catalysts

Supplementary Information: Transient kinetic experiments within the high conversion domain: The case of ammonia decomposition

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Catalyst structure and chemical composition

Figure S1A shows the pre-reaction XRD patters of Fe, CoFe and Co. Fe and Co samples were recorded at 550 °C in vacuum following *in situ* H_2 pre-treatment overnight (also at 550 °C). The CoFe spectra was recorded at room temperature. The pattern for Fe indicates cubic α-Fe with (110) as the predominant peak. The pattern for Co indicates predominant cubic structure with (111) the majority crystal plane exposed. A hexagonal structure for Co cannot be excluded completely. The XRD pattern for CoFe was similar to Fe. Peaks that could be assigned to cobalt oxides or pure cobalt metals were not observed. *Figure S1*Figure*B*, *C* and *D* indicate the XRD patterns recorded at room temperature for Fe, CoFe and Co, respectively, after exposure to 15% NH_3/He at 50 mL/min for 1 hour at 550 °C. For the iron sample, Fe_3N and Fe_4N were found indicating reaction between iron and ammonia lead to the formation of iron nitride. In addition, Fe_2N was observed over the CoFe sample.

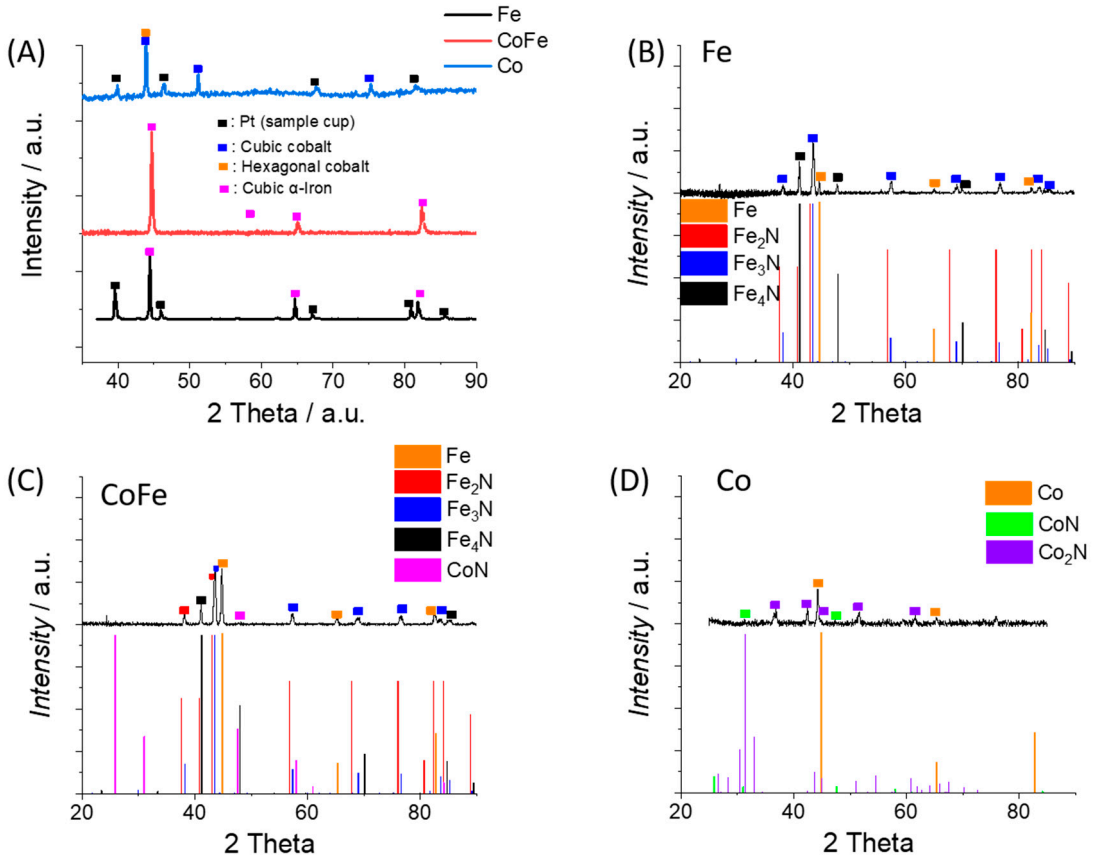

Figure S1. A) Pre-reaction XRD patterns for Fe and Co at 550 °C, CoFe at room temperature; post-reaction XRD patterns following exposure to 15%NH_3/He at 50 mL/min for 1 h at 550 °C, B) Fe, C) CoFe, D) Co.

Pulse Response Data

NH_3 conversion (X) is related to normalized zeroth moment (M_0) which represents the total amount of NH_3 molecules that exits the reactor divided by pulse intensity. The M_0 of exit flow rates are given by the general equation:

$$M_0 = \int_0^0 f(t)dt$$

where t is the time and f(t) is the exit flux. Therefore, Conversion (X) is calculated *via* X=1-M_0

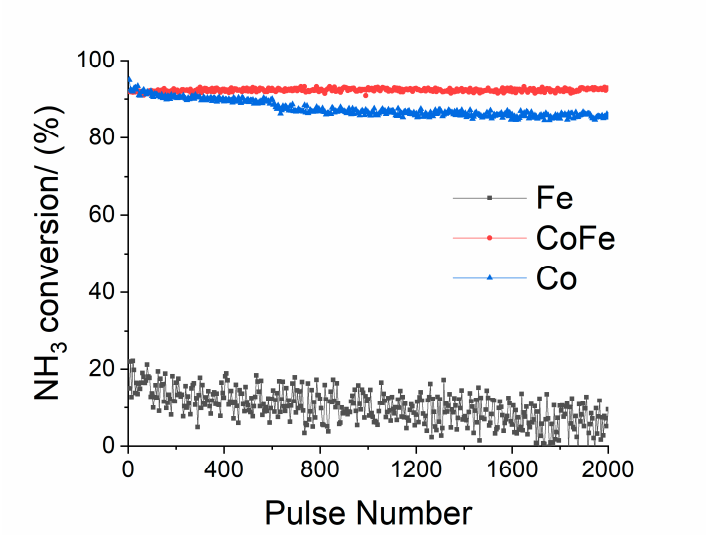

Figure S2. A) NH_3 conversion over the course of 2000 pulses NH_3 pulses at 550 °C over Fe, CoFe and Co materials in the TAP reactor.

