

View Article Online View Journal

# **RSC Advances**

This article can be cited before page numbers have been issued, to do this please use: D. Xie, Y. Sun, T. Zhu, X. Fan, X. Hong and W. Yang, *RSC Adv.*, 2016, DOI: 10.1039/C6RA21351K.



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. This Accepted Manuscript will be replaced by the edited, formatted and paginated article as soon as this is available.

You can find more information about *Accepted Manuscripts* in the **Information for Authors**.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard <u>Terms & Conditions</u> and the <u>Ethical guidelines</u> still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.



www.rsc.org/advances

1	Ammonia synthesis and by-products formation from $H_2O$ , $H_2$
2	and $N_2$ by dielectric barrier discharge combined with Ru/Al <sub>2</sub> O <sub>3</sub>
3	catalyst
4	Deyuan Xie <sup>a1</sup> , Ye Sun <sup>a1</sup> , Tianle Zhu <sup>a,*</sup> , Xing Fan <sup>b,*</sup> , Xiaowei Hong <sup>a</sup> , Wenhao Yang <sup>a</sup>
5	<sup>a</sup> School of Space and Environment, Beihang University, Beijing 100191, PR China.
6	<sup>b</sup> College of Environmental and Energy Engineering, Beijing University of Technology,
7	Beijing 100124, PR China.
8	* Corresponding author: Tel./fax: +86-10-82314215
9	E-mail address: zhutl@buaa.edu.cn (Tianle Zhu); fanxing@bjut.edu.cn (Xing Fan).
10	<sup>1</sup> These authors contributed equally.
11	Abstract:
12	$NH_3$ synthesis from $H_2O + N_2$ , $H_2 + N_2$ or $H_2O + H_2 + N_2$ by dielectric barrier
13	discharge combined with $Ru/Al_2O_3$ catalyst was studied at atmospheric pressure and
14	room temperature. The effects of reaction gas compositions, energy density, and
15	discharge frequency on NH <sub>3</sub> yield and by-products formation were investigated. The
16	results show that $NH_3$ can be formed from the reaction gases consisted of $H_2O$ and $N_2$ .
17	$NH_3$ yield of reaction gases containing $H_2$ is much higher than that of reaction gas
18	consisted of $H_2O$ and $N_2. The presence of H_2O has a promotion effect on NH_3$
19	synthesis from $H_2$ and $N_2$ , especially for the reaction gases with $H_2$ content less than
20	10%. The $NH_3$ yield first increases and then decreases with the increase of the energy
21	density. The maximum yield of 680 mg/kWh occurs at the energy density of 1400 J/L
22	and in the reaction gases of $0.14\%$ H <sub>2</sub> O, $40\%$ H <sub>2</sub> and N <sub>2</sub> . The discharge frequency has

RSC Advances Accepted Manuscript

a great effect on the NH<sub>3</sub> yield, and the maximum NH<sub>3</sub> yield is obtained at frequency
of 13 kHz. Besides NH<sub>3</sub>, some by-products such as N<sub>2</sub>O and NO<sub>2</sub> are also formed in
the reaction gases containing H<sub>2</sub>O. However, the formation can be suppressed in the
presence of H<sub>2</sub>, which is attributed to the reduction effect of H<sub>2</sub> on the by-products.

# 27 Keywords: NH<sub>3</sub> synthesis, DBD, Ru, Al<sub>2</sub>O<sub>3</sub>, H<sub>2</sub>O

## 28 1. Introduction

29 As the most important aftertreatment techniques for NO<sub>x</sub> emission from 30 combustion processes, selective catalytic reduction (NH<sub>3</sub>-SCR) and selective non-catalytic reduction (NH<sub>3</sub>-SNCR) with NH<sub>3</sub> as the reductant have gained a wide 31 attention both in research field and in practical applications.<sup>1-4</sup> Although their 32 excellent denitration (DeNO<sub>x</sub>) performance have been generally recognized, the 33 supply of  $NH_3$  remains a problem because of its toxicity and explosivity. To make 34 35 sure the safety, harsh measures have to be adopted for transport, storage and usage of liquid and aqueous NH<sub>3</sub>. One effective approach for overcoming these shortcomings 36 37 is to generate  $NH_3$  in site where and when the need arises. Actually, the on-board synthesis of NH<sub>3</sub> for NO<sub>x</sub> removal in truck and car exhausts was already investigated.<sup>5</sup> 38 The conventional ammonia synthesis technology such as Haber-Bosch process is 39 only suitable for large scale and continuous production as it requires high operating 40 temperatures (400-500  $^{\circ}$ C) and pressures (150-300 bar) over magnetite (Fe<sub>3</sub>O<sub>4</sub>) 41 catalyst.6,7 Nowadays. non-thermal plasma characterized 42 process, bv operating/stopping instantaneously, emerges as an alternative method of treating air 43 pollutants<sup>8</sup>, as well as a potential way to synthesize gas products at atmospheric 44

46

47

#### **RSC Advances**

pressure and close to ambient gas temperature.<sup>9,10</sup>. Actually, the NH<sub>3</sub> synthesis from

