Modified Pechini synthesis of perovskite-type oxide catalysts for CO_2 utilization

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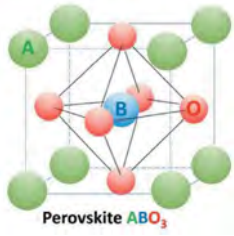
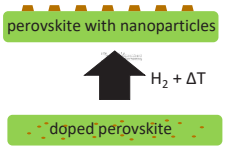
Introduction

Perovskites-type oxides with the general composition ABO_3 are promising catalysts for CO_2 utilization applications due to their flexible composition. For example, $Nd_{0.6}Ca_{0.4}Fe_{0.9}Co_{0.1}O_{3-\delta}$ (NCF-Co10) was found to be a good catalyst in the reverse water-gas shift reaction (rWGS). [1] Moreover, perovskites can form under reducing conditions metallic nanoparticles on the surface in a process called exsolution.

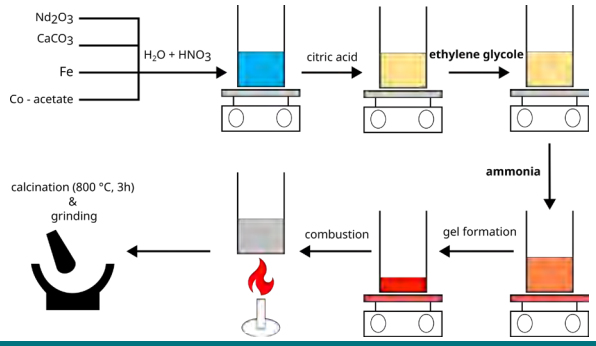
Synthesis of perovskite-type oxide catalysts is often carried out using the Pechini method. The reaction conditions employed in this process vary across literature. [2] In this work the effect of the synthesis conditions on the surface area and thus the performance of the final catalyst was investigated.



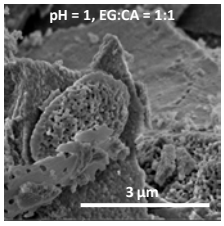


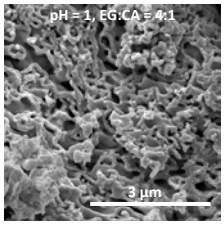
Approach

A modified Pechini method was used to synthesize NCF-Co10 with the addition of varying amounts of **ethylene glycol** (EG) and **ammonia** (pH adjustment). Morphology and surface areas were determined. Additionally catalytic activity in rWGS and reducibility (TPR) were investigated in a plug-flow reactor.



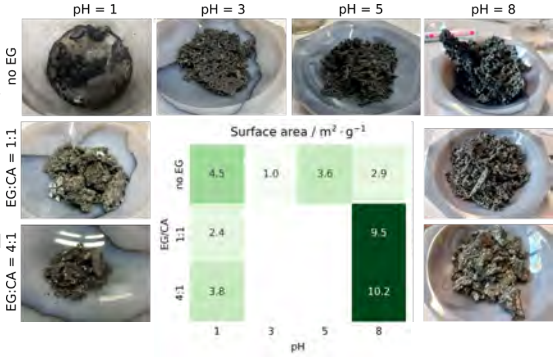
Effects on Morphology and Surface Area





Addition of Ethylene glycol at pH = 1 showed different effects depending on the ratio of citric acid (CA) to EG. While stoichiometric ratios (EG:CA = 1:1) decreased surface area, excess EG increased porosity.

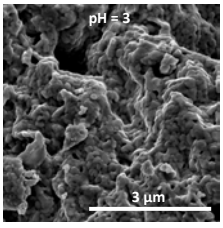
Combination of basic pH and ethylene glycol, produced the highest surface areas with the ratio of EG to CA being seemingly less important.

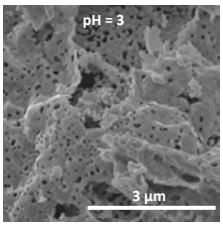


Photographs of the perovskite sponge after calcination at 800 °C for 3 h (outside) and the surface area of the powders obtained after grinding determined using Brunnauer-Emmet-Teller (BET) isotherms and nitrogen adsorption (inside).

Addition of ammonia caused a reduction in surface area. The effect is pH dependent with the lowest surface area observed at pH = 3 with 1 $m^2 \cdot g^{-1}$.

Notably the volume of the obtained foam increased with ammonia addition, likely due to the increased amounts of ammonium nitrate formed.

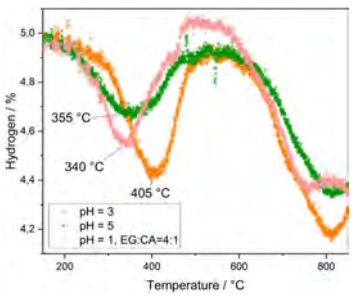


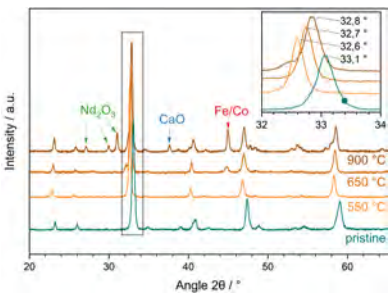


Reduction and Catalytic Activity

Reductive Behaviour

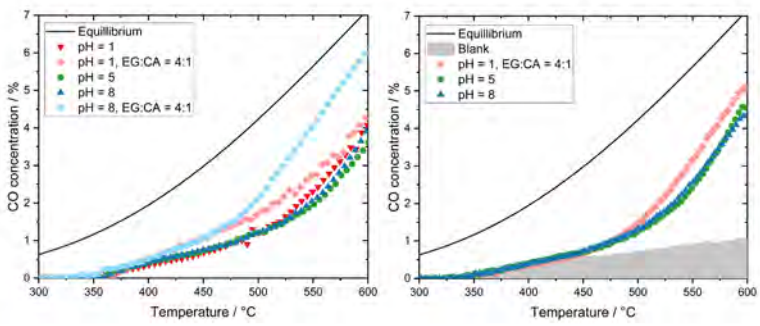
of catalysts tested in a 5 % H_2 in Ar showed slight differences between the syntheses. Primarily a shift of the first hydrogen consumption peak to lower temperatures was observed when ethylene glycol was added. XRDs after reduction at 550 °C show no formation of metallic nanoparticles indicating the formation of oxygen vacancies.





Catalytic Activity

in the rWGS reaction was measured using a mixture of H_2:CO_2:Ar = 1:1:2 and increases with the accessible catalyst surface area. Preliminary results indicate higher catalytic activity at low temperatures for synthesis using ethylene glycol.



Conclusion & Outlook

- A combination of high pH and addition of ethylene glycol produced the catalysts with the highest surface area
- Addition of EG caused earlier onset of exsolution, further testing is needed for confirmation
- Investigate possible effects on the size of exsolved nanoparticles during reaction using SEM
- Perform long term tests to investigation the effect of morphology on catalyst deactivation

References

[1] L. Lindenthal, J. Popovic, R. Rameshan, J. Huber, F. Schrenk, T. Ruh, A. Nenning, S. Löffler, A.K. Opitz, C. Rameshan, Novel perovskite catalysts for CO2 utilization - Exsolution enhanced reverse water-gas shift activity, Applied Catalysis B: Environmental, Volume 292, 2021, 120183

[2] Sunde, T. O. L. et al. Handbook of Sol-Gel Science and Technology, Chapter: Modified Pechini Synthesis of Oxide Powders and Thin Films, 2016

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