure time were used.

Products analysis



Figure S2. Qualitative analysis of the main products. (a) Gas chromatography-mass spectrometry (GC-MS) of HCN, (b) standard mass spectrometry (MS) of HCN, (c) GC-MS of CH₃CN and (d) standard MS of CH₃CN. The a and c are obtained by GC-MS measurement of gas products from plasma-catalytic ARM reaction, while the b and d are from a standard spectrogram library for mass spectrometry, aiming to determine the products.



Figure S3. Quantitative analysis of the products by GC. (a) HCN and CH₃CN in the tail gas by flame ionization detector, (b) H₂ and N₂ in the tail gas by thermal conductivity detector.

The energy consumption of the process was defined as follows:

The energy efficiency of the process was defined as follows:

efferigency % =
$$\frac{n \Delta H HCN + n \Delta H GEN}{discharge power}$$
 [100%]

 n_1 = rate of HCN produced (mol/s)

$$n_2 = rate of CH_3CN produced (mol/s)$$

 ΔH_{HCN} (673K) = 278.98 kJ/mol ΔH_{CH3CN} (673K) = 275.48 kJ/mol



Figure S4. (a) Discharge power, (b) energy efficiency and energy consumption, for plasma only, plasma + S-1, and plasma + Cu/S-1 at 673 K.



Figure S5. Waveforms of (a) discharge voltage and (b) discharge current, for plasma only, plasma + S-1, and plasma + Cu/S-1 at 673 K.

Reaction results



Figure S6. Effect of (a) reaction temperature and (b) Cu loading on CH₄ conversion and products selectivity (error bars are obtained through five repetitions of experiment).



Figure S7. Influence of support material of Cu-based catalysts on the reaction performance.

Samples	$S_{\text{BET}}(m^2/g)$	$S_{EXT}(m^2/g)$	$S_{\rm MIC}(m^2/g)$
NaZSM-5	259	220	39
TiO ₂	66	59	6.37
CeO ₂	30	29	0.57
HZSM-5	437	39	397
γ -Al ₂ O ₃	123	115	8.40
ZrO_2	33	30	2.39
TS-1	429	243	186.82
fumed SiO ₂	192	180	12.53
S-1	367	272	95.69

Table S1. Morphological information of the supports (obtained by N₂-physisorption)

Table S2. Morphological information of Cu-based catalysts with 10 wt.% loading (obtained by N2-physisorption)

Samples	$S_{BET}(m^2/g)$	$S_{EXT}(m^2/g)$	$S_{MIC}(m^2/g)$
Cu/NaZSM-5	273	38	235
Cu/TiO ₂	32	28	4.2
Cu/CeO ₂	43	41	2.5
Cu/HZSM-5	307	56	251
Cu/γ - Al_2O_3	119	101	18
Cu/ZrO ₂	28	24	4.1
Cu/TS-1	399	143	256
Cu/fumed SiO ₂	163	140	23
Cu/S-1	366	105	221



Figure S8. . Influence of metal type on reaction performance using S-1 as support.

Table S3. Comparison of TOF of Cu and Pt catalysts

	Sample	Metal loading (wt %)	CH ₄ conversion (%)	HCN selectivity (%)	Metal dispersion (%)	Concentration of active sites (10 ⁻⁵ mol/g)	TOF (h ⁻¹)
	TS-1	-	19.8	61.5	-	-	-
	1% Pt/TS-1	$\approx 1\%$	25.9	80.9	70	3.59	17.66
rate of HCN	produced ¹	(mōl/h)	15.6	58.2	-	-	-
catalyst(g) []	con centratios of	activeo.sites ((mol/g)30	79	26.5	42.12	2.54
rate HCN	15% Cu/S-1	15.2	31.3	81.9	17.5	41.86	3.16
duc-	20% Cu/S-1	20.4	31.8	84.8	8.7	27.93	5.53
_ of	25% Cu/S-1	25.2	32	85	4.7	18.64	8.42
N duc-	30% Cu/S-1	29.3	32.4	86.2	3.8	17.52	9.59
by							

asma + catalyst" - rate of HCN produced by "plasma + support" (The rate of HCN produced at 4 hour time on stream was used to calculate TOF values)



Figure S9. Influence of Cu/S-1 granule size on reaction performance (0.85-2.00mm: 10-20mesh; 0.42-0.85mm: 20-40 mesh; 0.25-0.42 mm: 40-60 mesh).

