Research Proposal for Master Thesis Project

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Topic: Investigation of the oxygen mobility in doped $SrFeO_{3-\delta}$ perovskites and its implications on their selectivity as redox catalysts for chemical looping

1. Why is this topic important?

In chemical looping, metal oxides are used as the oxidation/reduction agent in chemical reactions for various different applications such as total combustion, air separation and partial oxidation for the production of chemicals. [1] One promising family of metal oxides in the context of chemical looping are perovskites with the general formula $ABO_{3-\delta}$. [2] Perovskites are able to generate a significant amount of oxygen nonstoichiometry δ in the lattice without major phase transition even at temperatures below 500 °C, making them an ideal candidate for the donation of oxygen in chemical looping redox reactions. [3] Additionally, perovskites have a high flexibility in the composition of A and B-site cations, which allows the tuning of the chemical-physical properties by doping. [2]

2. What has been done so far? What was observed? What are the research gaps?

So far, many different compositions of perovskites have been investigated. Many effects which influence the oxygen mobility and therefore the performance of the perovskites have been detected. One main characteristic which affects the oxygen mobility of the perovskites is structural distortion. [4] Structural distortions are caused by doping the perovskite with cations, which have a smaller/larger ionic radius than the cation they are replacing. [4] Further, doping cations with different charges can change the oxygen vacancy concentration of the perovskite since the overall charge neutrality needs to be maintained. [5] A higher amount of oxygen vacancies has been reported to be beneficial for diffusion of oxygen in the lattice. [5] This suggests that higher oxygen vacancy concentrations promote fast oxygen release. [5] In the context of chemical looping catalysis, a fast oxygen release has been correlated with the tendency of perovskites to totally combust hydrocarbons to CO_2. However, the effects of doping on the oxygen release are still hard to predict and reasons for the overoxidation of carbonaceous feedstock are not fully understood. Therefore, further research is needed to obtain a better understanding of the oxygen mobility in doped perovskites and its effect on their selectivity as redox catalysts in chemical looping.

3. What will be done? What research gap am I filling?

This project aims at improving our understanding of the oxygen release and mobility of doped $SrFeO_{3-\delta}$ perovskites and its implications on their selectivity as redox catalysts in chemical looping partial oxidation applications. In this study, the effects of structural distortions introduced by A- and B-site doping with cations (e.g. Ca^{2+}, Ba^{2+}, Co^{4+}, Mn^{4+}) will be investigated by synthesizing a series of doped perovskites from a sol-gel method. As an indicator for the oxygen mobility, the reducibility of the synthesized metal oxides will be assessed by temperature-controlled reduction (TPR) experiments in a thermogravimetric analyzer (TGA). In addition, conductivity relaxation measurements will be carried out to explicitly determine the effect of doping on the oxygen diffusivity within the perovskite structure. The tendency of the perovskites towards overoxidation of carbonaceous feedstock to CO_2 will be evaluated by catalytic experiments in a fixed-bed reactor. To quantify and understand the structural changes caused by doping, the synthesized perovskites will

be analyzed by powder X-ray diffraction (XRD). Our goal is to correlate the structural changes imposed by doping the perovskites on their oxygen mobility and ultimately their catalytic performance for partial oxidation reactions.

References:

[1] Z. Xing, „Chemical looping beyond combustion – a perspective," *Energy Environ. Sci.*, Bd. 13, Nr. 3, pp. 772-804, 2020.

[2] G. Luongo, „Structural and thermodynamic study of Ca A- or Co B-site substituted SrFeO3−δ perovskites for low temperature chemical looping applications," *Physical Chemistry Chemical Physics,* Bd. 22, Nr. 17, 2020.

[3] D. Jian, „A- and B-site Codoped SrFeO3 Oxygen Sorbents for Enhanced Chemical Looping Air Separation," *ChemSusChem,* Bd. 13, Nr. 2, pp. 385-393, 2020.

[4] J. Ting, „Effective Ca2+-doping in Sr1-xCaxFeO3-δ oxygen carriers for chemical looping air separation: A theoretical and experimental investigation," *Applied Energy,* Bd. 281, 2021.

[5] H. Fang, „La1-xSrxFeO3 perovskite-type oxides for chemical-looping steam methane reforming: Identification of the surface elements and redox cyclic performance," *International Journal of Hydrogen Energy,* Bd. 44, Nr. 21, pp. 10265-10276, 2019.

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