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Rh promoted $La_{0.75}Sr_{0.25}(Fe_{0.8}Co_{0.2})_{1-x}Ga_xO_{3-\delta}$ perovskite catalysts: Characterization and catalytic performance for methane partial oxidation to synthesis gas

R. Palcheva[a,*], U. Olsbye[a], M. Palcut[a,1], P. Rauwel[b], G. Tyuliev[c], N. Velinov[c], H.H. Fjellvåg[a]

[a] InGAP Centre for Research-based Innovation, SMN, University of Oslo, PO Box 1033, Blindern, Oslo 0315 Norway
[b] Department of Physics, SMN, University of Oslo, PO Box B 1048 Blindern, Oslo 0316, Norway
[c] Institute of Catalysis, Bulgarian Academy of Sciences, G. Bonchev Str., Bldg. 11, Sofia 1113, Bulgaria

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ABSTRACT

Synthesis gas production via selective oxidation of methane at 600 °C in a pulse reaction over $La_{0.75}Sr_{0.25}(Fe_{0.8}Co_{0.2})_{1-x}Ga_xO_{3-\delta}$ ($x = 0.1, 0.25, 0.4$) perovskite-supported rhodium catalysts, was investigated. The perovskite oxides were prepared by sol–gel citrate method and characterized by X-ray Diffraction (XRD), Moessbauer Spectroscopy (MS), Temperature Programmed Reduction (TPR-H_2), X-ray Photoelectron Spectroscopy (XPS) and High Resolution Transmission Electron Microscopy (HRTEM). According to XRD analysis, the synthesized samples were a single perovskite phase. The perovskite structure of Ga substituted samples remained stable after TPR-H_2, as confirmed by XRD. Data of MS identified Fe^{3+} ions in two distinctive coordination environments, and Fe^{4+} ions. The Rh_2O_3 thin overlayer was detected by the HRTEM for the Rh impregnated perovskite oxides. During the interaction of methane with oxidized perovskite-supported Rh (0.5 wt.%) catalysts, besides CO, H_2, and surface carbon, CO_2 and H_2O were formed. The Rh perovskite catalyst with $x = 0.25$ gallium exhibits the highest catalytic activity of 83% at 600 °C. The CO selectivity was affected by the reducibility of $La_{0.75}Sr_{0.25}(Fe_{0.8}Co_{0.2})_{1-x}Ga_xO_{3-\delta}$ perovskite materials.

1. Introduction

Using methane to produce synthesis gas $H_2 + CO$ and/or hydrogen can be realised through three reactions, i.e. steam reforming, dry reforming and catalytic partial oxidation [1]. The steam reforming is the most widely used process to produce syngas with a high H_2/CO molar ratio (>3). Catalytic partial oxidation (CPO) of CH_4 is more compact and energy-efficient process for syngas production than steam reforming. However, partial oxidation usually requires the use of pure oxygen, which results in high costs due to air separation. In addition, CPO occurs between gas-phase oxygen and methane, which limits the selectivity of CO and hydrogen due to complete oxidation of methane. An alternative approach is the anaerobic catalytic partial oxidation of methane to syngas via chemical looping applications [2,3]. Chemical looping combustion is a concept where the oxygen is added to the combustion process as a reducible metal oxide often called an oxygen carrier. This method involves a reduction process in which the metal oxide is reduced upon oxidation of the fossil fuel, and an oxidation process in which the metal is reoxidized by air [4,5].

Perovskite-like mixed oxides—ABO_3 (where A and B are usually rare earth and transition metal cations, respectively) can be tailored to create a wide family of catalysts by varying either the A-site or the B-site metal ion, or both [6]. Thus, the substitution of La by Ca, Sr or Ba is known to improve oxygen ion mobility and, hence, the reducibility of the cation at B site. Similarly, the multiple substitutions at catalytically active B sites by some aliovalent transition metal cations lead to enhanced catalytic activity due to synergistic valence changes and resultant non-stoichiometry related micro-structural defects introduced into the lattice [7]. Howerver, too high oxygen mobility may lead to significant lattice strain, eventually reducing the metal-oxygen structure and causing its failure [8]. By partially reducing the perovskite surface it may be

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[*] Corresponding author. Present address: Institute of Catalysis, Bulgarian Academy of Sciences, G. Bonchev str., bldg. 11, 1113 Sofia, Bulgaria. Tel.: +359 2 979 25 03; fax: +359 2 971 29 67.
E-mail address: radost@ic.bas.bg (R. Palcheva).