N<sub>2</sub>-H<sub>2</sub> gas mixtures induced by non-thermal plasma at ambient temperature was

reported by Brewer as early as 1929.11 Up to now, a various forms of plasma

View Article Online DOI: 10.1039/C6RA21351K

48	including microwave discharge plasma <sup>12</sup> , radio frequency discharge plasma <sup>13</sup> , ECR
49	(electron cyclotron resonance) plasma <sup>14</sup> , expanding thermal plasma <sup>7</sup> were employed
50	for $NH_3$ synthesis from gas mixtures of $N_2$ and $H_2$ . The apparatus for generating these
51	types of plasma, however, were operated under reduced pressure (several hundreds of
52	Pa atmospheric pressure), so they are unsuitable for practical applications.
53	Recently, the application of atmospheric pressure DBD plasma in NH <sub>3</sub> synthesis
54	was reported by Mizushima using a catalyst-loaded membrane as dielectric material <sup>15</sup> ,
55	Hong using a DBD packed bed reactor filled with dielectric spheres <sup>16</sup> and Bai
56	applying a microgap DBD reactor <sup>17</sup> . Furthermore, Bai also pointed out that NH <sub>3</sub> yield
57	increased by about 1.54-1.75 times when MgO powder was coated on the surface of
58	the electrode plate. <sup>18</sup> Improvement of NH <sub>3</sub> yield was also achieved by loading the
59	alumina tube with Ru, Pt, Ni, and Fe catalysts placed between the electrodes. <sup>19</sup>
60	Previous researches generally thought that the reaction occurs on the surface of
61	catalysts. <sup>20,21</sup> Excited nitrogen molecules are absorbed on the surface of catalyst and
62	then dissociated to an adsorbed nitrogen atoms N (a). The nitrogen atoms N (a)
63	combines with hydrogen from the gas phase or on the surface of catalyst to form
64	successively NH (a) and NH <sub>2</sub> (a) and finally become ammonia. $^{21}$

In this study, we focused on the NH<sub>3</sub> synthesis from H<sub>2</sub>O, H<sub>2</sub> and N<sub>2</sub> by 65 DBD-type plasma combined with Ru/Al<sub>2</sub>O<sub>3</sub> catalyst at atmospheric pressure and room 66

RSC Advances Accepted Manuscript

67	temperature. Ru was selected as the catalyst and dielectric barrier material because it
68	is seen as the second generation of non-iron catalyst for NH <sub>3</sub> synthesis from reaction
69	gases of $H_2$ and $N_2$ . <sup>6,22</sup> Meanwhile, $H_2O$ also acted as the source of hydrogen because
70	hydrogen atoms can be produced by dissociating water molecules with the help of
71	non-thermal plasma, in which contains abundant reactive species such as high-energy
72	electrons, ions, excited atoms and molecules, and active radicals . For this reason, a
73	gas stream containing $H_2O$ , $H_2$ and $N_2$ was used as the reaction gases. And the effects
74	of reaction gas compositions, energy density, and discharge frequency on NH <sub>3</sub> yield
75	were investigated.

# 76 2. Experimental Section

## 77 2.1 Experimental setup

A schematic diagram of the experimental setup is shown in Fig. 1. It consists of a 78 gas feeding system, a cylinder DBD reactor with an AC high-voltage power supply 79 (Dalian University of Technology, China), a digital oscilloscope (Tektronix DPO3034, 80 81 America) with discharge parameters detection unit and a set of analytical instruments.  $H_2 + N_2$ ,  $H_2O + N_2$  or  $H_2O + H_2 + N_2$  were used as the reaction gases and the gas flow 82 rates were controlled with mass flow controllers (MFC). The H<sub>2</sub>O was introduced by 83 bubbling  $N_2$  in deionized water at 25 °C and the relative humidity of the reaction 84 gases was detected by a humidity meter (Cole Parmer, America). Then the H<sub>2</sub>O 85 content was calculated based on the relative humidity. The total gas flow rate was 500 86 mL/min except otherwise stated. 87

**RSC Advances Accepted Manuscript** 



Fig. 1 Schematic diagram of the experimental setup

90 2.2 Plasma reactor

88

89

Fig. 2 shows a schematic illustration of the concentric DBD reactor used in this 91 study. An aluminium rod with discharge length and outer diameter of 100 mm and 21 92 mm serving as the high-voltage electrode was placed in a quartz tube with length and 93 inner diameter of 200 mm and 25 mm. An aluminum tape wrapped on the outer 94 surface of the quartz tube was connected to a 10 nF capacitor before grounded. The 95 Ru/Al<sub>2</sub>O<sub>3</sub> catalyst was packed in the space between the high-voltage electrode and 96 thequartz tube. By applying AC high voltage, intense discharge plasma could be 97 98 generated around the contact point of the catalysts without arcing.

