



Exsolution of Re-alloy catalysts with enhanced stability for methane dry reforming



Daria Zubenko, Sarika Singh, Brian A. Rosen*

Department of Materials Science and Engineering, Tel Aviv University, 55 Haim Levanon Street, Ramat Aviv 69987001, Israel

ARTICLE INFO

Article history:

Received 21 December 2016
Received in revised form 13 March 2017
Accepted 18 March 2017
Available online 19 March 2017

Keywords:

Solid phase crystallization
Rhenium
Perovskites
Methane dry reforming

ABSTRACT

The valorization of natural gas is a highly important process which could enable the production of hydrogen or clean synthetic fuels. Methane reforming with carbon dioxide provides an environmentally friendly route for methane conversion to synthesis gas while consuming two green-house gasses. Large-scale implementation of this process has been stalled by the lack of stable catalysts owing to variety of deactivation mechanisms such as carbon accumulation (coking) and sintering. We created doped perovskite precursors based on lanthanum ferrite (LaFeO_3) and subsequently doped them with Ni and Re phases. Under reducing conditions, these composite precursors exsolved Re-alloy nanoparticles which were found to be active and stable under dry reforming conditions. The solid-phase crystallization process was studied by *in-situ* synchrotron XRD, and compared to the temperature programmed reduction of each precursor. No carbon accumulation or nanoparticle sintering was observed after 70 h of operation. Furthermore, the evaporation of catalytic Re phases, a major problem under reforming conditions, was shown to be completely blocked due to strong catalyst-support interactions imbued by this synthesis technique.

© 2017 Elsevier B.V. All rights reserved.

1. Introduction

The development of stable and active methane reforming catalysts has received a lot of attention due to the increasing number of natural gas discoveries worldwide. Methane, the primary component of natural gas, is a dangerous greenhouse gas, but also a potential feedstock for the production of synthetic fuels [1,2]. The dry reforming of methane (Reaction 1) is an attractive process for natural gas valorization owing to its ability to consume two greenhouse gasses as reactants and produce synthesis gas with an H_2 -to-CO ratio of 1:1. Such a ratio is favorable for the downstream synthesis of heavy synthetic hydrocarbon fuels [3].



Despite these advantages, large-scale utilization of methane dry reforming has been blocked due to the lack of stable catalysts under reaction conditions. Among the two largest contributors to catalyst instability are the accumulation of carbon (coking) which can block active sites and clog pores, and the sintering of active sites causing a drop in active surface area [4–6]. Rhenium (Re) is a common catalyst

component used in the reforming industry owing to its ability to behave as both a promoter and catalyst for alkane activation [7–9]. In the case of reforming catalysts containing Re, it has been shown that rhenium phases can oxidize and subsequently sublime owing to the high vapor pressure of Re_2O_7 [10]. The sublimation of Re under reaction conditions not only leads to a decrease in activity, but also the loss of an expensive component of the catalyst system.

Reforming catalysts are typically prepared by various metal-oxide techniques such as impregnation, suspension, vapor deposition, electroless deposition, or hybrids thereof [11]. Although widely used, a potential drawback with many of these methods is the tendency for the catalyst phase to have only a superficial interaction with the support. Such a weak catalyst-support interaction can lead to the formation of carbon nanotubes (coking) via the “tip-growth” mechanism, and provides little protection against sintering or sublimation [12].

An alternative method for catalyst preparation is the use of solid-phase-crystallization. When ordered perovskite (ABO_3) frameworks are utilized as catalyst precursors, they have the capability of exsolving certain B-site atoms under reducing conditions through a solid-phase reaction. For example, the reduction of LaNiO_3 by hydrogen leads to the formation of $\text{Ni/La}_2\text{O}_3$, where the Ni nanoparticles are firmly “socketed” into the support thereby giving rise to a comparably strong catalyst-support interaction.

* Corresponding author.

E-mail address: barosen@post.tau.ac.il (B.A. Rosen).

