## **Supplementary Information**

# NH<sub>3</sub> decomposition for H<sub>2</sub> production by thermal and plasma catalysis using bimetallic catalysts

Shengyan Meng<sup>a</sup>, Shangkun Li<sup>a</sup>, Shuaiqi Sun<sup>a</sup>, Annemie Bogaerts<sup>b</sup>, Yi Liu<sup>a</sup>\*, Yanhui Yi<sup>a</sup>\*

<sup>a</sup> State Key Laboratory of Fine Chemicals, School of Chemical Engineering, Dalian University of

Technology, Dalian 116024, Liaoning, China.

<sup>b</sup> Research group PLASMANT, Department of Chemistry, University of Antwerp, Universiteitsplein 1,

BE-2610 Wilrijk-Antwerp, Belgium.

\* Corresponding author: Prof. Dr. Yi Liu, Prof. Dr. Yanhui Yi

E-mail address: <u>diligenliu@dlut.edu.cn</u>, <u>yiyanhui@dlut.edu.cn</u>

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# 1. Summary of the catalysts and performance

**Table S1** Summary of the catalysts and performance of thermal catalysis and plasma catalysis for ammonia decomposition.

Catalyst	Temperature (°C)	Conversion (%)	$H_2$ production rate (mmol g <sup>-1</sup> s <sup>-1</sup> )
Ru/SiO <sub>2</sub> <sup>1</sup>	450	36	0.19
Ru/TiO <sub>2</sub> <sup>2</sup>	500	12	0.32
$Ru/ZrO_2^3$	500	86	—
Ni@SiO <sub>2</sub> <sup>4</sup>	600	87	0.49
Ni/Al <sub>2</sub> O <sub>3</sub> <sup>5</sup>	450	15	0.08
Ni/BaTiO <sub>3</sub> <sup>6</sup>	550	75	—
Ni/CeO <sub>2</sub> <sup>7</sup>	400	13	—
Ni/SBA-15 <sup>8</sup>	550	89	0.5
Ni/ZSM-5 <sup>9</sup>	650	98	0.55
Fe@SiO <sub>2</sub> <sup>10</sup>	450	8	0.5
Fe/Al <sub>2</sub> O <sub>3</sub> <sup>11</sup>	500	25	_
Fe/SBA-15 <sup>12</sup>	550	18	_
Co@SiO <sub>2</sub> <sup>13</sup>	450	4	
Co/Al <sub>2</sub> O <sub>3</sub> <sup>14</sup>	500	44	0.9
Co/MgO-Al <sub>2</sub> O <sub>3</sub> <sup>15</sup>	550	32	
Mo/Al <sub>2</sub> O <sub>3</sub> <sup>16</sup>	500	22	
Mo/C <sup>17</sup>	600	66	
Mo <sub>2</sub> N <sup>18</sup>	550	94	0.4
Mo <sub>2</sub> N <sup>19</sup>	550	69	
MoS <sub>2</sub> /laponite <sup>20</sup>	600	35	0.16
Fe <sub>3</sub> C <sup>21</sup>	550	23	
Co-Mo/MCM-41 <sup>22</sup>	500	52	—
Fe-Mo/CeO <sub>2</sub> -ZeO <sub>2</sub> <sup>23</sup>	550	16	
Fe-Ni/TiO <sub>2</sub> <sup>24</sup>	500	9	
NiMoN <sup>25</sup>	650	100	
Fe-Ni/SiO <sub>2</sub> (this work)	460	60	0.16