[1] Present address: Slovak University of Technology in Bratislava, Faculty of Materials Science and Technology in Trnava, Institute of Materials Science, Paulínska 16, 91724 Trnava, Slovak Republic.

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possible to obtain small, yet exposed metal particles embedded in a metal-oxygen lattice structure [8]. A combination of stability and redox properties is reported for $La_{0.8}Sr_{0.2}Co_{0.2}Fe_{0.8}O_{3-\delta}$ system [9]. The substitution of iron by cations having a stable oxidation state, such as Al^{3+} or Ga^{3+} should decrease oxygen non-stoichiometry variations [10].

Dai et al. [11] studying $LaFeO_3$ for CPO suggested that full combustion products are formed from chemisorbed oxygen at particle surfaces, while selective oxidation products are formed from oxygen diffusing from the bulk. Kharton et al. [12] reported a correlation between the degree of reduction and the selectivity for syngas formation over $La_{0.3}Sr_{0.7}Fe_{0.8}M_{0.2}O_{3-\delta}$ (M = Ga, Al) and $SrFe_{0.7}Al_{0.3}O_{3-\delta}$.

Combining noble metals with perovskites could facilitate partial insertion of the metal to the support, which leads to retardation of metal particles sintering [13]. It has been observed that the noble metal based catalysts are highly active for partial oxidation of methane, but their activity and stability depends strongly on the kind of carrier [14,15] and Rh is one suitable component for syngas and hydrogen production [16,17]. Slagtern and Olsbye [18] reported the formation of active metal species for synthesis gas production on $LaBO_3$ (B = Rh, Ni, Co) perovskites. The best system, $LaRhO_3$, displayed a high activity at 800 °C and exhibited a good dispersion of Rh particles on the La_2O_3 phase [18]. Recent investigations in our laboratory of Rh promoted $La_{0.8}Sr_{0.2}Fe_{0.8}Co_{0.2}O_{3-\delta}$ perovskites or with Al substitution ($La_{0.75}Sr_{0.25}Fe_{0.6}Co_{0.15}Al_{0.25}O_{3-\delta}$) and of $Pt/Ce_xZr_{1-x}O_2$ catalysts points out the correlation between the syngas selectivity and the bulk oxidation potential of Rh supported perovskites and $Pt/Ce_xZr_{1-x}O_2$ catalysts during CPO at 685 °C in the absence of the gas-phase oxygen [19,20].

The purpose of this study is to adjust the redox properties of the perovskite by varying the stoichiometry of the B element $La_{0.75}Sr_{0.25}(Fe_{0.8}Co_{0.2})_{1-x}Ga_xO_{3-\delta}$ (x = 0.1, 0.25, 0.4) and to evaluate the effect of gallium addition on the performance of Rh promoted perovskites for partial oxidation of CH_4 to synthesis gas at 600 °C. Furthermore, XPS analysis enabled determination of the catalysts surface concentration, while the iron and cobalt redox properties were evaluated by temperature programmed reduction under H_2 and flowing titration method.

2. Experimental

2.1. Sample synthesis

Perovskite materials of nominal composition $La_{0.75}Sr_{0.25}(Fe_{0.80}Co_{0.20})_{(1-x)}Ga_xO_{3-\delta}$ (x = 0.10, 0.25, 0.40) were prepared by sol–gel citrate method. $Sr(NO_3)_2$ (Fluka, ≥99.0), Co(II)acetate tetrahydrate (Fluka, ≥99.0), La_2O_3 (Sigma–Aldrich, 99.99), $Ga(NO_3)_3{\cdot}9H_2O$ (Merck, ≥99.0) and $Fe(NO_3)_3{\cdot}9H_2O$ (Merck, ≥99.0) were used as reagents. La_2O_3 was dissolved in nitric acid while metal nitrates were dissolved in water and mixed in respective concentrations with a surplus of citric acid (4:1). The resulting transparent solution was heated and continuously stirred. Water and residual NO_x gases were removed by careful evaporation at 100–120 °C over the course of several hours. The remaining gel was dried in a heating cabinet at 200 °C overnight. Next day, the precursor powder was crushed in an agate mortar and further calcined at 450 °C for 5 h. The final ceramic powders were prepared by annealing at 1000 °C in air. The heat-treatment was carried out twice, with an intermediate powder crushing between annealing steps. Rhodium (0.5 wt.%) was deposited on the sample grains by incipient-wetness technique. $Rh(NO_3)_3{\cdot}2H_2O$ from Alfa-Aesar was used. After impregnation, the samples were heat-treated at 800 °C for 10 h.

