Supporting Information for

Plasma driven ammonia decomposition on Fe-catalyst: eliminating surface nitrogen poisoning

Contents:

- 1. Scheme of the DBD plasma-driven catalysis reactor, Scheme S1.
- 2. XRF analysis of fresh commercial fused iron catalyst used for ammonia synthesis, table S1.
- 3. XRD, EA and FTIR analysis of Fe-based catalyst obtained by thermal treatment in NH₃ flow, Figures S1, S2, Table S2, Figures S3 and S4.
- 4. Energy efficiency and rates of H₂ formation from ammonia decomposition with different methods, Table S3.
- 5. Investigation of the role of the catalyst in the synergy obtained in ammonia decomposition by the plasma-driven catalysis method, Figures S5, S6 and Scheme S2.
- 6. On-line MS investigates the accelerating effect of DBD plasma on surface-adsorbed N atoms from metallic Fe catalyst in ammonia decomposition, Figure S7.
- Optical emission spectroscopy (OES) analyzed the species existed in ammonia decomposition by plasma-driven catalysis, Figure S8 and Table S4.
- 8. ¹⁵NH₃ isotope tracing experiments, Scheme S3, Figures S9 and S10.
- 9. Spectra of reaction temperature in the ${}^{15}NH_3$ decomposition on Fe_2N^{14} catalyst without or with DBD plasma, Figures S11 and S12.
- 10. Temperature distribution across the reactor for NH₃ decomposition in plasma-driven catalysis mode, Scheme S4 and Figure S13.

Electronic Supplementary Material (ESI) for Chemical Communications This journal is O The Royal Society of Chemistry 2013

1. Scheme of the DBD plasma-driven catalysis reactor.



Scheme S1. Scheme of the experimental setup used for H_2 generation from NH_3 decomposition.

2. XRF analysis of fresh commercial fused iron catalyst used for ammonia synthesis, Table. S1.

FeO	Al ₂ O ₃	K ₂ O	V_2O_5	SiO ₂	TiO ₂	SO ₃
691.9 KCps	2.5 KCps	5.0 KCps	2.8 KCps	0.7 KCps	2.8 KCps	0.9 KCps
94.4%	2.19%	0.166%	0.835%	0.477%	0.446%	0.235%
MgO	MnO	Lu_2O_3	Cl	CuO	NiO	MoO ₃
0.3 KCps	0.5 KCps	0.1 KCps	0.2 KCps	0.2 KCps	0.1 KCps	0.5 KCps
0.968%	0.0605%	0.0376%	0.0762%	0.0282%	0.0205%	0.0191%
				_		
ZnO	Compton	Rayleigh	Sum			
0.1 KCps]		
0.0117%	1.11	1.03	100.00%]		

Table S1. X-ray fluorescence (XRF) analysis of fresh commercial fused iron catalyst

(X-ray fluorescence: SRS-3400, Germany, 40 kW, 60 kV, 150 mA, 75 mm, ±0.01°C)

3. XRD, EA and FTIR analysis of Fe-based catalyst obtained by thermal treatment in NH₃ flow, Figures S1, S2, Table S2, Figures S3 and S4.

The samples were analyzed before and after NH_3 thermal treatment by X-ray diffraction (XRD, Figure S1), Element Analysis (EA, Table S2), and Fourier Transform Infrared Spectroscopy (FITR, Figure S2) techniques. All the results showed that Fe_2N was obtained after NH_3 thermal treatment.



Figure S1. X-ray diffraction patterns of catalysts before and after NH₃ thermal treatment. (X-ray diffraction: D/MAX-2400, Japan, 12 kW, 0.01, Cu, $\lambda = 0.1541$ nm)

Table S2. Element Analysis (EA) of Fe-based catalyst after NH₃ thermal treatment.

Wght.	Info.	02	Content [%]	Peak Area
			N: 10.27	7145
2.0500	CuHu	Index 1	C: 0.183	88
			H: 0.246	422

(Elementar Analysensysteme GmbH: vario EL III, Germany, 0.0001mg, CHN Mode)



Figure S2. IR spectra of catalysts before and after NH_3 treatment (FTIR: Nicolet 6700 FTI-IR Spectrometer, Thermo Electron Corporation in USA, 7800-350 cm⁻¹)

The stability of Fe_2N in high temperature or in the presence of DBD plasma is shown in Figures S3 and S4. Obviously, Fe_2N is unstable and it is easy to desorb N from Fe at high temperature or in the presence of plasma, which means that the structure of the catalyst changes depending on the reaction conditions during ammonia decomposition.