#### 2. Experimental

#### 1.1 Catalysts Preparation

The monometallic catalysts (Fe, Co, Ni and Mo), bimetallic catalysts (Fe-Co, Mo-Co, Fe-Ni and Mo-Ni) with 5:5 metal molar ratio, and the Fe-Co bimetallic catalysts with varying Fe/Co molar ratios were prepared using the incipient-wetness impregnation method, with fumed SiO<sub>2</sub> as the support. Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O, Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O and (NH<sub>4</sub>)<sub>2</sub>MoO<sub>4</sub> were used as the precursors of Fe, Ni, Co and Mo, respectively. Before the incipient-wetness impregnation, the fumed SiO<sub>2</sub> support was calcined at 500 °C for 3 hours to remove adsorbed molecules (mainly H<sub>2</sub>O and CO<sub>2</sub>). Subsequently, metal component solution was prepared according to 10 wt.% loading (metal content) and water adsorption capacity of fumed SiO<sub>2</sub>, before being mixed with the fumed SiO<sub>2</sub> support. The wet samples were standing for 8 hours before being dried in an oven at 120 °C overnight. Next, the dried sample was calcined in a furnace at 540 °C for 5 hours under an air atmosphere. Before the plasma catalytic NH<sub>3</sub> decomposition reaction, the calcined samples were pressed and sieved to obtain particles with diameter of 20-40 mesh. Prior to catalytic tests, the samples are reduced in a pure ammonia flow (50 mL/min NH<sub>3</sub>) at 500 °C for 1 h.

The mixture of Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O (12.12 g) and Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (2.908 g) with an Fe/Ni molar ratio of 3/1 was dissolved in 90 g of deionized water. Then, 10 ml of ammonia solution (25%) was added dropwise to obtain a precipitate product. The precursor solution was aged in a beaker at 90 °C in a water bath for 2 hours, followed by washing until the pH was below 8. The resulting solid product was then dried in an oven at 110 °C for 12 hours before being calcined for 5 hours to obtain NiFe<sub>2</sub>O<sub>4</sub>. The catalyst was nitrided under a pure ammonia flow, raising the temperature to 700 °C at a rate of 5 °C/min and maintaining it for 2 hours. After cooling to room temperature, the catalyst is passivated with 1% O<sub>2</sub>/He at room temperature for 2 hours.

#### 1.2 Activity Test

As shown in Figure S1, the hybrid plasma catalytic NH<sub>3</sub> decomposition was operated in a dielectric barrier discharge (DBD) reactor. The DBD reactor consisted of a glass cylinder and two coaxial electrodes. The cylinder was made of quartz glass with an inner diameter (id) of 8 mm and an outer diameter (od) of 10 mm. The quartz glass wall of the cylinder served as the dielectric barrier. A stainless-steel rod was used as the high-voltage electrode (HVE), and it was installed along the axis of the glass cylinder and connected to the AC plasma power supply (High performance plasma generators CTP-2000K). An aluminum foil, tightly wrapped on the outside of the quartz cylinder, was used as the ground

electrode (GE), and a thermocouple was connected with the GE to monitor the temperature of the reactor wall. The temperature of the catalyst bed was calibrated by FLIR equipment. A cylindrical discharge space with a length of 50 mm and a volume of 2.36 ml was formed between the HVE and GE. Before igniting the DBD, the NH<sub>3</sub> gas flowed through the discharge space for about 10 minutes, to make sure that air was pushed out of the reactor (for safety reasons).



Figure S1. Schematic diagram of the experimental setup for the plasma catalytic NH<sub>3</sub> decomposition

The reactor was set in a tube furnace. In the case of pure plasma-driven NH<sub>3</sub> decomposition and plasma catalytic NH<sub>3</sub> decomposition, the voltage of the HVE was adjusted by the AC plasma power supply to initiate the DBD discharge. The discharge voltage, discharge current and input power were monitored on site by a digital oscilloscope (Tektronix DPO 3012) with a HV probe (Tektronix P6015A) and a current probe (Pearson 6585). The temperature of the reactor wall was in-site monitored by the thermocouple, and the temperature of the catalyst bed was calibrated using FLIR equipment (Figure S2-S3). In the case of thermal catalytic NH<sub>3</sub> decomposition, the reaction temperature was adjusted by the tube furnace, and it was recorded by a thermocouple too. The exhaust gas was analyzed using an on-line gas chromatograph (GC) equipped with a TCD detector. The NH<sub>3</sub> conversion was measured using an external standard method. During the reaction process, only H<sub>2</sub> and N<sub>2</sub> were produced, corresponding to a 100% mass balance.