The impregnated samples were named Rh/Ga10, Rh/Ga25, Rh/Ga40, where the number indicates the nominal content of Ga, i.e. 100× at the B site. The Rh deposited on $La_{0.8}Sr_{0.2}Fe_{0.8}Co_{0.2}O_{3-\delta}$ is named Rh/Ga0.

2.2. Characterization

XRD spectra were collected within the 2θ range from 5° to 80°, with a constant step of 0.02°, on Bruker D8 Advance diffractometer with Cu Kα radiation and LynxEye detector.

MS of synthesized perovskite type oxides were recorded at 295 K on a Wissel electromechanical Moessbauer spectrometer (Wissenschaftliche Elektronik GmbH, Germany) working in a constant acceleration mode at room temperature. A $^{57}Co/Cr$ (activity ≈10 mCi) source and α-Fe standard were used. The experimental spectra were treated using the least squares method. The parameters of hyperfine interaction such as isomer shift (IS), quadrupole splitting (QS) and effective internal magnetic field (Heff) as well as the line widths (FWHM) and the relative weight (G) of the partial components of the spectra were determined.

TPR-H_2 experiments were carried out in the measurement cell of a differential scanning calorimeter (DSC), directly connected to a gas chromatograph (GC), in the 10–700 °C range at a 10 K/min heating rate in a flow of H_2/Ar = 1:9, the total flow rate being 20 ml/min. A cooling trap between DSC and GC removes the water produced during the reduction.

The XPS measurements were carried out in the analysis chamber of the electron spectrometer ESCALAB-MkII (VG Scientific) with base pressure of $\sim 2 \times 10^{-10}$ mbar. The spectra were excited with nonmonochromatized Al K_α radiation with energy 1486.6 eV. Due to the overlap of Co2p and OKLL Auger lines using the Mg K_α radiation is not appropriate in this study. Powder samples were pressed into standard holders and pumped before analysis in the preparation chamber down to pressure of $\sim 1 \times 10^{-9}$ mbar. All samples possess rather good electrical conductivity but in a number of cases small surface charge was observed, i.e. it was necessary to calibrate the energy scale by using the C1s signal of adventitions carbon centered at 285.0 eV. All samples were analyzed also after TPR measurements. After reduction treatment the samples were allowed to cool to room temperature in H_2/Ar gas mixture and then within few minites were inserted into spectrometer for XPS analysis.

The surface atomic concentrations were derived from the photoelectron intensities divided by the corresponding photo ionization cross sections taken from Scofield [21].

HRTEM of fresh and spent Rh/Ga25 samples was carried out in a JEOL 2010F field emission electron microscope operating at 200 keV. The samples were prepared by sonicating a small amount of the catalyst suspended in ethanol and placing a drop of the suspension on a carbon coated grid for observations.

2.3. Equilibrium measurement

The oxygen non-stoichiometry of perovskite samples was investigated at low oxygen partial pressures by modification of method previously developed by Kim et al. [22]. The authors investigated the thermodynamic properties of zirconium-doped ceria samples equilibrated in H_2O/H_2 mixtures at 600–900 °C. Our perovskite sample (0.5 g) was mounted in a tubular quartz reactor (inner diameter 8 mm) and heated to 600 °C in a constant air flow (5 ml/min). Once the peak temperature was achieved, the gas feed was switched to a mixture of CO_2 and H_2. A specific oxygen partial pressure was established through the equilibrium of the following reactions

$$CO_2 \rightleftarrows CO + \frac{1}{2}O_2 \quad p_{O_2} = \left[K_1 \frac{p_{CO_2}}{p_{CO}}\right]^2 \tag{1}$$