Page 6 of 26 View Article Online DOI: 10.1039/C6RA21351K



100

# Fig. 2 Schematic diagram of the DBD plasma reactor

# 101 2.3 Preparation of $Ru/Al_2O_3$ catalyst

Aluminum oxide powder was provided by Aladdin Co. Ltd (Shanghai, China) and RuCl<sub>3</sub> was obtained from Shenyang Jinke Reagent Co. Ltd (China). All the chemicals were used as received without any further purification. Ru (1 wt%) was added by incipient wetness impregnation with aqueous RuCl<sub>3</sub> solution, followed by evaporation in rotavapor and drying ( $105^{\circ}$ C) in an oven for overnight. Then the as-prepared sample was reduced in hydrogen at 400°C for 4 h to obtain Ru/Al<sub>2</sub>O<sub>3</sub>.

# 108 2.4 Characterization of the catalysts

X-ray powder diffraction (XRD) measurements were performed using a
PANalytical X' Pert PRO diffractometer (Cu Pd radiation) at 40 kV and 40 mA.
HRTEM micrographs were obtained with a JEM-2100F microscope at 200 kV. The
surface chemical states of the Ru/Al<sub>2</sub>O<sub>3</sub> catalysts were investigated *via* XPS (PHI
Quantro SXM ULVAC-PHI, Japan) using an Al Kα X-ray source (1486.7 eV) at 15
kV and 25 W with the binding energy calibrated by C 1s at 284.8 eV.

Published on 13 October 2016. Downloaded by Cornell University Library on 16/10/2016 19:57:17.

# 115 2.5 Experimental method

116	The NH <sub>3</sub> was absorbed by dilute sulphuric acid and then quantitatively analyzed
117	using a visible spectrophotometer based on Nessler's reagent colorimetric method. <sup>23</sup>
118	Other gas phase products were qualitatively confirmed by Fourier transform infrared
119	spectrometer (FTIR, Nicolet 6700, America) and/or mass spectrometer (MS,
120	OmniStar GSD300, Germany). The applied voltage and the voltage drop through the
121	capacitor were monitored with a high voltage probe (EP-50 K, Japan) and a low
122	voltage probe (Tektronix P5100, America), respectively. The Q-U Lissajous method
123	was used to calculate the discharge power of the DBD reactor $(P)$ , which is defined as
124	follows:

125 
$$P(W) = f \times C \times A \tag{1}$$

where f, C and A are the frequency of discharge, capacitance of the external capacitor (10 nF) and the area of Lissajous diagram, respectively.

128 The energy density (*ED*) is defined as the energy deposited per unit volume of 129 the reaction gas:

$$ED = \frac{P \times 60}{Q} \tag{2}$$

131 where Q denotes the total gas flow rate in L/min.

132 In this study, the yield of NH<sub>3</sub> ( $\eta$ , mg/kWh) is defined as follows:

133 
$$\eta = \frac{C_{\rm NH_3}}{ED} \times 3.6 \times 10^6 \tag{3}$$

134 where  $C_{NH_3}$  (mg/L) is the concentration of NH<sub>3</sub> detected at the outlet of the reactor.

# 135 **3. Results and Discussion**

Fig. 3 shows the XRD spectra of  $Ru/Al_2O_3$  catalysts before and after discharge reaction (5% H<sub>2</sub> + N<sub>2</sub>, ED = 1400 J/L). The pattern of the both catalysts contain only diffraction peaks from alumina. No peak correlated to Ru was observed, probably due to the relatively low contents.



141

Published on 13 October 2016. Downloaded by Cornell University Library on 16/10/2016 19:57:17.

Fig. 3 X-ray diffraction patterns of  $Ru/Al_2O_3$  catalysts: (a) before discharge, (b) after discharge (5% H<sub>2</sub> + N<sub>2</sub>, ED = 1400 J/L)

The distribution of Ru particles on the  $Al_2O_3$  support has been determined by TEM (Fig. 4). It shows that Ru nanoparticles ( $\sim 3$  nm) appear to be uniformly distributed on the  $Al_2O_3$  support and the size and distribution of the Ru particles are almost unchanged after the discharge reaction.

**RSC Advances Accepted Manuscript** 



148Fig. 4 Transmission electron micrograph of Ru/Al<sub>2</sub>O catalysts: (a) before149discharge, (b) after discharge (5%  $H_2 + N_2$ , ED = 1400 J/L)

150 XPS analysis was performed on both  $Ru/Al_2O_3$  catalysts before and after 151 discharge reaction (Fig. 5). The peak at 461.9 eV can be assigned as metallic  $Ru^{24}$ . As 152 shown in Fig. 5, the valence state of Ru remains the same after the discharge reaction.





after discharge (5%  $H_2 + N_2$ , ED = 1400 J/L)

<sup>155 3.2</sup> Discharge characteristics

RSC Advances Accepted Manuscript

156 Fig. 6 shows the relationship between energy density and discharge voltage for 157 different reaction gases at the same discharge frequency of 11.0 kHz. For the representative reaction gases, the energy density remains zero until the voltage 158 reaches the discharge inception value and then the energy density is dramatically 159 increased with the increase of discharge voltage. The introduction of H<sub>2</sub>O results in an 160 161 increase of the discharge inception value and a decrease of energy density at a given 162 discharge voltage, which can be attributed to the strong electron affinities of  $H_2O$ 163 molecules. The ability of  $H_2O$  molecules attaching the dissociative electrons is larger than that of H<sub>2</sub>.<sup>25</sup> Therefore, higher discharge inception voltage is needed to achieve 164 the same energy density in the reactor for 0.14% H<sub>2</sub>O + N<sub>2</sub>, compared with the 165 reaction gases consisted of 5%  $H_2 + N_2$  or 0.14%  $H_2O + 5\% H_2 + N_2$ . 166