Figure S2. FLIR results of plasma catalytic NH<sub>3</sub> decomposition packed by a catalyst. (A) FLIR image;





**Figure S3**. FLIR results of thermal catalytic NH<sub>3</sub> decomposition (heated by furnace) packed by a catalyst. (A) FLIR image; (B) temperature profiles.

The NH<sub>3</sub> conversion ( $X_{NH3}$ ) is defined as equation 1, in which  $C_{NH3}$  is the moles of NH<sub>3</sub> converted (measured by the GC), and  $I_{NH3}$  is the moles of the inputted NH<sub>3</sub>. The synergistic capacity between a catalyst and a DBD plasma (Q) is defined as equation 2, in which  $X_{NH3(p-c)}$ ,  $X_{NH3(p)}$  and  $X_{NH3(c)}$  correspond to the NH<sub>3</sub> conversion in the case of "plasma + catalyst", "plasma alone" and "catalyst alone", respectively.

#### **1.3 Catalyst Characterization**

The powder XRD patterns of the samples were collected using an X-ray diffractometer (XRD, Rigaku, D-max 2400) with Cu Ka radiation. The measurement was operated at 100 mA and 40 kV, with a scanning rate of 10°/min in the range of 5-80°. The exact metal loadings were measured using an X-ray fluorescence (XRF, SRS-3400, Germany, 40 kW), which was operated at 60 kV and 150 mA. The H<sub>2</sub>temperature programmed reduction (H<sub>2</sub>-TPR) was performed on a Quanta chrome ChemBET Pulsar Chemisorption instrument. Before the analysis, the samples (0.20 g) were pretreated with He from ambient temperature to 150 °C, and kept at 150 °C for 60 minutes. Afterward, the samples were cooled to 50 °C in He atmosphere. Finally, the H<sub>2</sub>-TPR was carried out in a flow of H<sub>2</sub>/Ar mixture (120 ml/min, 10% H<sub>2</sub>) from 100 °C to 1000 °C at a heating rate of 10 °C/min. X-ray photoelectron spectroscopy (XPS) was conducted by Thermo Fisher ESCALAB XI<sup>+</sup> with Al Ka X-ray source. The C 1s binding energy value (284.8 eV) was taken as a reference level to calibrate binding energy. The morphology and particle size of the catalysts were examined with high resolution transmission electron microscopy (HRTEM, FEI, TF-30 device) and high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM), while energy dispersive X-ray (EDX) spectrometry was used to analyze the chemical composition of the catalysts, applying 300 kV operating voltage. The specific surface area, total pore volume, and pore diameter of the samples were measured using a nitrogen adsorption-desorption technique (Micromeritics, TriStar II physical adsorption) at -196 °C. Before the measurement, the samples (0.1500g) were degassed at 350 °C for 4 h. The specific surface area of the samples was calculated based on the BET approach. The total pore volume of the samples was measured at a relative pressure (P/P<sub>0</sub>) of 0.98. The ammonia temperature programmed desorption (NH<sub>3</sub>-TPD) of the spent catalysts were carried out using a ChemBET Pulsar Chemical Adsorbent (Quantachrome, USA), to characterize the acidity and NH<sub>3</sub>-adsorption-desorption property. About 0.1 g sample was treated in a He atmosphere from 40 °C to 600 °C at a heating rate of 20 °C/min, and was maintained at 600 °C for 30 min; after cooling to 100 °C, plenty of NH<sub>3</sub> was supplied for saturated adsorption on the surface of the spent sample; then, the sample was purged by He at 100 °C for 90 min to eliminate physically adsorbed NH<sub>3</sub>; at last, NH<sub>3</sub> desorption was examined in a He atmosphere from 100 °C to 600 °C at a heating rate of 20 °C/min, and a thermal conductivity cell detector was used to detect NH<sub>3</sub> desorption. The exhaust gas of NH<sub>3</sub>-TPD was collected using two tandem absorption flask, in which deionized water was placed to dissolve NH<sub>3</sub> desorbed from the surface of the catalysts. After that, the ammonia solution was titrated using standard hydrochloric acid solution (0.001 mol/l), and the consumption of hydrochloric acid was