Figure S3. Stability of Fe₂N as function of temperature in He flow (He 40 ml/min, 2 g catalyst)



Figure S4. Stability of Fe₂N in NH₃ flow in the presence of DBD plasma (NH₃ 40 ml/min, 2 g catalyst)

4. Energy efficiency and rates of H₂ formation from NH₃ decomposition with different methods, Table S3.

	Fe-based catalyst			DBD plasma		Fe-	Fe-based catalyst + DBD plasma		
Reaction temp. °C	NH ₃ conv. %	H_2 formation rate, mol·L ⁻¹ ·h ⁻¹	NH ₃ conv. %	Energy efficiency of H_2 formation, mol $(kW \cdot h)^{-1}$	H_2 formation rate, mol·L ⁻¹ ·h ⁻¹	NH ₃ conv. %	Energy efficiency of H_2 fromation, mol $(kW \cdot h)^{-1}$	H_2 formation rate, mol·L ⁻¹ ·h ⁻¹	
300	0.4	0.32	5.2	0.41	4.17	1.5	0.09	1.21	
350	0.8	0.64	6.2	0.43	4.98	4.1	0.20	3.29	
380	2.5	2.01	7.2	0.44	5.79	16.8	0.80	13.50	
390	3.6	2.89	7.4	0.43	5.95	31.0	1.50	24.91	
400	5.4	4.34	7.6	0.43	6.11	90.8	4.56	72.96	
410	7.4	5.95	7.8	0.43	6.27	> 99.9	4.96	80.00	
430	17.6	14.14	8.3	0.42	6.67	-	-		
450	35.4	28.44	8.6	0.42	6.91	-	-		
470	65.0	52.23	9.7	0.43	7.79	-	-		
500	87.7	70.47	-	-		-	-		
550	> 99.9	80.00	-	-		-	-		

Table S3 Energy efficiency and rates of H₂ formation from NH₃ decomposition with different methods. (NH₃ feed flow 40 ml/min, 10 g catalyst, volume 2 ml, discharge frequency 12 kHz)

Energy efficiency of H_2 formation: the amount of H_2 production per kilowatt hour. H_2 formation rate: the amount of H_2 production per hour and per volume.

5. Investigation of the role of the catalyst in the synergy obtained in NH₃ decomposition by the plasma-driven catalysis method, Figures S5, S6 and Scheme S2.

When the DBD reactor worked at fixed condition (input power 26 W), the NH₃ conversion gradually increased from 10% to ~99%. Although XRD showed that FeO was transformed into Fe/Fe₃N/Fe₄N, in fact, metallic Fe dominates during on-site reaction process. The reason is that the XRD analysis of the catalyst after the reaction was done by turning off the plasma and keeping the catalyst in NH₃ flow until the catalyst was totally cooled. During this process the ammonia decomposition reaction is still occurring. Thus, parts of metallic Fe catalysts were inevitably transformed into Fe₃N/Fe₄N by strong adsorbed N atoms. In addition, the O atoms of iron oxide (FeO) were consumed to form H₂O not NO_x, see Figure S6 and Scheme S2. From Scheme S2, we know that the product H₂O was condensed on pipe wall, so the MS signal of H₂O was intermittent.



Figure S5. X-ray diffraction patterns of FeO after NH₃ decomposition in plasma-driven catalysis mode. (X-ray diffraction: D/MAX-2400, Japan, 12 kW, 0.01, Cu, $\lambda = 0.1541$ nm)



Figure S6. MS signals of products from ammonia decomposition on FeO catalyst in the presence of plasma. (NH₃ flow 40 ml/min, 2 g FeO catalyst, the reactor temperature was kept at 500 °C with input power 27 W.)



Scheme S2. Photograph of reactor outlet in the process of ammonia decomposition on FeO catalyst in the presence of plasma. (camera Nikon D7000, exposure time 0.5 s)

6. On-line MS investigates the accelerating effect of DBD plasma on surface-adsorbed N atoms on metallic Fe catalyst in ammonia decomposition, Figure S7.



Figure S7. XRD analysis of metallic Fe catalyst used in ammonia decomposition by thermal catalysis method (Reaction for 25 min, at 450 °C)

7. Optical emission spectroscopy (OES) analyzed the species existed in ammonia decomposition by plasma-driven catalysis, Figure S8 and Table S4.