Fig. 6 The energy density as a function of discharge voltage (f = 11.0 kHz)

<sup>169 3.3</sup> Effect of  $H_2O$  content on  $NH_3$  yield

<sup>170 3.3.1</sup> Reaction gases consisting of  $H_2O$  and  $N_2$ 

<sup>Fig. 7 illustrates the variation of NH<sub>3</sub> yield with energy density for the H<sub>2</sub>O
content of 0.07%, 0.14%, and 0.21%, respectively. For all the H<sub>2</sub>O content, NH<sub>3</sub> yield</sup> 

first increases and then decreases with the increase in energy density, with maximum ammonia yields of 8.5 mg/kWh, 17.6 mg/kWh and 16.1 mg/kWh at energy density of 500 J/L, 670 J/L and 550 J/L for H<sub>2</sub>O content of 0.07%, 0.14%, and 0.21%, respectively. The NH<sub>3</sub> yield enhances by about 2 times when the H<sub>2</sub>O content increases from 0.07% to 0.14%, while it almost keeps same for H<sub>2</sub>O content of 0.14% and 0.21%.



186  $H_2$  (Fig. 8) and NO<sub>x</sub> (Fig. 9).



187

189

Fig. 8 Hydrogen ion current for different energy density

(reaction gases: 0.14% H<sub>2</sub>O + N<sub>2</sub>, f = 11.0 kHz)



190

191

192

Fig. 9 FTIR spectra of the effluents after the DBD reactor

(reaction gases: 0.14% H<sub>2</sub>O + N<sub>2</sub>, f = 11.0 kHz)

As can be seen from Fig. 8, the  $H_2$  yield, represented by ion current detected by MS, increases with increasing energy density, indicating that more H atoms can be generated at higher energy density, which explains the phenomenon that  $NH_3$  yield increases with the increase of energy density (Fig. 7). On the other hand, the FTIR results which are shown in Fig. 9 prove that  $NO_x$  (mainly  $NO_2$  and  $N_2O$ ) are also

View Article Online DOI: 10.1039/C6RA21351K

200 dis 201 (re 202 end 203 occ 204 wit 205 mc 206 Fo 207 yie 208 209 210

Published on 13 October 2016. Downloaded by Cornell University Library on 16/10/2016 19:57:17.

produced during the DBD process and the concentration of NO<sub>x</sub> greatly enhanced when the energy density is higher than a certain value. A portion of N species and discharge energy used for NH<sub>3</sub> synthesis can be consumed in NO<sub>x</sub> formation (reactions R6-R8), which thus results in the decrease of NH<sub>3</sub> yield with increasing the energy density after the peak point (Fig. 7). Besides, Mizushima pointed out that the occurrence of backward reaction is a possible reason for the decreasing NH<sub>3</sub> yield with increasing energy density.<sup>15</sup> In other words, at a higher energy density, more NH<sub>3</sub> molecules are formed, meanwhile their decomposition to H<sub>2</sub> and N<sub>2</sub> are also promoted. For this reason, there exists an optimum energy density for obtaining a maximum NH<sub>3</sub> yield in the plasma process.

208 
$$N_2 + e \rightarrow N_2^+ (X^2 \sum g^+, A^2 \Pi u, B^2 \sum u^+, C^3 \sum u^+) + 2e$$
 (R1)

209 
$$N_2 + e \rightarrow N^+({}^{3}P) + N^+({}^{4}S, {}^{2}D) + 2e$$
 (R2)

210 
$$N_2^+ + H_2O \rightarrow N_2 + H_2O^+$$
 (R3)

211 
$$H_2O^+ + H_2O \rightarrow H_3O^+ + OH$$
 (R4)

$$e+H_2O+\rightarrow H+OH \tag{R5}$$

213 
$$N + OH \rightarrow NO + H \cdot k_1 = 5.05 \times 10^{-11} \text{ cm}^3 \cdot \text{molecule}^{-1} \cdot \text{s}^{-1}$$
 (R6)

214 
$$\text{NO} + \text{O} \rightarrow \text{NO}_2$$
  $k_2 = 3.01 \times 10^{-11} \text{ cm}^3 \cdot \text{molecule}^{-1} \cdot \text{s}^{-1}$  (R7)

215 
$$NO_2 + N \rightarrow N_2O + O$$
  $k_3 = 1.2 \times 10^{-11} \text{ cm}^3 \cdot \text{molecule}^{-1} \cdot \text{s}^{-1}$  (R8)

216 3.3.2 Reaction gases consisting of  $H_2O$ ,  $H_2$  and  $N_2$ 

The effect of  $H_2O$  content on  $NH_3$  yield is plotted in Fig. 10 when the basic compositions of reaction gases are 5%  $H_2$  and  $N_2$ . With the increase of energy density from 0 to 2000 J/L, the  $NH_3$  yield increases to a peak value and then decreases to a