used to estimate the quantity of the active sites for NH<sub>3</sub> chemisorption.

#### **1.4 Plasma Diagnostics**

The NH<sub>3</sub> plasmas (in the presence and absence of catalysts) were diagnosed using optical emission spectra (OES). The OES were collected by an ICCD spectrometer (Princeton Instruments SP 2758) in the range of 300-800 nm, using a 300 G/mm grating in the monochromator. The light emitted by the NH<sub>3</sub> 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 near the inlet of the feed gas (Figure S1), since the light emitted from other regions in the plasma was influenced by the NH<sub>3</sub> conversion (i.e., different gas composition yields different OES intensities). The distance between the head of the lens and the upper edge of the NH<sub>3</sub> plasma was fixed at ca. 4 cm. During the OES analysis, a 50 µm slit width of the spectrometer and 5 s exposure time was used.

# 3. Results of activity test

Table S2  $NH_3$  conversion and parameters in the case of "plasma alone", "catalyst alone" and "plasma

Plasma alone		Catalyst alor		st alone	Plasma + catalyst			Synergistic
P (w)	X <sub>NH3</sub> (%)	Catalyst	T (°C)	X <sub>NH3</sub> (%)	T (°C)	P (w)	X <sub>NH3</sub> (%)	capacity (%)
29.3	3.9		360	0.5	360	29.3	7.6	3.2
34.2	8.4	_	405	2.2	405	34.2	16.7	6.1
38.5	11.4	Fe	440	7.1	440	38.5	28.5	10.0
41.0	14.4		460	9.9	460	41.0	37.6	13.3
30.0	4.7		368	2.3	368	30.0	11.2	4.2
35.9	10.2		420	6.0	420	35.9	24.8	8.6
38.5	11.4	Со	440	13.2	440	38.5	35.9	11.3
41.0	14.4		460	18.6	460	41.0	49.4	16.4
29.3	3.9		360	2.0	360	29.3	7.0	1.1
32.7	7.2		392	2.8	392	32.7	12.1	2.1
38.5	11.4	N1	440	9.4	440	38.5	24.8	4.0
41.0	14.4		460	16.3	460	41.0	35.1	4.4
29.3	3.9		360	1.0	360	29.3	6.0	1.1
32.7	7.2		392	2.8	392	32.7	12.6	2.6
38.5	11.4	Мо	440	10.6	440	38.5	25.7	3.7
41.0	14.4		460	14.3	460	41.0	33.2	4.5
27.8	2.4		345	4.1	345	27.8	8.5	2.0
32.2	6.7	E G	388	8.6	388	32.2	18.5	3.2
38.3	11.4	Fe-Co	439	15.9	439	38.3	33.6	6.3
41.0	14.4		460	21.5	460	41.0	43.5	8.7
27.3	1.9		340	2.1	340	27.3	7.2	3.2
32.0	6.5	N. G	386	3.1	386	32.0	15.2	5.6
37.7	11.1	Mo-Co	434	8.9	434	37.7	30.1	10.1
41.0	14.4		460	13.4	460	41.0	41.3	13.6
28.1	2.7		348	2.7	348	28.1	11.8	6.4
33.3	7.6		397	3.1	397	33.3	27.4	16.7
39.1	12.2	Fe-Ni	445	11.8	445	39.1	50.3	26.3
41.0	14.4		460	13.7	460	41.0	59.6	31.5
27.8	2.4		345	2.0	345	27.8	6.9	2.5
32.6	7.0	M N	391	2.7	391	32.6	14.1	4.4
38.3	11.4	Mo-N1	439	10.1	439	38.3	27.8	6.3
41.0	14.4		460	14.0	460	41.0	35.5	8.2

+ catalyst".