6 Mass spectrometry profile of products



Figure S10. In-situ MS signal of H₂, HCN and CH₃CN species in the product gas of CH₄/NH₃ plasma packed by (a) fresh Cu/S-1 and (b) spent Cu/S-1 sample.

7 DFT calculations

Fully periodic density functional theory (DFT) calculations were conducted using the Quickstep² module of the CP2K³ package. The general gradient approximation (GGA) Perdew-Burke-Ernzerhof (PBE)⁴ was used by employing molecularly optimized DZVP-MOLOPT⁵ basis sets and Goedecker-

Teter-Hutter (GTH) pseudopotentials.^{6,7} Dispersion corrections were considered by applying Grimme's DFT-D3 approximation alongside Becke-Johnson damping.^{8,9} A lattice constant of 3.615 Å¹⁰ was used for making four-layered Cu (111), Cu (200) and Cu (220) slabs with the two bottom layers fixed to their bulk structures. The supercell dimensions chosen for each slab are provided in the supporting information (SI). Fermi-Dirac smearing with the electronic temperature of 300 K was used for the calculations, and sampling of the Brillouin zone was limited to the Γ -point only.

For the geometry optimization of the end points for the calculation of the MEP, the Broyden-Fletcher-Goldfarb-Shanno (BFGS) scheme was used by applying maximum force tolerance of 0.02 eV/Å and employing an energy cutoff of 800 Ry for auxiliary plane wave basis sets.

The energy profiles and activation energies were achieved using the climbing image nudged elastic band (CI-NEB)¹¹ method implemented in the CP2K code. Depending on the distance that atoms needed to travel, between 9 to 28 images were interpolated along the path. The transition state was identified as the highest point between two minima in the energy profile. The plane wave cutoff energy was set to 400 Ry for the NEB calculations.

For most of the exothermic reactions, no saddle point was detected along the reaction coordinate. Consequently, the reaction barrier was reported as zero (barrier-less) for these reactions. For the endothermic reactions without detected transition state, the reaction energy is reported.

• Dimensions of the supercells used for the calculations (all in Å):

Cu (111): 10.23 × 08.86 × 30.00 Cu (200): 10.23 × 10.23 × 30.00 Cu (220): 10.23 × 10.85 × 30.00

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Figure S11. Minimum energy path (MEP; black curve, left y-axis) and C-N distance (red curve, right y-axis) for (a) the interaction of pre-adsorbed NH and CH, (b) gas phase NH with pre-adsorbed CH and (c) gas phase CH with pre-adsorbed NH to form HCNH(s) on the Cu (111) surface. All energies are with respect to that of the pre-adsorbed NH and CH on Cu (111). The insets illustrate the configurations of initial state, transition state (TS) and final state, where brown, black, blue and yellow colors correspond to Cu, C, N and H atoms, respectively.



Figure S12. Minimum energy path (MEP; black curve, left y-axis) and C-N distance (red curve, right y-axis) for (a) the interaction of pre-adsorbed NH_2 and CH, (b) gas phase NH_2 with pre-adsorbed CH and (c) gas phase CH with pre-adsorbed NH_2 to form $HCNH_2(s)$ on the Cu (111) surface. All energies are with respect to that of the pre-adsorbed NH_2 and CH on Cu (111). The insets illustrate the configurations of initial state, transition state (TS) and final state, where brown, black, blue and yellow colors correspond to Cu, C, N and H atoms, respectively.