220 certain value regardless of the  $H_2O$  content in the reaction gases. For the reaction 221 gases consisted of 5%  $H_2$  and  $N_2$  (dry case), the maximum NH<sub>3</sub> yield is 270 mg/kWh at 1386 J/L, which is much higher than the case for  $H_2O$  and  $N_2$  (Fig. 7). The 222 introduction of H<sub>2</sub>O to reaction gases of 5% H<sub>2</sub> and N<sub>2</sub> results in an increase of the 223 NH<sub>3</sub> yield. For the same energy density of 1400 J/L, the NH<sub>3</sub> yield increases from 270 224 225 mg/kWh (dry case) to 300 mg/kWh, 380 mg/kWh and 310 mg/kWh in the presence of 226 0.07% H<sub>2</sub>O, 0.14% H<sub>2</sub>O, and 0.21% H<sub>2</sub>O, respectively, which can be attributed to the 227 formation of more H-containing species in favor of NH<sub>3</sub> synthesis in the presence of  $H_2O$ . Kikuchi studied the effect of  $H_2O$  on atomic hydrogen generation in hydrogen 228 plasma and proposed that the relative concentration of hydrogen atoms increased 229 when water vapor was added.<sup>26</sup> 230



231

232

233

Fig. 10 Effect of adding H<sub>2</sub>O on the NH<sub>3</sub> yield

(basic reaction gases 5%  $H_2$ +  $N_2$ , f = 11.0 kHz)

Fig. 11 shows the FTIR spectra of effluents after the DBD reactor for different  $H_2O$  content under the same energy density of 1400 J/L. It can be seen that the presence of  $H_2O$  does promote NH<sub>3</sub> formation. Besides, only nitrous oxide (N<sub>2</sub>O) is

Published on 13 October 2016. Downloaded by Cornell University Library on 16/10/2016 19:57:17.

237	detected as the byproduct and its concentration increases with increasing H <sub>2</sub> O content
238	$NO_2$ , which is observed when $H_2O$ and $N_2$ were used as the reaction gases (Fig. 9), is
239	not detected in the presence of $H_2$ (Fig. 11). This may be due to that more NH and
240	NH <sub>2</sub> radicals exist in the discharge region as precursors of NH <sub>3</sub> . These free radicals
241	are strongly reductive and can reduce NO and $NO_2$ to $N_2O$ quickly, as shown in
242	equations R9-R11.

243 NO+NH
$$\rightarrow$$
N<sub>2</sub>O+H·  $k_4$ =8.39×10<sup>-1</sup> cm<sup>3</sup>·molecule<sup>-1</sup>·s<sup>-1</sup> (R9)

244 
$$NO_2 + NH \rightarrow N_2O + \cdot OH$$
  $k_5 = 4.1 \times 10^{-1} \text{ cm}^3 \cdot \text{molecule}^{-1} \cdot \text{s}^{-1}$ 

246 
$$NO_2 + NH_2 \rightarrow N_2O + H_2O$$
  $k_6 = 1.4 \times 10^{-1} \text{ cm}^3 \cdot \text{molecule}^{-1} \cdot \text{s}^{-1}$  (R11)

Obviously, the rate constants of these reduction reactions are several orders of 247 magnitude higher than those of nitrogen oxides (NO and NO<sub>2</sub>) formation reactions 248 (equations R6, R7). As a result, NO and NO<sub>2</sub> formed during the plasma process would 249 be immediately consumed by NH and NH<sub>2</sub> radicals. On the other hand, increase the 250  $H_2O$  content results in the increase of  $N_2O$  concentration by providing more oxidizing 251 species (e.g. O, OH) for NO<sub>x</sub> formation (equation R6, R7), which may not be favor 252 for the  $NH_3$  synthesis and the  $NH_3$  yield decreases when the  $H_2O$  content is higher 253 254 than the optimum value of 0.14%.



256

Fig. 11 FTIR spectra of the effluents after the DBD reactor

257 (reaction gases: 5%  $H_2+H_2O+N_2$ , f=11.0 kHz)

# 258 **3.4 Effect of H<sub>2</sub> content on NH<sub>3</sub> yield**

3.4.1 Reaction gases consisting of H<sub>2</sub> and N<sub>2</sub>

260 The effect of  $H_2$  content on  $NH_3$  yield without  $H_2O$  is shown in Fig.12. The  $NH_3$  yield increases to a peak value at an energy density of about 1400 J/L regardless of the H<sub>2</sub> 261 content. At this point, the NH<sub>3</sub> yield reaches to 270 mg/kWh, 440 mg/kWh, 620 262 mg/kWh, 640 mg/kWh, and 580 mg/kWh for  $H_2$  contents of 5%, 10%, 20%, 40%, and 263 60%, respectively. In a traditional NH<sub>3</sub> synthesis process, the H<sub>2</sub> content of reaction 264 gases is usually around 75% ( $N_2$ :H<sub>2</sub>=1:3). In this study, the observed optimum H<sub>2</sub> 265 266 content (40%) is lower than the calculated value from the stoichiometric ratio of  $H_2$ and N<sub>2</sub> in NH<sub>3</sub>. Previous studies about NH<sub>3</sub> synthesis in the presence of non-thermal 267 268 plasma also indicated that the NH<sub>3</sub> yield depends on the  $N_2/H_2$  ratio in the reaction gases and similar optimal ratio was reported.<sup>18, 27</sup> 269