### 4. XRD results



Figure S4. XRD patterns of 10Mo, 10Co and 5Mo-5Co catalysts. (A) fresh and (B) spent catalysts.



Figure S5. XRD patterns of 10Mo, 10Ni and 5Mo-5Ni catalysts. (A) fresh and (B) spent catalysts.



Figure S6. XRD patterns of 10Fe, 10Co and 5Fe-5Co catalysts. (A) fresh and (B) spent catalysts.



Figure S7. XRD patterns of the 10Fe, 10Ni and 5Fe-5Ni catalysts. (A) fresh and (B) spent catalysts.



Figure S8. XRD patterns of Fe-Co bimetallic catalysts with varying Fe/Co ratio. (A) fresh and (B)

spent catalysts.

### 5. XRF results

Catalysts	Fe <sub>2</sub> O <sub>3</sub>	Co <sub>3</sub> O <sub>4</sub>	NiO	MoO <sub>3</sub>
10Fe	13.4%	-	-	-
10Co	-	12.6%	-	-
10Ni	-	-	12.6%	-
10Mo	-	-	-	13.8%
5Fe-5Co	6.4%	6.4%	-	-
5Mo-5Co	-	5.0%	-	9.0%
5Fe-5Ni	6.7%	-	6.3%	-
5Mo-5Ni	-	-	4.5%	8.6%

**Table S3.** X-ray fluorescence (XRF) analysis of fresh 10Fe, 10Co, 10Ni, 10Mo, 5Fe-5Co, 5Mo-5Co,5Fe-5Ni and 5Mo-5Ni catalysts (metal oxide weight percentage content).

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

**Table S4**. X-ray fluorescence (XRF) analysis of fresh 10Fe, 10Co, 10Ni, 10Mo, 5Fe-5Co, 5Mo-5Co,5Fe-5Ni and 5Mo-5Ni catalysts (metal weight percentage content calculated by the data from Table

S2).

Catalysts	Fe	Co	Ni	Мо
10Fe	9.8%	-	-	-
10Co	-	9.5%	-	-
10Ni	-	-	10.1%	-
10Mo	-	-	-	9.7%
5Fe-5Co	4.6%	4.8%	-	-
5Mo-5Co	-	3.8%	-	6.2%
5Fe-5Ni	4.8%	-	5.1%	-
5Mo-5Ni	-	-	3.6%	5.9%

Со
-
2.8%
3.9%
5.4%
7.6%
0.3%
2.6%

Table S5. X-ray fluorescence (XRF) analysis of fresh Fe-Co bimetallic catalysts

(Metal oxide weight percentage content).

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

Table S6. X-ray fluorescence (XRF) analysis of fresh Fe-Co bimetallic catalysts

Catalysts	Fe	Co
10Fe	9.8%	-
8Fe-2Co	8.0%	2.1%
7Fe-3Co	6.7%	3.0%
5Fe-5Co	4.6%	4.9%
4Fe-6Co	3.9%	5.8%
2Fe-8Co	1.9%	7.9%
10Co	-	9.6%

(Metal weight percentage content calculated by the data from Table S5).

# 6. HRTEM results



Figure S9. HRTEM images of Fe, Co, Ni, Mo, Fe-Co, Mo-Co, Fe-Ni and Mo-Ni catalysts.



**Figure S10** Particle size distribution of the catalysts derived from HRTEM images. (A) 10Fe; (B) 10Co; (C) 10Ni; (D) 10Mo; (E) 5Fe-5Co; (F) 5Mo-5Co; (G) 5Fe-5Ni; (H) 5Mo-5Ni.

