Ammonia oxidation on perovskites for ammonia SOFCs

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Highlights

- A promising candidate for ammonia oxidation has been found
- Measured reaction orders indicate Mars van Krevelen mechanism
- Experiment design allowed a wide systematic screening with reduced cost and effort

1. Introduction

The activity of perovskites in ammonia oxidation to nitric oxide has been investigated extensively[1], [2], [3], but corresponding kinetic data is scarcely reported. In addition, doping strategies of those mixed oxide catalysts have mostly focused on a narrow range of compositions with only one component varying in concentration. In this work, a Design of Experiment approach has been implemented to screen a wide range of perovskite materials with the general formula $LaFe_xCo_yNi_zO_3$, followed by a detailed kinetic study over the candidate showing highest selectivity to the desired product.

2. Methods

All the perovskite materials have been synthesized using coprecipitation followed by calcination in air at 700-800°C depending on the sample. Selectivity screening tests and kinetic studies have been performed in an R&D rig. Perovskite samples diluted in alumina were placed in a tubular quartz reactor enclosed in a furnace. Inlet flow was controlled by MFCs, and outlet gas evolution was measured using MS. The results were processed, and ternary contour plots were generated using a python script.

3. Results and discussion

Selectivity screening led to results shown in Figure 1. Based on the screening, an optimal catalyst candidate – $LaFe_{0.25}Ni_{0.75}O_3$ – has been suggested and synthesized. The NO selectivity for the optimized catalyst was confirmed to be highest of all tested catalysts. A kinetic study of ammonia oxidation to nitric oxide over the optimized candidate led to the following conclusions: First order in ammonia, between 0[th] and 1[st] order in oxygen (see Figure 2), oscillatory behavior at lower oxygen partial pressures (indicates MvK mechanism), linear Arrhenius behavior for the desired product, and inverted "V" Arrhenius behavior for undesired products, making the selected perovskite a promising candidate for ammonia SOFC anode material.

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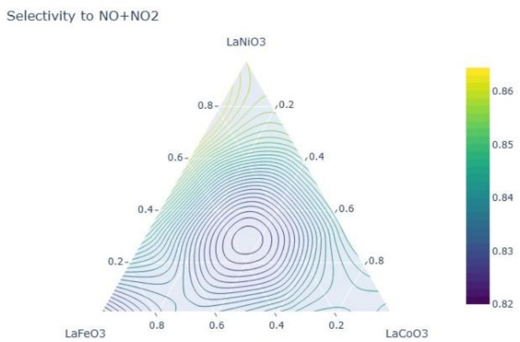

Figure 1 Selectivity screening results

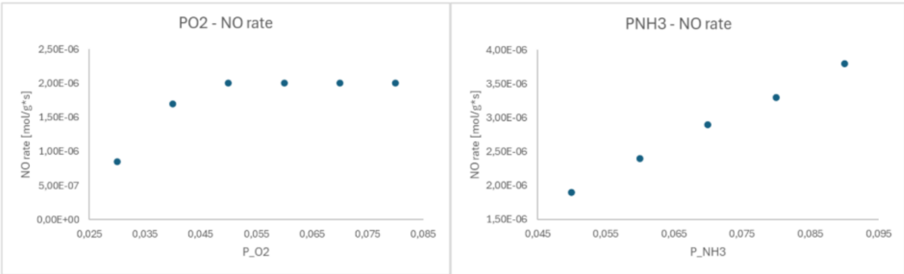

Figure 2 Reaction orders in oxygen and ammonia

4. Conclusions

Implementation of a DoE approach successfully allowed systematic screening encompassing a relatively wide range of perovskite compositions. A promising candidate for ammonia oxidation to nitric oxide has been identified. The kinetic study performed provided results proving that the catalyst and its operating conditions are favorable for the desired product (NO). In addition, valuable insights into the possible mechanistic pathway have been obtained.

References

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