271

# **RSC Advances**

Being different from the traditional NH<sub>3</sub> synthesis process, in which the molecules are

dissociated on a catalytic surface at high temperatures (400- 550°C) and high

View Article Online DOI: 10.1039/C6RA21351K

272	pressures (15-35 MPa), under the non-thermal plasma condition, the precursor
273	molecules $H_2O$ , $H_2$ and/or $N_2$ are dissociated to N and H atoms. Thus, the surfaces of
274	catalyst are exposed to high concentration atomic N and H radicals. The $\mathrm{NH}_3$
275	formation turns out to be strongly dependent on the content of atomic N and H
276	radicals. <sup>14</sup> When the $H_2$ content is lower than the optimum $H_2/N_2$ ratio, the reaction
277	possibility between the $H_2$ and $N_2$ on the surface of catalysts increases with increasing
278	$\mathrm{H}_2$ content, which is due to more reaction gases dissociated in favorable of $\mathrm{NH}_3$
279	synthesis. However, if the $H_2$ content further increased above the optimum value, the
280	NH <sub>3</sub> synthesis would be restrained mainly due to the following two reasons. Firstly,
281	more discharge power would be consumed for activating $\mathrm{H}_2$ molecules other than $\mathrm{N}_2$
282	molecules, as the dissociation energy of $\mathrm{H}_2$ (4.5 eV) is much lower than that of $\mathrm{N}_2$
283	(9.8 eV), which results in shortage of nitrogen atoms for NH <sub>3</sub> synthesis. Secondly,
284	with increasing $H_2$ content, more hydrogen atoms would occupy the catalyst surface,
285	reducing the number of adsorbed nitrogen atoms and also increasing the possibility of
286	hydrogen atoms recombination to hydrogen molecules.



# Fig. 12 Effect of H<sub>2</sub> content on NH<sub>3</sub> yield

(reaction gases:  $H_2 + N_2$ , f=13kHz)

289

290

# 3.4.2 Reaction gases consisting of 0.14% H<sub>2</sub>O, H<sub>2</sub> and N<sub>2</sub>

291 Fig. 13 shows NH<sub>3</sub> yield versus H<sub>2</sub> contents of reaction gases in the presence of 0.14% H<sub>2</sub>O and a given energy density of 1400 J/L. It can be seen 292 293 that NH<sub>3</sub> yield also first increases and then decreases with the increase of  $H_2$ 294 content, with the highest NH<sub>3</sub> yield of 680 mg/kWh at the H<sub>2</sub> content of 40%. It is interesting to find that the presence of H<sub>2</sub>O has a promotion effect on NH<sub>3</sub> 295 synthesis from H<sub>2</sub> and N<sub>2</sub>, and the effect for the reaction gases with H<sub>2</sub> content 296 297 less than 10% is much stronger than that for the reaction gases with H<sub>2</sub> content 298 higher than 10%, which may be ascribed to the fact that H<sub>2</sub>O molecules make 299 more contribution to generate hydrogen atoms for NH<sub>3</sub> synthesis when the H<sub>2</sub> 300 content is lower than 10%.



302

303

Published on 13 October 2016. Downloaded by Cornell University Library on 16/10/2016 19:57:17.

# Fig. 13 Effect of H<sub>2</sub> content on NH<sub>3</sub> yield

(reaction gases:  $H_2+N_2$  or  $H_2O+H_2+N_2$ , f=13kHz)

As shown in Fig. 14, N<sub>2</sub>O is the main by-product when the H<sub>2</sub> content is less than 40% and it disappears for higher H<sub>2</sub> content, which is likely due to the reduction of N<sub>2</sub>O into N<sub>2</sub> by hydrogen atoms through the reaction (R12) when the H<sub>2</sub> content is enough high.

308 
$$N_2O + H \rightarrow OH + N_2$$
  $k_7 = 3.0 \times 10^{14} \exp(-16000/RT) \text{ cm}^3 \cdot \text{molecule}^{-1} \cdot \text{s}^{-1}$  (R12)



309

Fig. 14 FTIR spectra of the effluents after the DBD reactor

311 (reaction gases: 
$$0.14\%$$
 H<sub>2</sub>O + H<sub>2</sub> + N<sub>2</sub>, *ED*= 1400 J/L and *f*=11 kHz)