### 7. HAADF-STEM results



Figure S11. HAADF-STEM and EDX line scanning results of the Fe-Co catalysts.



Figure S12. HAADF-STEM and EDX line scanning results of the Fe-Ni catalysts.



Figure S13. HAADF-STEM and EDX-Mapping images of the fresh Mo-Ni catalysts.



Figure S14. HAADF-STEM and EDX-Mapping images of the fresh Mo-Ni catalysts.

### 8. N<sub>2</sub>-physisorption results

Samples	$S_{BET} (m^2/g)^a$	Pore Volume (cm <sup>3</sup> /g) <sup>b</sup>	Pore Diameter (nm)
SiO <sub>2</sub>	211.4	0.69	11.3
Fe/SiO <sub>2</sub>	169.9	0.51	11.9
Co/SiO <sub>2</sub>	164.6	0.52	12.5
Ni/SiO <sub>2</sub>	168.7	0.52	12.3
Mo/SiO <sub>2</sub>	168.1	0.52	12.4
Fe-Co/SiO <sub>2</sub>	175.5	0.65	15.4
Mo-Co/SiO <sub>2</sub>	173.3	0.59	14.6
Fe-Ni/SiO <sub>2</sub>	182.6	0.60	13.5
Mo-Ni/SiO <sub>2</sub>	173.6	0.64	15.1

Table S7. BET surface area, pore volume and average pore diameter of the SiO<sub>2</sub> support and the catalysts.

<sup>a</sup> The BET surface area was calculated from the adsorption branch of the  $N_2$  adsorption-desorption isotherm. <sup>b</sup> The pore volume was calculated from the adsorption branch of the  $N_2$  adsorption-desorption isotherm at a relative pressure of 0.98.

**Table S8**. BET surface area, pore volume and average pore diameter of the SiO<sub>2</sub> support and Fe-Co/SiO<sub>2</sub> catalysts with varying Fe/Co ratio.

	$S_{BET} (m^2/g)$	Pore Volume (cm <sup>3</sup> /g)	Pore diameter (nm)
SiO <sub>2</sub>	211.4	0.69	11.3
10Fe/SiO <sub>2</sub>	169.9	0.51	11.9
7Fe-3Co/SiO <sub>2</sub>	173.3	0.59	14.6
5Fe-5Co/SiO <sub>2</sub>	175.5	0.65	15.4
4Fe-6Co/SiO <sub>2</sub>	173.6	0.64	15.1
2Fe-8Co/SiO <sub>2</sub>	168.1	0.58	13.7
10Co/SiO <sub>2</sub>	164.6	0.52	12.5

# 9. MS signal of H<sub>2</sub> during TPSR



Figure S15. MS signal of H<sub>2</sub> during the TPSR experiments.

### 10. OES diagnostics results



Figure S16. OES of NH<sub>3</sub> plasma in the absence of the catalyst (NH<sub>3</sub> feed rate 120 ml/min, discharge gap 3mm, discharge frequency 10kHz).



Figure S17. OES of NH<sub>3</sub> plasma in the presence of the catalyst. The other conditions are the same as in Figure S16.

11. In comparison to Fe<sub>3</sub>NiN catalyst



Figure S18. XRD patterns of (A) NiFe<sub>2</sub>O<sub>4</sub> and (B) Fe<sub>3</sub>NiN catalyst <sup>24</sup>.



**Figure S19**. The Fe-Ni/SiO<sub>2</sub> and Fe<sub>3</sub>NiN catalysts for (A) Results of plasma catalytic NH<sub>3</sub> decomposition; (B) NH<sub>3</sub>-TPD profiles; (C) NH<sub>3</sub> chemisorption active site numbers and TOF.



Figure S20. Relative dielectric constants of Fe-Ni/SiO<sub>2</sub> and Fe<sub>3</sub>NiN catalysts.

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