Figure S8. Species of ammonia decomposition as function of input power in plasma-driven catalysis system by OES

Speices	NH·	N_2^*	NH ₃ *	$\mathbf{H}_{\mathbf{a}}$
λ, nm	336	337max	564.3 and 568.1 continuum	656.3
Electronic transition	$A^3 \Pi \rightarrow X^3 S^-$	$C^3 \Pi_{\mathrm{u}} \rightarrow B^3 \Pi_{\mathrm{g}}$	Schuster's emission bands	$2p^2p^0_{\ 3/2}-3d^2D_{3/2}$

Table S4. Species indentified by OES in NH₃ plasma-driven catalysis system (28 W)

(SP2758, produced by Princeton instrument company).

Electronic Supplementary Material (ESI) for Chemical Communications This journal is C The Royal Society of Chemistry 2013

8. ¹⁵NH₃ isotope tracing experiments, Scheme S3, Figures S9 and S10.



Scheme S3 Scheme of the desorption of adsorbed N atoms



Figure S9. XRD profiles of Fe₂N¹⁴ prepared by ¹⁴NH₃ thermal nitridation (X-ray diffraction: D/MAX-2400, Japan, 12 kW, 0.01, Cu, $\lambda = 0.1541$ nm)

X-ray photoelectron spectroscopy (XPS) was used to analyze the chemical environments of the surface components of the catalysts. The binding energy of Fe 2p3/2 and 2p1/2 of iron nitride centers at around 706 and 720 eV (Figure S10), respectively. The N 1s binding energy is 396.3 eV, which is characteristic of an iron nitride phase.



Figure S10. Fe 2p and N 1s spectra of Fe₂N¹⁴ prepared by ¹⁴NH₃ thermal nitridation (X-ray photoelectron spectroscopy: ESCALAB250, American Thermo VG company; ESCA: AlKa=1486.6 eV, P=150W, Spot Size=500 um, Pass Energy=50.0 eV, Energy Step Size=0.05 eV)

9. Spectra of reaction temperature in the ¹⁵NH₃ decomposition on Fe²N₁₄ catalyst without or with DBD plasma, Figures S11 and S12.



Figure S11. Reaction temperature obtained by thermal couple in NH₃ decomposition with thermal catalysis method (Without plasma, temperature-programmed heating using external heating furnace, 15 °C/min)



Figure S12. Reaction temperature obtained by thermal couple in NH_3 decomposition with plasma-driven catalysis method (The reaction system was heated internally by DBD plasma with 40~50W input power, without using external heating furnace)

10. Temperature distribution across the reactor for NH₃ decomposition in plasma-driven catalysis mode, Scheme S4 and Figure S13.

In the absence of DBD plasma, the thermal desorption (TD) of the Fe_2N^{14} was carried out in ${}^{15}NH_3$ flow with external temperature-programmed heating furnace (15 °C/min), identical to the temperature-programmed desorption technique (TPD). In the presence of DBD plasma, the plasma desorption (PD) of the Fe_2N^{14} was carried out in the DBD reactor in identical ${}^{15}NH_3$ flow. In this case, the sample was heated internally by DBD (input power 40-50 W) without using external heating furnace, and the temperature increased automatically, see Figure S12. Because of the high-voltage discharge inside the DBD reactor, it is impossible to follow the temperature of the catalyst bed in situ with an inside thermal couple. Therefore, the real-time temperature was determined by a thermal couple tightly attached to the reactor surface (connected to the ground electrode) and an infrared camera (Scheme S4 and Figure S13, ESI[†]).

Measurement of temperature: An infrared camera was focused on a 9×9 mm window of the reactor (Scheme S4) to measure the catalyst bed temperature. Results showed that the temperature of the catalyst bed was lower than that of the reactor wall (Figure S13). Thus, it was reasonable to compare desorption temperature in plasma-driven catalysis with that in only catalyst according to the temperature obtained by the thermal couple measurement, which is tightly attached to the reactor wall.



Scheme S4. The configuration of N₂ desorption from Fe₂N detected by mass spectrometry (MS) and temperature recorded by infrared camera in the presence of DBD plasma.



Figure S13. Temperatures of inside and outside reactor when NH₃ decomposition on Fe₂N in the presence of DBD plasma (Infrared camera: FLIR A 40, NH₃ flow 40 ml/min)