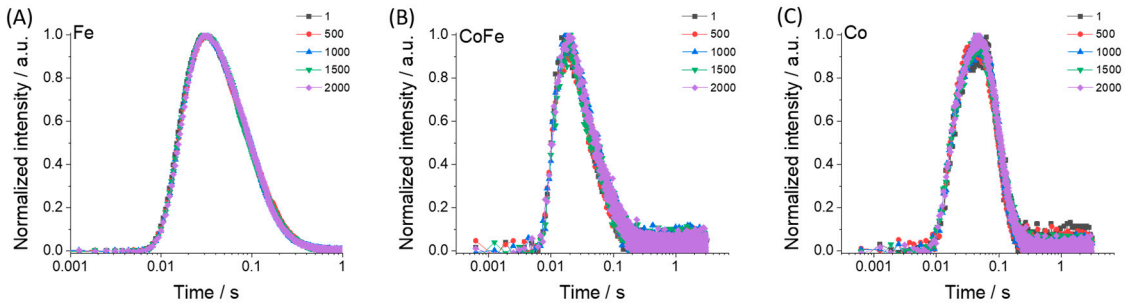

Figure S3. Height normalized NH_3 reaction rate at different pulses over the 2000 pulse sequence for A) Fe, B) CoFe and C) Co.

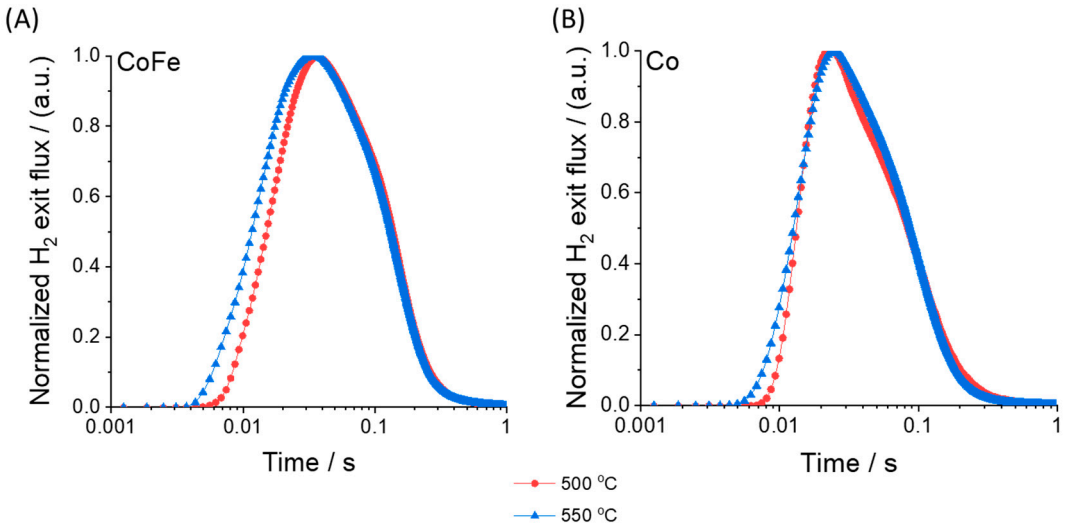

Figure S4. Height normalized hydrogen pulse response for A) CoFe and B) Co during ammonia decomposition experiments at 500 and 550 °C.

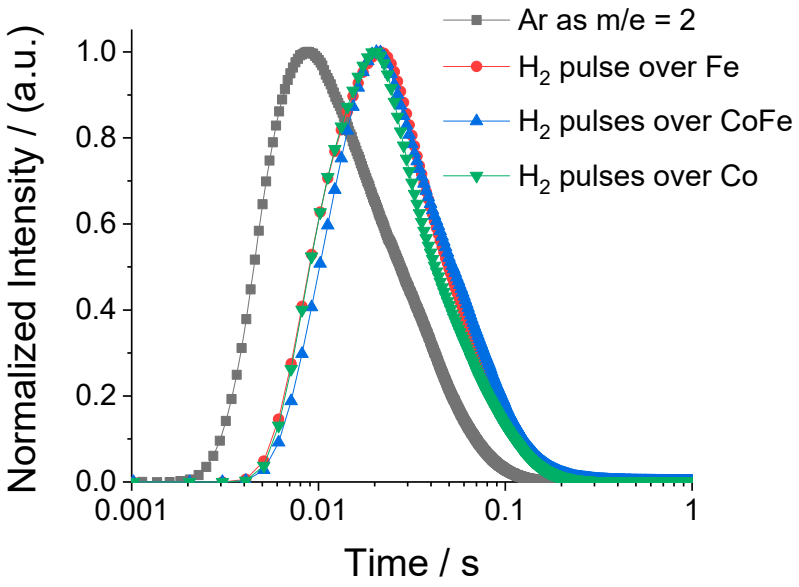

Figure S5. Height normalized hydrogen and argon (internal standard) pulse response during H_2/Ar direct pulsing at 550 °C over Fe, CoFe and Co. Argon diffusion time was corrected by Graham's law.