312 3.5 Effect of discharge frequency on NH<sub>3</sub> yield

As shown in Fig. 15, the discharge frequency has a great effect on the NH<sub>3</sub> 313 yield at a given energy density, with the maximum NH<sub>3</sub> yield of 680 mg/kWh at 13 314 kHz for reaction gases consisting of 0.14% H<sub>2</sub>O + 40% H<sub>2</sub> +N<sub>2</sub>. For discharge 315 316 frequency lower than 13 kHz, the increase of discharge frequency results in the 317 increase of the microdischarge, which is in favor of the formation of N- and 318 H-containing species and the synthesis of NH<sub>3</sub>. However, further increase of the 319 discharge frequency over 13 kHz results in the decrease of NH<sub>3</sub> yield, possibly due to the dissociation of NH<sub>3</sub> by the excessive energetic electrons. Thus, the NH<sub>3</sub> yield 320 decreases to 600 mg/kWh at 14.5 kHz. These findings are in a fairly good agreement 321 with Bai's experimental results.<sup>17</sup> 322



Fig. 15 Effect of discharge frequency on NH<sub>3</sub> yield

325 (reaction gases: 0.14% H<sub>2</sub>O +40% H<sub>2</sub>+N<sub>2</sub>, *ED*=1400 J/L)

326 **4. Reaction routes** 

Published on 13 October 2016. Downloaded by Cornell University Library on 16/10/2016 19:57:17.

327

# **RSC Advances**

Based on the results described above, we propose the reaction routes for the NH<sub>3</sub>

View Article Online DOI: 10.1039/C6RA21351K

328	synthesis and the by-products formation by a hybrid plasma-catalytic process, as
329	shown in Fig. 16. It is well known that the rate-limiting step of the NH <sub>3</sub> synthesis in
330	the conventional Haber-Bosch process is the dissociative chemisorption of $N_{\rm 2}$
331	molecules on the surface of the catalyst and the dissociation process only occurs at the
332	temperature of 400-500 $^\circ C$ due to the high binding energy of 9.6 eV of $N_2.$ In a DBD
333	reactor, atomic N (a) species can be produced on the surface of catalyst through the
334	dissociative adsorption of $N_2^*$ molecules excited by electron impacts at atmospheric
335	pressure and room temperature. Plasma discharge also generates activated hydrogen
336	species such as H atoms and $H_2^*$ molecules. Then, the $NH_3$ can be produced by
337	reactions of the N (a) atoms with H (a) atoms with the help of Ru/Al <sub>2</sub> O <sub>3</sub> . Actually,
338	this research showed that a little amount of NH3 (several mg per kWh) was detected
339	over alumina when DBD reactor is on. The presence of Ru significantly promoted the
340	production of $NH_3$ (Fig. 16 (a)).
341	Both NH <sub>3</sub> and NO <sub>2</sub> , N <sub>2</sub> O were formed from H <sub>2</sub> O and N <sub>2</sub> , because H <sub>2</sub> O is
342	dissociated to give H atoms and O, OH active species with the help of non-thermal

plasma (Fig. 16 (b)). For the reaction gas of H<sub>2</sub>O, H<sub>2</sub> and N<sub>2</sub>, only N<sub>2</sub>O, as by-product, 343

344 was detected when H<sub>2</sub> content is less than 40% and N<sub>2</sub>O also disappeared when the H<sub>2</sub> content is above 40% (Fig.16 (c)). 345

RSC Advances Accepted Manuscript



Fig. 16 Reaction routes for  $NH_3$  synthesis and by-products formation by DBD-type plasma combined with  $Ru/Al_2O_3$  catalyst under different reaction gases: (a)  $H_2 + N_2$ ;

(b)  $H_2O + N_2$ ; (c)  $H_2O + H_2 + N_2$ 

# 351 **5. Conclusions**

350

NH<sub>3</sub> can be synthesized from the reaction gases consisted of  $H_2O + N_2$ ,  $H_2$ +  $N_2$  or  $H_2O + H_2 + N_2$  by DBD-type plasma combined with catalyst at atmospheric pressure and room temperature. The largest NH<sub>3</sub> yields from  $H_2 +$ N<sub>2</sub> (640 mg/kWh) and  $H_2O + H_2 + N_2$  (680 mg/kWh) are much higher than that from  $H_2O + N_2$  (18 mg/kWh), which is attributed to the dissociation of  $H_2$ molecules into hydrogen atoms more easily than  $H_2O$  molecules.

The dissociation degrees of  $H_2O$ ,  $H_2$  and  $N_2$  enhance with increasing energy density, which results in the increase of  $NH_3$  yield. However, it is unfavorable

