

## **Supplementary Information**

### **Elucidating the role of potassium addition on the surface chemistry and catalytic properties of cobalt catalysts for ammonia synthesis**

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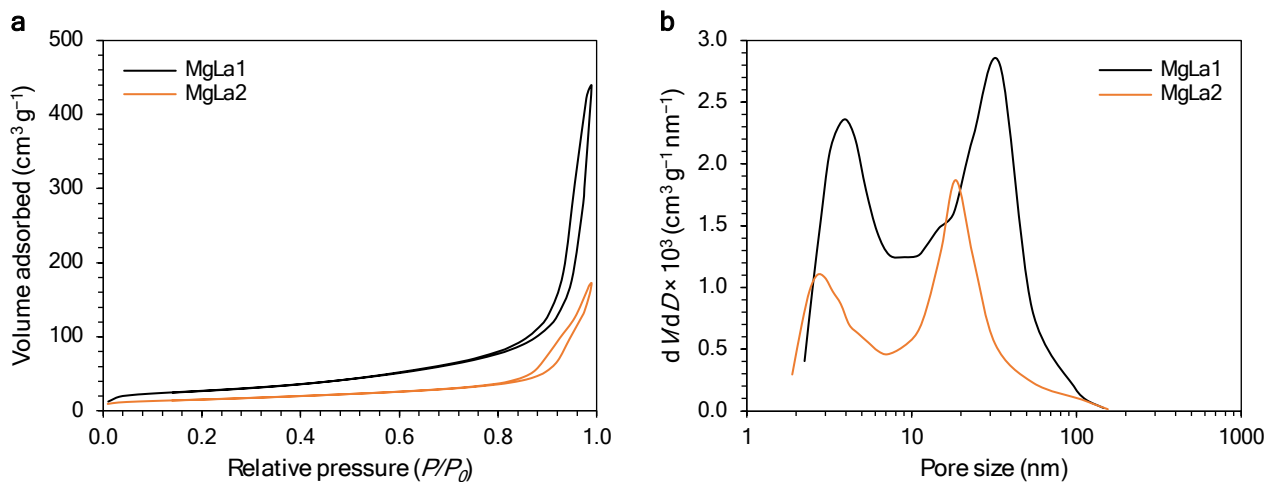
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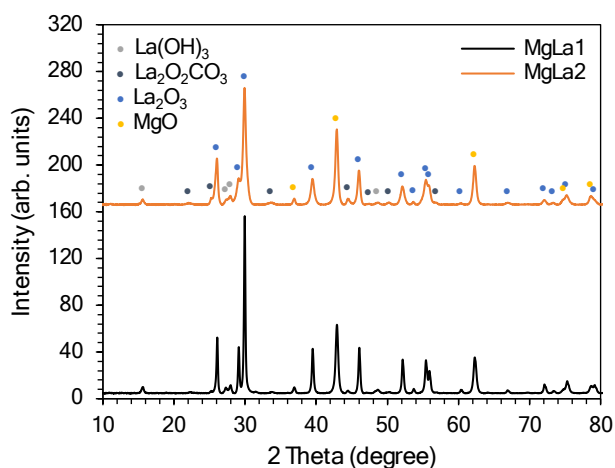
**Figure S1.** (a)  $N_2$  adsorption-desorption isotherms and (b) the corresponding pore size distribution curves of the support materials.

**Table S1.** Textural parameters of the support materials.

Support	MgLa1	MgLa2
Specific surface area <sup>a</sup> ( $m^2 g^{-1}$ )	96.7	53.9
Total pore volume <sup>b</sup> ( $cm^3 g^{-1}$ )	0.681	0.268
Average pore diameter <sup>b</sup> (nm)	21.2	17.7

<sup>a</sup> Determined by BET method.

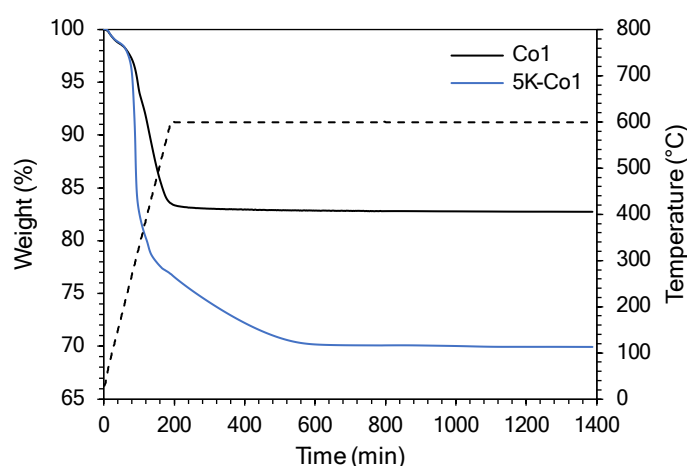
<sup>b</sup> Determined by BJH method from the desorption branch of the isotherm curves.



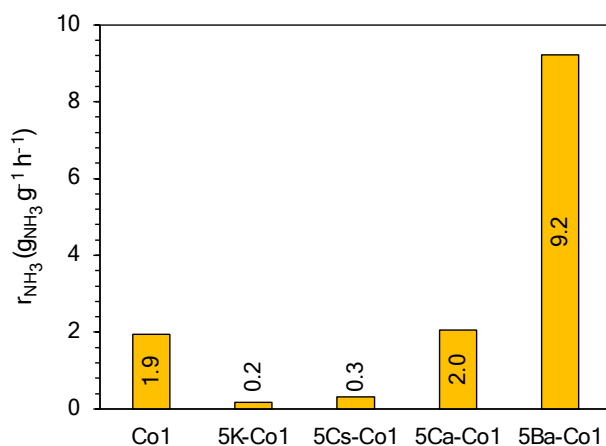
**Figure S2.** XRD patterns of the support materials.

