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journal homepage: www.elsevier.com/locate/apcatbTemplate-free mesoporous $\text{La}_{0.3}\text{Sr}_{0.7}\text{Ti}_{1-x}\text{Fe}_x\text{O}_{3\pm\delta}$ for CH_4 and CO oxidation catalysisBuğra Kayaalp^{a,1}, Siwon Lee^{b,1}, Kurt Klauke^a, Jongsu Seo^b, Luca Nodari^{c,d}, Andreas Kornowski^e, WooChul Jung^{b,*}, Simone Mascotto^{a,*}^a Institut für Anorganische und Angewandte Chemie, Universität Hamburg, Martin-Luther-King-Platz 6, D-20146, Hamburg, Germany^b Department of Materials Science and Engineering, Korea Advanced Institute of Science and Technology, 291 Daehak-ro, Yuseong-gu, Daejeon, 34141, Republic of Korea^c Istituto di Chimica della Materia Condensata e di Tecnologie per l'Energia, ICMATE-CNR, C.so Stati Uniti 4, Padova, 35127, Italy^d Dipartimento di Scienze Chimiche, Università di Padova, Via Marzolo 1, Padova, 35131, Italy^e Institut für Physikalische Chemie, Universität Hamburg, Grindelallee 117, D-20146 Hamburg, Germany

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ABSTRACT

The design of perovskite oxides with improved textural properties in combination with tunable composition variations is a forward-looking strategy for the preparation of next generation catalytic converter. In the present work we report the template-free synthesis of mesoporous solid solutions of $\text{La}_{0.3}\text{Sr}_{0.7}\text{Ti}_{1-x}\text{Fe}_x\text{O}_{3\pm\delta}$ ($0 \leq x \leq 0.5$) and the study of their catalytic performance towards CH_4 and CO oxidation. Using an innovative polymer complex route, phase pure perovskite solid solutions with specific surface area of $65 \text{ m}^2 \text{ g}^{-1}$ and average pore size of 15 nm were prepared. The iron concentration increase led to a progressive enhancement of not only both concentration and transport of the charge carriers but also reducibility and oxygen desorption capability on the catalyst. As a result, we observed almost complete conversion of CH_4 and CO at 600 °C and 300 °C, respectively. Kinetic studies on methane oxidation showed that competing *suprafacial* and *intrafacial* reaction mechanisms coexist, and that the concentration of 30% of Fe maximizes the *suprafacial* contribution. Under reducing conditions at 600 °C the materials retained their structural and morphological integrity, showing superior stability. Finally, the reaction rate of CH_4 and CO conversion evidenced that our systems are by a maximum of 90 times more performing than other bulk and nanoporous Fe-based perovskites in literature (e.g. $\text{La}_{0.66}\text{Sr}_{0.34}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3\pm\delta}$), as a result their large surface area, intimate gas-solid contact and short intragrain oxygen diffusion pathways induced by the mesoporous structure.

1. Introduction

The growing demand for efficient power generation systems with minimized emission of pollutants is at the moment a major driving force pushing for the development of cost-effective, non-toxic, stable and active catalyst materials. In this respect perovskite oxides are currently experiencing a renaissance in many fields of the energy sector from Li-batteries [1] to solar fuels [2,3], fuel cells [4] and diesel soot combustion [5]. It is well known that the versatility of this class of materials is given by their ease in accommodating nonstoichiometry without compromising their structural stability. The rational introduction of doping species in A and/or B position of the perovskite lattice is a feature largely exploited for the design of the materials for energy conversion devices, because it significantly influences their ionic and electronic mobility as well as electronic structure. Along with the optimization of the composition, the improvement of the morphological

properties of the oxides is a further essential requirement for such applications. In comparison to nanoparticulate systems, nanoporous materials possess higher concentration of active sites thanks to their larger specific surface area. In particular, the realization of well-connected networks of mesopores, i.e. pores between 2 and 50 nm, is highly desired, because the size related enhancement of the pore wall adsorption potential improves the fluid-solid interactions. Furthermore, the existence of mesoscaled pore walls guarantees short intragrain diffusion pathways favoring the transport of ionic and electronic charge carriers. Hence, the design of perovskite oxides, which combine mesoporosity with controlled cationic substitution, represents an ultimate goal for the development of high performance catalytic devices [6].

Even though the preparation of nanoporous and mesoporous perovskite oxide powders is meanwhile reported by several wet-chemistry studies [7–12], to the best of our knowledge, the simultaneous

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