The effectiveness of solid-phase-crystallization for catalyst development is highly dependent on the reducibility of the B-site cation, and more subtly on the microstructure, shape, and non-stoichiometry of the perovskite precursor [13,14]. This technique has been extensively studied in recent years as a sustainable technique for synthesizing a wide variety of catalysts through the use of LaCoO_3 [15,16], LaFeO_3 [16–27], LaNiO_3 [2,5,28–30] or their mixtures as precursor materials. Furthermore, the doping of these precursor structures with heteroatoms such as Ru, Pd [20], Cu, and Mg [29] has given rise to catalytic materials with enhanced activity towards methane reforming reactions. The use of Re-substituted precursors, or the creation of a composite precursor containing Re, have yet to be detailed despite the fact that Re is used as a co-catalyst in industrial reforming processes [31,32].

Here, we report the use of solid-phase-crystallization in order to transform several lanthanum ferrite (LaFeO_3)-based precursors containing nickel (Ni) and/or rhenium (Re). While LaFeO_3 itself is not active, it provides high oxygen mobility and flexible redox character, properties which are instrumental in designing stable reforming catalyst [33]. The precursor materials reported in this study are LaFeO_3 (LF), $\text{LaNi}_{0.2}\text{Fe}_{0.8}\text{O}_3$ (LNF), $\text{LaRe}_x\text{Fe}_{0.8}\text{O}_{3+\delta}$ - La_3ReO_8 (LRF), and $\text{LaNi}_{0.2}\text{Re}_x\text{Fe}_{0.6}\text{O}_{3+\delta}$ - La_3ReO_8 (LNRF) where $x < 0.2$. The incorporation of heptavalent Re into an $\text{A}^{+3}\text{B}^{+3}\text{O}_3$ perovskite such as LaFeO_3 necessarily results in an oxygen non-stoichiometry (δ) in order to maintain charge balance. It has been shown that non-stoichiometric Re substitutions in the B-site can be made to a limited extent (< 0.2) to form stable perovskite-like materials [34–36]. The Re that did not enter the perovskite went to form the competing La_3ReO_8 phase ultimately forming a composite precursor material. For simplicity, the shorthand naming of these materials will be used throughout the paper.

We report the structure of these precursor materials before and after solid-phase crystallization, thereby exsolving nanoparticles containing metallic Ni, Re, and some Fe which function as catalytic active sites. We describe the catalytic activity and stability under methane dry reforming conditions in light of gas conversion and materials characterization.

2. Experimental

2.1. Materials synthesis

The catalyst precursors were prepared by the Pechini method described in detail elsewhere [28,37]. Briefly, the solution was prepared by dissolving the desired ratio of metal precursor salts using lanthanum nitrate hexahydrate ($\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$), iron nitrate nonahydrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) (or iron (II) oxalate dihydrate ($\text{C}_2\text{FeO}_4 \cdot 2\text{H}_2\text{O}$) for Re-containing perovskites), nickel nitrate hexahydrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) and ammonium perrhenate NH_4ReO_4 in Milli-Q water. Citric acid and ethylene glycol were added in excess as complexing agents. The molar ratio of total cations, citric acid, and ethylene glycol was 1:3:3 [38]. The resulting solution was evaporated at 140°C on hot plate under stirring until the solution volume decreased by approximately 33%. Afterwards, the temperature was reduced to 120°C and kept overnight to remove the solvent resulting in an aerogel. The aerogel was then ground and calcined at 400°C for 2 h and then at 700°C for 6 h in air at 1 atm [37].