**Table S2.** The K content in the as-prepared catalysts measured by XRF.

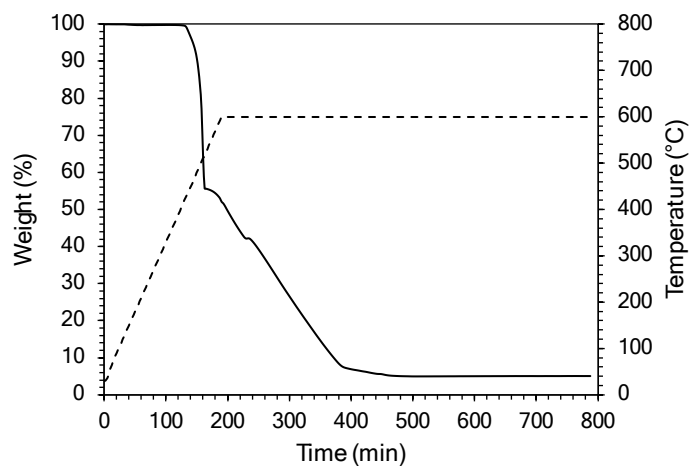
Catalyst	K content (wt%)
Co1	0.08
0.5K-Co1	0.46
1K-Co1	0.91
3K-Co1	2.59
5K-Co1	4.19
7K-Co1	5.71
9K-Co1	7.18



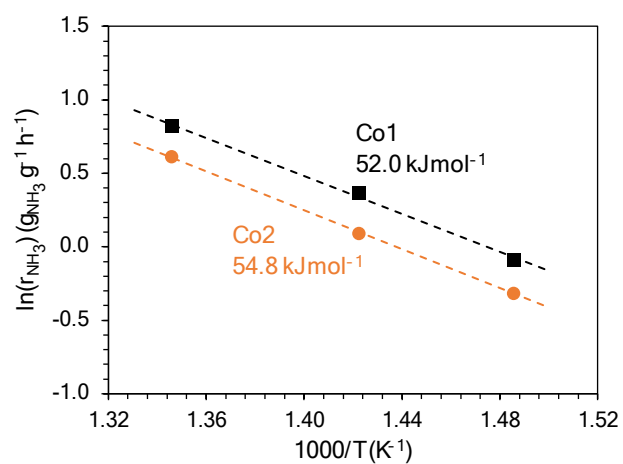
**Figure S3.** TPR-TGA profiles of the as-prepared Co catalysts. The TGA-TPR profile of the as-prepared Co1 revealed that the reduction was completed at around 600 °C, suggesting that the loaded Co metal species was reduced to the metal phase. When holding at 600 °C for 20 h, no further mass losses were observed. The TGA-TPR profile of the as-prepared 5K-Co1 revealed that the reduction was notably more hindered compared to the as-prepared Co1. This was caused by the potassium addition. The activation of 5K-Co1 was completed after 10 h of heating at 600 °C. However, it seems that the reduction of Co metal species was completed at around 600 °C and further heating at 600 °C for 10 h made it possible to reduce  $K_2O$  to metallic K, which was subsequently evaporated. This is very likely since  $KNO_3$  exhibited a similar TGA-TPR profile (Figure S5) to that of the as-prepared 5K-Co1. Moreover, based on the total mass loss, it was deduced that almost all K introduced was evaporated; XRF and ICP analyses confirmed it (Table 1). *Measurement conditions: 100 mL min<sup>-1</sup> H<sub>2</sub>/Ar (50/50 vol%), 100 mg sample, 30–600 °C (3 °C min<sup>-1</sup>) with holding at 600 °C for 20 h.*



**Figure S4.** Comparison of the catalytic performance for ammonia synthesis of the Co catalysts. Reaction conditions: 470 °C, 6.3 MPa, 70 L h<sup>-1</sup> H<sub>2</sub>/N<sub>2</sub> (75/25 mol%).



**Figure S5.** TGA-TPR profile of the KNO<sub>3</sub> salt. The TGA-TPR profile revealed a total mass loss of ~95% related to the decomposition of KNO<sub>3</sub> to K<sub>2</sub>O. K<sub>2</sub>O was then reduced to metallic K, which was prone to evaporate (K volatilises at around 400 °C [1]). This explains why almost complete mass loss of KNO<sub>3</sub> salt was observed; however, some residual amount of K<sub>2</sub>O was not reduced. Measurement conditions: 100 mL min<sup>-1</sup> H<sub>2</sub>/Ar (50/50 vol%), 100 mg sample, 30–600 °C (3 °C min<sup>-1</sup>) with holding at 600 °C for 10 h.



**Figure S6.** Arrhenius plots for ammonia synthesis over the Co1 and Co2 catalysts at 6.3 MPa.

## References

- [1] J.-H. Kim, T.-Y. Dai, M. Yang, J.-M. Seo, J. S. Lee, D. H. Kweon, X.-Y. Lang, K. Ihm, T. J. Shin, G.-F. Han, Q. Jiang, J.-B. Baek. Achieving volatile potassium promoted ammonia synthesis via mechanochemistry. *Nat. Commun.*, 2023, **14**, 2319. <https://doi.org/10.1038/s41467-023-38050-2>