Al₂O₃-supported transition metals for plasma-catalytic NH₃ synthesis in a DBD plasma: Metal activity and insights into mechanisms

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Figure S1. XRPD diffractograms of the catalysts used in our work. (a) Fe₂O₃/Al₂O₃ (after calcination, before reduction); (b) Co₃O₄/Al₂O₃ (after calcination, before reduction); (c) Ru/Al₂O₃ (after calcination, after reduction).

Table S1. Measured active surface area ($S_{BET}$) and pore volume (V) for the 10 wt% Co/Al₂O₃ catalyst before (fresh) and after (spent) the plasma-catalytic NH₃ synthesis experiments, showing no difference before and after the plasma experiments. The other catalysts showed similar behaviour.

| Material          | $S_{BET}$ (m²/g) | V (cm³/g) |
|-------------------|------------------|-----------|
| 10 wt% Co/Al₂O₃ (fresh) | 175              | 0.37      |
| 10 wt% Co/Al₂O₃ (spent)  | 177              | 0.37      |
Figure S2. Typical SEM-EDX images of the catalysts, for the example of 10 wt% Co and Cu/Al₂O₃ catalysts with EDX maps applied for visualisation of the respective metals. (a) SEM image of the 10 wt% Co/Al₂O₃; (b) SEM EDX map of Co on the surface of the 10 wt% Co/Al₂O₃; (c) SEM image of the 10 wt% Cu/Al₂O₃; (d) SEM EDX map of Cu on the surface of the 10 wt% Cu/Al₂O₃. Green and cyan colours indicate the particles of the respective metal on the surface of Al₂O₃.
Figure S3. Current and voltage waveforms for the plasma-catalytic NH₃ synthesis experiments with different Al₂O₃-supported catalysts and pristine Al₂O₃, at different H₂:N₂ ratios in the feed gas. (a) Al₂O₃ at the 1:1 H₂/N₂ gas ratio; (b) 10 wt% Fe/Al₂O at the 1:1 H₂/N₂ gas ratio; (c) 10 wt% Ru/Al₂O₃ at the 1:1 H₂/N₂ gas ratio; (d) 10 wt% Co/Al₂O₃ at the 1:1 H₂/N₂ gas ratio; (e) 10 wt% Cu/Al₂O₃ at the 1:1 H₂/N₂ gas ratio; (f) 10 wt% Co/Al₂O₃ at the 3:1 H₂/N₂ gas ratio; (g) 10 wt% Co/Al₂O₃ at the 3:1 H₂/N₂ gas ratio.
Figure S4. Lissajous figures for the plasma-catalytic NH₃ synthesis experiments with different Al₂O₃-supported catalyst and pristine Al₂O₃, at the different H₂:N₂ ratios in the feed gas. (a) Al₂O₃ at the 1:1 H₂/N₂ gas ratio; (b) 10 wt% Fe/Al₂O at the 1:1 H₂/N₂ gas ratio; (c) 10 wt% Ru/Al₂O at the 1:1 H₂/N₂ gas ratio; (d) 10 wt% Co/Al₂O at the 1:1 H₂/N₂ gas ratio; (e) 10 wt% Cu/Al₂O at the 1:1 H₂/N₂ gas ratio; (f) 10 wt% Co/Al₂O at the 1:3 H₂/N₂ gas ratio; (g) 10 wt% Co/Al₂O at the 3:1 H₂/N₂ gas ratio.
Table S2. The amount of the used catalyst, and the production rate of NH₃ (in mg/(h×g cat)) in our work compared to literature reports.

| Reference in the main text | Catalyst amount (g) | NH₃ production rate |
|---------------------------|--------------------|---------------------|
|                           |                    | mg/h                |
|                           |                    | mg/(h × g cat)      |
| [35]                      | 17                 | 119                 |
| [36]                      | 173                | 32                  |
| [39]                      | 3.6                | 76                  |
| [42]                      | 100                | 17                  |
| [46]                      | 0.5                | 25                  |
| this work                 | 12                 | 42                  |
|                           |                    | 3.5                 |