Plasma-catalytic ammonia synthesis: Packed catalysts act as plasma modifiers

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Table S1: A summary of studies on NH_3 production from N_2 and H_2 in dielectric barrier discharge (DBD) plasma reactors, as well as comparison with our work. The catalysts, experimental details, and the calculated values of NH_3 yield and production rate correspond to the lowest energy consumption (EC) reported in the respective publications. This table was adapted from [1].

| Ref | Catalyst | T (°C) | Plasma power (W) | H2:N2 ratio | EC (MJ/mol) | NH3 yield (%) | NH3 production rate (mg/h) |
|------|--|--------|------------------------|----------------|----------------|---------------------|----------------------------------|
| [2] | Ru/Al ₂ O ₃ | 20 | 127 | 3:1 | 244 | 2.4 | 16 |
| [3] | Cu | n/a† | n/a | 1:1 | 19 | 1.4 | 71 |
| [4] | DLC- coated Al ₂ O ₃ | 160 | 70 | 3:1 | 350 | n/a | 12 |
| [5] | PZT | 60 | n/a | 3:1 | 94 | 7 | 34 |
| [6] | Ru-Cs-K- Ba/ /Si-MCM- 41 | 150 | n/a | 1:1 | 36 | <0.1 | n/a |
| [7] | RuO- MgO/Al ₂ O ₃ | 300 | 4 | 1:4 | 2 | <0.1 | 113 |
| [8] | Ni/SiO ₂ + BaTiO ₃ | 140 | 87 | 3:1 | 81 | 12.0 | 32 |
| [9] | Au | n/a | 100 | 1:1 | 79 | 2.5 | 77 |
| [10] | Co/Al ₂ O ₃ | 200 | 10 | 2:1 | 36 | 1.0 | 17 |
| [11] | Ni/Al ₂ O ₃ | 35 | 10 | 2:1 | 56 | 0.7 | 10 |
| [12] | Co/Al ₂ O ₃ | 200 | 10 | 1:3 | 102 | 0.1 | 6 |
| [13] | Ru/Al ₂ O ₃ | 118 | 38 | 1:2 | 32 | 1.1 | 76 |
| [14] | Ru/MgO | 200 | 26 | 1:2 | 47 | 0.1 | 25 |
| [15] | alkaline Al ₂ O ₃ | >105 | 24 | 3:1 | 9 | <0.1 | 159 |

⁺ Not available: the data were missing, and the absence of the needed experimental data did not allow us to calculate the numerical values.

| [16] | Rh/Al ₂ O ₃ | 300 | n/a | 1:2 | 65 | 1.1 | 29 |
|--------------|--|------|-----|-----|----|-----|----|
| [17] | Ru/AC | n/a | 13 | 3:1 | 85 | 0.5 | 10 |
| [18] | Ru-K/MgO | 390 | 4 | 1:1 | 46 | 0.6 | 5 |
| [1] | Co/Al ₂ O ₃ | <120 | 67 | 1:1 | 99 | 1.0 | 42 |
| [19] | Co- Ni/Al ₂ O ₃ | 200 | 31 | 1:1 | 37 | 0.6 | 51 |
| [20] | Ru/AC | 110 | 9 | 1:1 | 96 | 0.3 | 6 |
| [21] | Zeolite 4A | 57 | 6.4 | 1:2 | 27 | 2.6 | 15 |
| [22] | Ni/MCM- 41 | 35 | 40 | 3:1 | 51 | 5.3 | 48 |
| This work | CoLa/Al ₂ O ₃ | <120 | 51 | 1:1 | 77 | 0.9 | 41 |

Non-dispersive infrared sensor (NDIR)

In this study a non-dispersive infrared sensor is used to determine the NH₃ concentration at the outlet of the DBD reactor. The NDIR was calibrated by measuring various concentrations of NH₃ diluted with helium. Plotting these values (Figure S1) generates the calibration equation:

 $2.10^{\text{-}10}\,{\rm C_{shown}}^3 - 3.10^{\text{-}6}\,{\rm C_{shown}}^2 + 0.9033\,\,{\rm C_{shown}} = {\rm C_{real}}$



Figure S1: Measured NH_3 concentration versus the actual NH_3 concentration during the NDIR calibration.

S2 Capacitances obtained from Lissajous figure

Various information can be obtained from Lissajous figures but in this section we focus on capacitances. Figure S2 shows an ideal Lissajous figure with characteristic parallelogram shape. Line AB and DC represent the two "plasma off" phases. During the plasma off phase no plasma is formed and the DBD reactor behaves as two capacitors in series namely the dielectric layer (C_{diel}) and the discharge gap (C_{gap}).[23] C_{diel} and C_{gap} are related to the overall DBD cell capacitance (C_{cell}) in the following way:

$$\frac{1}{C_{cell}} = \frac{1}{C_{diel}} + \frac{1}{C_{gap}}$$

S1

On the other hand, lines BC and DA represent the "plasma on" phase when the plasma is formed inside the discharge gap. The slope indicates the effective capacity (C_{eff}) of the DBD reactor.[24] In a plane-parallel DBD plasma reactor, the discharge gap is uniformly spaced and therefore the ignition voltage across the gap will be roughly constant. In this case C_{eff} is equal to C_{diel} . However, when the discharge gap is filled with catalysts, the plasma ignites over a range of gap voltages and as a result lines BC and DA will not be