8 Synthesis of S-1 support

The support material of silicalite-1 (S-1) was synthesized by a hydrothermal method (Figure S13) from the silica source of tetraethylorthosilicate (TEOS) using 25 wt.% TPAOH as an organic structure-directing agent. Firstly, 25.78g of TPAOH was added to the 27.33g of distilled water, and stirred for 10 minutes. Then 30 g of TEOS was slowly dripped into the above solution and the mixture was stirred at room temperature for 3 hours to fully hydrolyze the TEOS. The solution was transferred into a Teflon-lined reactor and crystallized at 443 K for 36 hours. After cooling to room temperature, the crystalline product was obtained by centrifugation and washed with deionized water to neutral pH (pH = 7), dried at 393 K overnight and then calcined in air at 813 K for 6 hours to remove the organic template.



Figure S13. Schematic diagram of Silicate-1 preparation.

9 Synthesis of Cu/Silicalite-1

The supported Cu catalyst with varied Cu loadings (10, 15, 20, 25, and 30 wt.%) was prepared by impregnation method (Figure S14). Copper nitrate was purchased from Tianjin (China) Kemiou Chemical Reagent Co. Ltd. and the reagents were used without further purification. The S-1 was

calcined at 673 K for 5 hours to remove impurities (H₂O) before they were used as supports. The catalyst (10 wt.%) preparation process was as follows. The 3 g supports were added to an aqueous solution containing 1.27 g Cu(NO₃)₂·3H₂O under stirring. After stirring for 30 minutes at room temperature, the samples were aged at room temperature for 12 hours and then dried overnight at 393 K. Finally, the sample was calcined by a muffle oven at 813 K for 5 hours in air condition, shaped and sieved (dp = 20-40 meshes) for further reaction.



Figure S14. Schematic diagram of Cu/S-1 preparation.

10 Experimental setup for activity test

A schematic diagram of the experimental equipment for the plasma-catalytic CH_4/NH_3 reaction was shown as Figure S15. The mixture of CH_4 (20 ml/min) and NH_3 (40 ml/min) was controlled by mass flow controllers (Beijing Sevenstar Electronics Co., Ltd). The reactor was a typical cylindrical Dielectric Barrier Discharge (DBD) quartz tube (11 mm o.d. × 8 mm i.d.), with a sieve plate to hold the catalyst and a stainless-steel rod (2 mm o.d.) placed along the axis of the reactor, acting as high voltage electrode, while an aluminum foil covering the outside of the quartz tube acts as the grounded electrode. The discharge length was 5 cm, and 1.5 g catalyst samples (20-40 meshes) were used to fill the entire discharge length. After reaction of CH_4 and NH_3 for 1 hour, the products were detected by a gas chromatograph (GC-7890F) equipped with a flame ionization detector (FID) using a free fatty acid phase (FFAP) capillary column. The temperature program used for the GC was as follows: an initial temperature of 313 K lasting for 5 minutes and then heating up to 473 K at a rate of 20 K/min, and finally keeping this temperature for 5 minutes. The injection temperature and the detector temperature were both set at 493 K.

The catalyst performance was expressed by the CH₄ conversion and HCN selectivity. The HCN (and CH₃CN) selectivity was determined by the peak area normalization method.

The CH₄ conversion was calculated as follows:

CH 4 conversion =
$$\frac{[CH]_{inflet} - [CH]_{outlet}}{[CH]_{inflet}} = 100\%$$

where [CH₄] _{inlet} and [CH₄]_{outlet} represented the mole of CH₄ in the inlet and outlet, respectively. The selectivity of HCN was defined as follows:

HCN selectivit y =
$$\frac{S_{HCN}}{S_{all}}$$
 100%

where S_{HCN} represented the peak area of HCN in the outlet. S_{all} represented the peak area of all the products in the outlet. The same was done for the CH₃CN selectivity.

The selectivity of the other products detected (N, N-dimethyl cyanamide, amino acetonitrile) was too low to be analyzed quantitatively by the GC (five repetitions of the experiment have been done).



Figure S15. Schematic diagram of the experimental plasma-catalytic setup for the CH₄-NH₃ coupling reaction

Safety Warning. It is worth noting that, in order to prevent poisoning and environmental pollution, the experimental operators should always wear a gas mask, a protection suit and gloves. Furthermore, the exhaust gas must be burned in a high temperature furnace. In addition, anyone who wants to repeat the experiments must read the file about HCN-Safety Warning and Matters Need Attention.

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