Ni–perovskite interaction and its structural and catalytic consequences in methane steam reforming and methanation reactions

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ABSTRACT

Metal–support interaction effects and their consequences in CO_2/CO methanation and methane steam reforming have been exemplarily studied on two complex Ni–perovskite powder catalyst systems, namely Ni–$La_{0.6}Sr_{0.4}FeO_{3-\delta}$ (lanthanum strontium ferrite, LSF) and Ni–$SrTi_{0.7}Fe_{0.3}O_{3-\delta}$ (strontium titanium ferrite, STF). Pre-reduction in hydrogen and treatment in catalytic gas mixtures cause a variety of structural effects, including exsolution of iron particles and formation of Ni–Fe alloy particles. These manifestations strongly depend on the reducibility of the perovskite and are hence much more pronounced on LSF. Reactivity differences are strongly influenced by the chemical properties of the respective perovskite support. The more reducible the perovskite support, the stronger the deviation from the catalytic behavior of a Ni/Al_2O_3 reference catalyst, rendering establishments of direct structure–activity/selectivity relationships difficult. The studies show the extreme variety of the metal–perovskite interface, which helps in judging similar systems of recent high catalytic importance, e.g. metals supported on spinel or other perovskite phases.

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1. Introduction

Perovskite materials have recently emerged as promising (electro-) catalytic materials with applications in a wide range of reactions, including oxidation reactions, pollution abatement, hydrogenation and hydrogenolysis, photo-catalysis or electrocatalysis [1,2]. The latter is usually either connected with oxygen reduction reactions or use as anode materials in SOFCs [1,2]. A particular interesting reaction, which has also been studied over different perovskite materials, is the methanation reaction from CO (or CO_2) and H_2 to CH_4 or its reverse reaction, the methane steam reforming reaction, respectively [3–15]. This also includes the dry reforming of methane [16]. Already known for over 100 years [17], especially the CO_2 methanation reaction $CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$ has attracted recent interest due to the search for CO_2 utilization in combination with energy-efficient storage solutions for renewable electricity. For the equivalent CO methanation reaction

$CO + 3H_2 \rightarrow CH_4 + H_2O$, this is linked to the generation of a natural gas substitute [3–5,7,12–14,18–20]. As a number of catalysts are active, including transition metals such as Rh, Ru, Co or Ni, which potentially steer the selectivity patterns also to higher hydrocarbons or alcohols, the available literature on the methanation reaction is vast [3–5,7,12–14,18–21]. Comprehensive reviews on almost all aspects already exist [3–5]. This also holds for the methane steam reforming reaction, which is also a promising method for efficient hydrogen production [6]. The reason for the employment of perovskite materials in these reactions is multifold, but unfortunately does not come without drawbacks: this is basically due to their inherent structural and chemical complexity. Nevertheless, various perovskites, including $LaFeO_3$, $LaNi_xFe_{1-x}O_3$, $LaNiO_3$ or $La_{1-x}Ce_xFe_{0.7}Ni_{0.3}O_3$ have been found to especially exhibit a high activity in the steam reforming of methane with minimal coke deposition under low steam-to-carbon ratios [3–15]. Suppression of coke formation in the latter reaction is of particular importance, as the commonly employed Ni catalyst is especially prone to carbon deposition and subsequent coke formation. However, despite their obvious advantages, the necessarily high operating temperatures (e.g. $T \geqslant 600\,°C$) of both methanation and methane

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reforming reactions eventually induce irreversible structural changes, including structural collapse and exsolution of (reactive or inactive) metal particles from the perovskite lattice [8,9–11,14,15]. This has a very strong influence on the catalytic material under scrutiny, but at the same time is structurally very difficult to control. This is not always per se detrimental: for instance, exsolution of Fe from LSF has been shown to improve its water-splitting capability [22]. Taking this idea even further, alloying or even intermetallic compound formation following metal exsolution from supported metal–perovskite systems might lead to catalytically interesting systems. In close correlation to the formation of Ni–Fe alloy particles eventually following Fe exsolution observed on impregnated Ni–perovskite systems under scrutiny here, Ni_3Fe intermetallic compounds or Ni–Fe alloy phases themselves already showed promising activity in methane and tar steam reforming [23,24]. Exsolution phenomena from perovskites are not uncommon and recently an elegant pathway of deliberately using their non-stoichiometry for generation of well-defined and dispersed metal particles by controlled exsolution has been reported [25–29]. These ideas must in principle be extended to the behavior of the perovskite systems in contact with the relevant reaction mixtures, which could again alter the structure obtained after activation treatments in situ. In that respect, detailed studies on the structure of perovskite systems after each step of activation and reaction have to be performed to gain a full picture of the structure–activity relationships in metal-on-complex oxide systems. Such studies have been already performed on the pure perovskite systems LSF and STF in (inverse) water gas shift reaction and methane oxidation and revealed significant differences in the extent of reduction and the reactivity of the respective lattice oxygen [30] and on metal-on-$LaFeO_3$ systems, where the influence of the perimeter of the metal–perovskite interface on catalytic properties has been highlighted [31,32].