View Article Online DOI: 10.1039/C6RA21351K

360	for $\rm NH_3$ synthesis when the energy density is higher than 500 J/L and 1400 J/L or so
361	for the reaction gases of $H_2O$ + $H_2$ and $H_2$ + ( $H_2O$ ) + $N_2$ , respectively, because
362	discharge power is more inclined to dissociate $\mathrm{H_2O}$ and $\mathrm{H_2}$ other than $\mathrm{N_2}$ and the N/H
363	ratio is thus below the optimal value.
364	Besides $NH_3$ , some by-products such as $N_2O$ and $NO_2$ are also formed in the
365	reaction gases containing $H_2O$ . However, the formation can be suppressed in the
366	presence of $H_2$ , which is attributed to the reduction effect of $H_2$ on the by-products.
367	What's more, the by-products disappear for reaction gases containing above 40% $H_2$
368	Acknowledgments
369	The authors wish to thank Prof. A. Mizuno from the Toyohashi University of
370	Technology for valuable discussions. The authors also gratefully acknowledge the
371	financial support by the National Natural Science Foundation of China (Nos.
372	21377009 and 21547004).
373	References
374	[1] G. Busca, L. Lietti, G. Ramis, F. Berti, Appl. Catal. B Environ., 1998, 18, 1 – 36.
375	[2] W. Fan, T. Zhu, Y. Sun, D. Lv, Chemosphere. , 2014, 113, 182 – 187.
376	[3] M.T. Javed, N. Irfan, B.M. Gibbs, J. Environ. Manage. , 2007, 83, 251 – 289.
377	[4] L. Wang, H. Chen, M. Yuan, S. Rivillon, E.H. Klingenberg, X. Li, R.T. Yang, Appl.
378	Catal. B Environ. , 2014, 152, 162 – 171.
379	[5] Y. Iitsuka, H. Yamauchi, S. Sato, K. Takashima, A. Mizuno, G. Prieto, IEEE Trans.
380	Ind. Appl. , 2012, 48, 872 – 877.
381	[6] N. Saadatjou, A. Jafari, S. Sahebdelfar, Chem. Eng. Commun. , 2015, 202, 420 -
382	448.

383	[7] R. Michalsky, B.J. Parman, V. Amanor-Boadu, P.H. Pfromm, Energy. , 2012, 42,
384	251 – 260.
385	[8] S. Samukawa, M. Hori, S. Rauf, K. Tachibana, P. Bruggeman, G. Kroesen, J.C.
386	Whitehead, A.B. Murphy, A.F. Gutsol, S. Starikovskaia, J. Phys. D: Appl. Phys. , 2012,
387	45, 1 – 5.
388	[9] X. Tu, J.C. Whitehead, Appl. Catal., B, Environ. , 2012, 125, 439 – 448.
389	[10] K. Zhang, B. Eliasson, U. Kogelschatz, Ind. Eng. Chem. Res., 2002, 41, 1462 -
390	1468.
391	[11] A.K. Brewer, J.W. Westhaver, J. Phys. Chem., 1930, 34, 153 – 164.
392	[12] H. Uyama, O. Matsumoto, Plasma Chem. Plasma Process. , 1989, 9, 421 – 432.
393	[13] H. Uyama, O. Matsumoto, 1989, 9, 13 – 24.
394	[14] H. Uyama, O. Matsumoto, Plasma Chem. Plasma Process. , 1996, 16, 547 – 562.
395	[15] T. Mizushima, K. Matsumoto, J.I. Sugoh, H. Ohkita, N. Kakuta, Appl. Catal. A.,
396	2004, 265, 53 – 59.
397	[16] J. Hong, S. Prawer, A.B. Murphy, IEEE T. Plasma Sci. , 2014, 42, 2338 – 2339.
398	[17] M. Bai, Z. Zhang, X. Bai, M. Bai, W. Ning, IEEE T. Plasma Sci. , 2003, 31, 1285
399	- 1291.

- 400 [18] M. Bai, X. Bai, Z. Zhang, M. Bai, Plasma Chem. Plasma Process. , 2000, 20, 511
  401 520.
- 402 [19] T. Mizushima, K. Matsumoto, H. Ohkita, N. Kakuta, Plasma Chem. Plasma
  403 Process., 2007, 27, 1 11.
- 404 [20] J.H. van Helden, W. Wagemans, G. Yagci, R.A.B. Zijlmans, D.C. Schram, R.

Published on 13 October 2016. Downloaded by Cornell University Library on 16/10/2016 19:57:17.

- 405 Engeln, G. Lombardi, G.D. Stancu, J. Appl. Phys., 2007, 101, 101 112.
- 406 [21] K. Sugiyama, K. Akazawa, M. Oshima, H. Miura, T. Matsuda, O. Nomura,
- 407 Plasma Chem. Plasma Process. , 1986, 6, 179 193.
- 408 [22] W. Rarog, Z. Kowalczyk, J. Sentek, D. Skladanowski, J. Zielinski, Chem. Lett.,
- 409 2000, 68, 163 168.
- 410 [23] GB/T 14668-93. Air quality-Determination of ammonia-Nessler's reagent
- 411 colorimetric method.
- 412 [24] F. Sen, G. Gokagac, Energy Fuel, 2008, 22, 1858 1864.
- 413 [25] A. Fridman. in Plasma Chemistry, Cambridge University, New York, 2008,
- 414 Chapter 2, 33.
- 415 [26] J. Kikuchi, S. Fujimura, M. Suzuki, H. Yano, Jpn. J. Appl. Phys., 1993, 32, 70 –
  416 76.
- 417 [27] J. Nakajima, H. Sekiguchi, Thin Solid Films. , 2008, 516, 4446 4451.

**RSC Advances Accepted Manuscript** 



Reaction routes for NH<sub>3</sub> synthesis and by-products formation by DBD-type plasma combined with  $Ru/Al_2O_3$  catalyst under different reaction gases: (a)  $H_2 + N_2$ ; (b)  $H_2O + N_2$ ; (c)  $H_2O + H_2 + N_2$