Figure S2: The ideal Lissajous figure with parallelogram shape.

a straight lines anymore, as shown in Figure 5. In this case C_{eff} is only equal to C_{diel} at the maximum observed slope.[23]

S3 Raman spectroscopy

The Raman spectra were recorded on a Horiba XploRA Plus Raman spectrometer equipped with a diodepumped solid-state laser of 532 nm and a power of 25 mW. The samples were measured with an acquisition time of 10 s, 10 accumulations and in a spectral range of 100-2000 cm⁻¹. The spectra were acquired in two different spots on two different beads, in order to verify the homogeneity of the catalysts.



Figure S3: Raman spectra of the fresh Co/Al₂O₃, CoCe/Al₂O₃, CoCeLa/Al₂O₃ and CoLa/Al₂O₃ catalysts.

All samples show Raman modes around similar shifts: ~190, ~477, ~520, ~622 and ~685 cm⁻¹. These modes are in good agreement with the values of pure Co₃O₄ spinel structure. For pure Co₃O₄ spinel structure with Co²⁺ and Co³⁺ located in the tetrahedral and octahedral sites, the space group theory predicts five Raman-active modes: A_{1g}, E_g and three F_{2g} modes.[25, 26] The A_{1g} band (~685 cm⁻¹) can be attributed to characteristics of the octahedral sites.[25-27] In addition, there is a general agreement that the E_g (~477 cm⁻¹) and F_{2g} (~190, ~520 and ~622 cm⁻¹) modes are related to the combined vibrations of the tetrahedral site and octahedral oxygen motions.[25, 27, 28] . Further, spent CoCeMg/Al₂O₃ and fresh and spent CoCeLa/Al₂O₃ all show a shoulder at ca. ~440 cm⁻¹, which could be attributed to the cubic fluorite structure of ceria (CeO₂) and/or to La₂O₃ in case of CoCeLa/Al₂O₃. The F_{2g} symmetry is the only Raman active mode of CeO₂[29] and is related to symmetrical stretch vibrations in the [CeO₈] cubic subunit of the CeO₂ structure.[30] In addition, fresh and spent CoLa/Al₂O₃ both show a shoulder around 445 cm⁻¹ which could be assigned to La₂O₃. The E_g mode of La₂O₃ is correlated to the La-O stretching vibration, while the A_{1g} mode of La₂O₃ is ascribed to the La-O bending vibration.[31]

| Sample | | F _{2g} (Co ₃ O ₄ (cm ⁻¹) | ı) | Eg (C03O4) cm ⁻¹ | A _{1g} (Co ₃ O ₄) (cm ⁻¹) | F _{2g} (CeO ₂) (cm ⁻¹) | E _g (La ₂ O ₃) (cm ⁻¹) | A _{1g} (La ₂ O ₃) (cm ⁻¹) |
|---------------------------------------|-----|---|-----|-----------------------------------|---|---|--|---|
| Co/Al ₂ O ₃ | 202 | 523 | 637 | 489 | 703 | - | - | - |
| CoCe/Al ₂ O ₃ | 180 | 523 | 605 | 480 | 680 | - | - | - |
| CoCeLa/Al ₂ O ₃ | 193 | 523 | 616 | 474 | 698 | 447 | 459 | 193 |
| CoLa/Al ₂ O ₃ | 196 | 523 | 604 | 444 | 665 | - | 447 | 196 |
| CoCeMg/Al ₂ O ₃ | 184 | 511 | 604 | 459 | 664 | 432 | - | - |

 $\label{eq:constraint} \textbf{Table S2:} Peak values of the Raman spectra of fresh Co/Al_2O_3, CoCe/Al_2O_3, CoLa/Al_2O_3, CoCeLa/Al_2O_3 and CoCeMg/Al_2O_3.$

S4 SEM – EDX



Figure S4: SEM image of (A) Co/Al₂O₃, (B) CoCe/Al₂O₃, (C) CoCeMg/Al₂O₃, (D) CoCeLa/Al₂O₃ and (E) CoLa/Al₂O₃. (F) Shows the elemental EDX map for Co on top of image (A). The brighter pixels indicate a higher Co concentration. As is confirmed by the radial distribution, the Co sample displays a Co-rich area at the edge of the bead. As indicated in (F), a circle is fitted to the edge of the bead, so the distance from the center can be determined for every pixel, as indicated by the red arrow. This results in the radial distribution for the various elements. The images were acquired in backscattered electron mode which is sensitive to local variations in the composition (average atomic number).