In the present study, we extend these studies to an even more complex system, namely small Ni particles deliberately deposited by non-aqueous impregnation on STF (strontium titanium ferrite, $SrTi_{0.7}Fe_{0.3}O_{3−\delta}$) and LSF (lanthanum strontium ferrite, $La_{0.6}Sr_{0.4}FeO_{3−\delta}$) perovskite supports. The reason to study such systems is multifold: addition of Ni eventually leads to hydrogen activation and possibly also to different pathways of perovskite structural changes during activation and reaction. Secondly, the deliberate addition of Ni should in principle help to create an improved methanation/methane reforming perovskite catalyst. Thirdly, which provides the connecting link to electro-catalysis and SOFC-research, impregnated catalyst systems with a lower Ni loading should in principle be favored over the so far used cermet anode materials. Cermet materials with percolated and sintered Ni bulk morphologies provide a lower surface area/electro-catalytic interface compared to smaller Ni particles. Furthermore, impregnation techniques are standard routines in catalyst preparation. The latter, however, poses additional problems: since especially LSF is suspected to become hydrolyzed under aqueous conditions [33], water-free alternatives in preparation are to be preferred, but at the same time are not straightforward. Here, we have chosen a preparation pathway using Ni(II)-acetylacetonate as catalyst precursor material. As shown below, this reproducibly creates Ni–LSF and Ni–STF catalysts with well-defined and dispersed Ni particles. In due course, these systems are perfect candidates to study the structural interaction and catalytic consequences of metal–perovskite interaction. Apart from catalytic measurements, dedicated electron microscopy techniques are used to establish the anticipated structure–activity correlations. As a result, the direct comparison of Ni–LSF and Ni–STF will reveal the different structural consequences of perovskite reducibility, associated metal exsolution and metal–perovskite interaction, also in correlation with a Ni–Al_2O_3 reference catalyst.

2. Experimental

2.1. Materials preparation

Synthesis of pure LSF and STF has been discussed in detail in Ref. [30]. The Pechini route was used to synthesize $La_{0.6}Sr_{0.4}FeO_{3−\delta}$ [34]. In case of the $SrTi_{0.7}Fe_{0.3}O_{3−\delta}$ a solid state reaction was performed [30]. As for the preparation of the Ni–LSF and Ni–STF samples (10 mol% of Ni), a synthesis routine avoiding water-containing solutions has been followed. Aqueous impregnation especially on LSF potentially may lead to alkaline oxide hydrolysis (e.g. La_2O_3 or SrO) [33]. Therefore, a solution of Ni-acetylacetonate $(Ni(acac)_2)$ has been used as Ni precursor material. $Ni(acac)_2$ was dissolved in 30 mL acetone and subsequently, a suspension with 1 g perovskite material was prepared. The resulting solution was vigorously stirred for 30 min, dried in air and finally calcined in pure oxygen at 600 °C for 2 h. Afterward, the structural integrity of the perovskite and the presence of NiO were verified by XRD (Fig. 1). Hence, the starting state of both materials is NiO–LSF and NiO–STF. Surface areas using the BET method were determined for both samples to be around 0.4 $m^2\ g^{−1}$. BET surface areas were measured with a Quantachrome Nova 2000 Surface and Pore Size Analyzer. The Ni/Al_2O_3 reference catalyst was prepared by initial co-precipitation of Ni and boehmite (AlOOH), closely following a routine outlined in detail in Ref. [35]. All the structural details except the catalytic data can be found in the Supporting Information. The reference catalyst was subjected to pre-oxidation (O_2, 400 °C, 1 h) and pre-reduction (H_2, 600 °C, 1 h) prior to catalytic testing.

2.2. Pre-treatments and catalytic experiments

All catalytic measurements discussed below are carried out in a 13 mL re-circulating quartz batch reactor constructed for ~100 mg catalyst. Details of the setup are given in [30]. The gas phase composition is detected online using a quadrupole mass spectrometer, connected via a capillary to the reactor. Before each experiment, a pre-treatment routine consisting of an oxidative and reductive
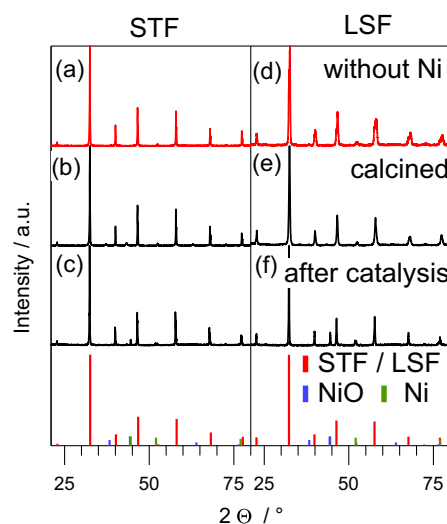

Fig. 1. Representative X-ray diffractograms of pure STF (a), pure LSF (d), calcined impregnated Ni–STF (b), Ni–LSF (e) and both catalysts after reductive activation at 600 °C followed by a catalytic CO_2 methanation reaction up to 600 °C (c and f), respectively. The bottom panels show the theoretical diffractograms of STF, LSF (red), NiO (blue) and Ni (green) on the basis of the ICDD PDF4+ database, patterns 04-013-9876 (STF) [36], 01-072-8136 (LSF) [37], 00-047-1049 (NiO) [38] and 00-001-1260 (Ni) [39].