2.2. Materials characterization

Ex-situ X-ray diffraction (XRD) patterns were recorded on a Scintag powder diffractometer equipped with liquid nitrogen-cooled germanium solid state detector and using $\text{Cu-K}\alpha$ radiation. *In-situ* XRD was performed at Argonne National Laboratory's Advanced

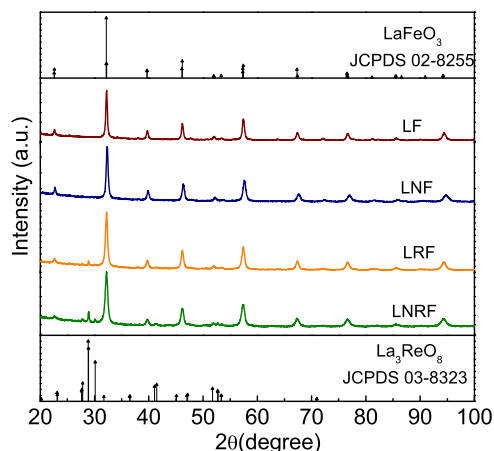


Fig. 1. XRD patterns of all four synthesized precursors along with the JCPDS entry for LF and La_3ReO_8 . Substitution of Ni and/or Re did not destroy the underlying LF structure. Precursors with Re contained a small amount of La_3ReO_8 contaminant.

Photon Source (beamline 6ID-D) using 85.152 eV (0.145586 \AA) synchrotron radiation. Approximately 50 mg of sample was placed in a fused quartz capillary and mounted between two resistive heaters in a transmission X-ray cell described in detail elsewhere [39]. The 2D X-ray detector (Perkin Elmer XRD1621 CN3-EHS) was mounted approximately 1 m from the cell and contained a grid of 2048×2048 pixels (pixel size $200\text{ }\mu\text{m}$). The incident beam size was set to $700\text{ }\mu\text{m} \times 700\text{ }\mu\text{m}$. Data analysis was carried out by Fit2D software and a NIST silicon 640c standard was used for calibration.

Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were performed on a Quanta 200 FEG (field-emission gun) environmental scanning electron microscope and field emission TEM (Tecnai[®] F20, Philips) operated at 200KV, respectively. BET surface area was measured by nitrogen adsorption at -196°C using a Quantachrome ChemBET. Temperature programmed reduction (TPR) and temperature programmed oxidation (TPO) were recorded using the same instrument. Prior to BET, TPR, or TPO measurements, catalysts were degassed at 300°C for 1 h under N_2 flow to remove any residual moisture, then cooled down to room temperature. For TPR and TPO measurements, fresh materials were reduced in a hydrogen mixture ($5\%\text{H}_2/\text{N}_2$) or oxidized in an oxygen mixture ($5\%\text{O}_2/\text{He}$) respectively, while the temperature of the furnace was increased at a heating rate of $10^\circ\text{C}/\text{min}$ to 1050°C . Thermo-gravimetric analysis (TGA) was carried out by TGA 2950 thermogravimetric analyzer in an ambient atmosphere. XPS analysis was performed on a 5600 AES/XPS system (PHI, USA) using an $\text{Al-K}\alpha$ anode ($h\nu = 1486.6\text{ eV}$) as the exciting source. The binding energies obtained in the XPS analysis were standardized for specimen charging using carbon (C 1s) as the reference at 285 eV. The conversion of methane and carbon dioxide into carbon monoxide and hydrogen was monitored using an SRI gas chromatograph fitted with MS-13X and Haysep-C packed columns. Hydrogen was detected using a nitrogen carrier and a TCD detector. CO_2 , CO, and CH_4 were detected using an argon carrier and FID detector with a methanizer placed directly upstream.

2.3. Catalytic activity

Temperature programmed catalytic tests were performed by using 35 mg of catalyst. The catalyst was placed between two pieces of quartz wool inside a 12-mm ID quartz tube ($L = 60\text{ mm}$, $\text{OD} = 15\text{ mm}$) in the isothermal zone of an Electrotherm tube furnace. Before catalytic testing, the sample was heated from room temperature up to 860°C at $20^\circ\text{C}/\text{min}$ in a $50\%\text{H}_2/\text{Ar}$ (50 sccm) atmosphere and held at that temperature for 1 h to activate catalyst

Download English Version:

<https://daneshyari.com/en/article/6454271>

Download Persian Version:

<https://daneshyari.com/article/6454271>

[Daneshyari.com](https://daneshyari.com)