Figure S5: Metal content as a function of distance from the center of the bead for (A) Co/Al_2O_3 , (B) $CoCe/Al_2O_3$, (C) $CoCeMg/Al_2O_3$, (D) $CoCeLa/Al_2O_3$ and (E) $CoLa/Al_2O_3$. From this plot it is clear that most of the metals are present on the outermost micrometers of the bead (except for $CoCeLa/Al_2O_3$), which is beneficial for the plasma-catalytic synthesis of NH₃, as more active sites will be exposed to the plasma. Furthermore, this can alter the conductivity of the packing material, which affects the plasma discharge.



Figure S6: EDX map of the cross-section of a Co/Al₂O₃ bead.



Figure S7: EDX map of the cross-section of a $CoCe/Al_2O_3$ bead.



Figure S8: EDX map of the cross-section of a CoCeMg/Al₂O₃ bead.



Figure S9: EDX map of the cross-section of a CoCeLa/Al₂O₃ bead.



Figure S10: EDX map of the cross-section of a CoLa/Al₂O₃ bead.

S5 N₂ sorption

All the isotherms can be classified as type IV(a) in the IUPAC classification of physisorption isotherms, which are typical for mesoporous materials.[32]



Figure S11: Physisorption isotherms of fresh and/or spent catalysts and pristine Al₂O₃.

S6 NH₃-TPD

The NH₃-TPD revealed information on the acidity of spent Al₂O₃, Co/Al₂O₃ and CoLa/Al₂O₃. These three samples were chosen because Al_2O_3 is used as a support for all catalysts, and out of all catalysts CoLa/Al₂O₃ showed the best results, while Co/Al₂O₃ performed in-between the two, see Figure 4 and Figure S15. In the weak acid site region (120-300°C)[11, 33], Al₂O₃ shows a desorption peak at 236 °C, while Co/Al₂O₃ and CoLa/Al₂O₃ both show a desorption peak at 222 °C, shown in Figure S12. Interestingly, the temperature of desorption decreased for the transition metal catalysts compared to Al₂O₃, indicating that the strength of the acid sites reduced. Weak acid sites, as opposed to medium or strong acid sites, can facilitate the desorption of the end product, which is beneficial for the production rate of the catalyst.[34] Moreover, in the medium/strong acid region[11, 33], Al₂O₃ and CoLa/Al₂O₃ show a desorption peak at 576 °C and 526 °C, respectively. The mass spectrometer however revealed that these peaks are not due to the desorption of NH₃ (m/z= 17), but due to water evolution (m/z=18), see Figure S13. It is possible that hydroxyl groups on the surface of the catalyst desorb in the form of water. Indeed, a slight increase in the signal of m/z=16 is visible at the same time of the water evolution, which could be attributed to the desorption of hydroxyl groups. A similar phenomenon with Al₂O₃-supported catalysts was observed by Lin et al. [35] Lastly, the amount of ammonia adsorbed on the acid sites, shown in Table S3, demonstrates that impregnating the support with metals reduces the number of available acid sites.[11] Taken together with the data in Table S3, we can conclude both catalysts show similar affinity for ammonia.



Figure S12: NH₃-TPD profiles of spent Al₂O₃, Co/Al₂O₃ and CoLa/Al₂O₃.



Figure S13: The MS Signal a function of time during the NH₃ TPD analysis of (a) Al₂O₃ and (b) CoLa/Al₂O₃.

| Catalyst | Amount of adorsbed NH₃ on the acid sites (μmol/g) |
|-------------------------------------|---|
| Al ₂ O ₃ | 257 |
| Co/Al ₂ O ₃ | 158 |
| CoLa/Al ₂ O ₃ | 150 |

| Table | S3: | Surface | acidity | of Al ₂ O ₃ , | Co/ | Al ₂ O ₃ and | CoLa Al ₂ O ₃ . |
|-------|-----|---------|---------|-------------------------------------|-----|------------------------------------|---------------------------------------|
|-------|-----|---------|---------|-------------------------------------|-----|------------------------------------|---------------------------------------|



S7 Plasma-catalytic performance

Figure S14: (A) NH_3 concentration, (B) production rate, (C) energy consumption and (D) specific energy input, as a function of the gas flow rate for an empty reactor and a reactor packed with Al_2O_3 and the Co-based catalysts at a 1:1 $H_2:N_2$ ratio.



Figure S15: (A) NH₃ concentration and power, and (B) energy consumption and production rate, for an empty DBD reactor, and a DBD reactor packed with Al₂O₃, Co/Al₂O₃, CoCe/Al₂O₃, CoCe/Al₂O₃, CoCe/Al₂O₃, CoCe/Al₂O₃, and CoLa/Al₂O₃ and CoLa/Al₂O₃ catalysts, operating at 200 mL/min and at three different H₂:N₂ ratios. The empty reactor was used with two different feed gas flow rates: 400 and 200 mL/min, to obtain the same residence time and same mass flow rate, respectively, as the packed reactor.



Figure S16: NH₃ concentration as a function of time for the reaction using CoLa/Al₂O₃ as packed catalysts. The



Figure S17: NH₃ concentration normalized over the surface area for a DBD reactor packed with Al₂O₃, Co/Al₂O₃, Co/Ce/Al₂O₃, Co/

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