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Tuning the dimensionality of layered $Sr_{n+1}Ti_{n-x}Ni_xO_{3n+1}$ perovskite structures for improved activity in syngas generation

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ABSTRACT

Interest in perovskite type oxides is growing due to their versatile catalytic applications. A series of Ruddlesden-Popper (RP) type layered perovskite oxides $Sr_{n+1}Ti_{n-x}Ni_xO_{3n+1}$ were prepared and evaluated for their catalytic activity in steam reforming, CO_2 reforming and bi-reforming of methane. These materials, prepared through citrate gel method were characterized to understand their structure and Ni reducibility. Substitution of Ni in RP phases was established through refinement of XRD powder pattern. During methane reforming, the catalytic activity increased with the order of RP phase of $SrTi_{1-x}Ni_xO_{3-\delta}$ ($n = \infty$). TPR results show variation in Ni reducibility with the order of RP phase, while TPD-O_2 study helped to estimate oxygen vacancies. These vacancies seem to influence catalytic activity during methane reforming. Transient pulse experiments show that CO_2 dissociates over oxygen vacancies to give CO and oxygen, with later replenishing lattice oxygen in $SrTi_{0.8}Ni_{0.2}O_{3-\delta}$ ($n = \infty$) phases. Highly labile oxygen vacancies generated in the bulk of $SrTi_{0.8}Ni_{0.2}O_{3-\delta}$ must be migrating to the surface, helping in the removal of coke formed. Characterization of catalysts after reaction helped in better understanding of coke precursors.

1. Introduction

Combustion of fossil fuels like coal, petroleum and natural gas are the main cause for the release of huge quantities of CO_2 to the atmosphere, which appears to be responsible for global warming. Moreover, the fossil fuel resources are fast depleting, while there is a continuous growth in energy consumption worldwide. Hence, the researchers are motivated for the development of new energy production routes that will leave low carbon footprint. In addition to its containment, if there are viable routes available for recycling of CO_2, it will be a huge incentive. Synthesis gas (syngas) is an important feed stock for the production of Fischer-Tropsch (FT) products like diesel, methanol, dimethyl ether and olefins. On further processing, syngas becomes a source of H_2 for fuel cells [1]. Hydrogen to carbon monoxide ratio (H_2/CO) plays an important role in synthesizing a desired hydrocarbon product. The conversion of natural gas to syngas or hydrogen is usually accomplished through (i) steam reforming (SR); (ii) dry reforming of methane (DRM) or (iii) partial oxidation (PO) of methane. Other processes like combined reforming and auto thermal reforming (ATR) are derived from these process. Steam reforming of methane was first commercialized in 1930s which is used for syngas or H_2 production as shown in Eq. (1).

$$CH_4(g) + H_2O(g) \leftrightarrow 3H_2(g) + CO(g) \quad \Delta H^{\circ}_{298K} = +206\ \text{kJ/mol} \quad (1)$$

Steam reforming is a highly endothermic process; hence it needs high temperatures to maximize conversion of methane. Such high temperatures lead to catalyst deactivation through coke formation and as a result of active metal sintering at high temperatures. Though as per stoichiometry in the above equation, only one mole of water is required to convert one mole of methane, usually excess water in the form of steam is used to avoid carbon formation on catalyst surfaces. Industrial plants operate at steam to carbon ratios in the range of 2.5–3.0 for natural gas [2,3]. In parallel to SR reaction, water gas shift reaction also takes place as represented in Eq. (2).

$$CO(g) + H_2O(g) \leftrightarrow H_2(g) + CO_2(g) \quad \Delta H^{\circ}_{298K} = -41\ \text{kJ/mol} \quad (2)$$

On the otherhand, syngas also can be produced by reacting methane with CO_2, which is called dry reforming of methane (DRM) as shown in Eq. (3). Recently, this reaction gained considerable attention in the academia and industries, as it converts two major greenhouse gases to value added products [4]. In addition

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to dry reforming reaction, the product H_2 also reacts with CO_2 to give additional CO through reverse water gas shift reaction (RWGS), as shown in Eq. (4).

$$CH_4(g) + CO_2(g) \leftrightarrow 2H_2(g) + 2CO(g) \quad \Delta H^{\circ}_{298K} = +247\ \text{kJ/mol} \tag{3}$$

$$CO_2(g) + H_2(g) \leftrightarrow CO(g) + H_2O(g) \quad \Delta H^{\circ}_{298K} = +41\ \text{kJ/mol} \tag{4}$$

The RWGS reaction is an endothermic reaction and predominant at high temperatures. Major drawback of this reaction is that it consumes valuable H_2, thus reducing the H_2/CO ratio in the syngas. In addition, higher CO content in the product can lead to domination of disproportionation of CO, which is called Boudouard reaction, leading to the formation of carbon over the catalyst (Eq. (5)). Apart from steam reforming, dry reforming, RWGS and Boudouard reactions, many other side reactions occur depending on the operating conditions and partial pressure of the reactants. One important reaction among them is that methane cracking or dissociation leading to the deposition of carbon on the surface of catalyst as given in Eq. (6).

$$2CO(g) \leftrightarrow C(s) + CO_2(g) \quad \Delta H^{\circ}_{298K} = -171\ \text{kJ/mol} \tag{5}$$

$$CH_4(g) \leftrightarrow C(s) + 2H_2(g) \quad \Delta H^{\circ}_{298K} = +75\ \text{kJ/mol} \tag{6}$$

As a consequence of the above side reactions, catalysts deactivate rapidly due to coke deposition on the surface of the catalyst. To overcome the coking problem, bi-reforming of methane, which is a combination of SR and DRM, could offer a solution. In addition, through bi-reforming, it is possible to obtain syngas with desirable H_2/CO ratio, based on the H_2O fraction (CH_4:CO_2:H_2O molar ratios) in the reaction feed. This combination of reactions need catalyst that is specifically designed to be active for both steam and dry reforming reactions without any deactivation, thus sustaining activity for thousands of hours.

$$3CH_4(g) + 2H_2O(g) + CO_2(g) \rightarrow 8H_2(g) + 4_{CO}(g)$$
$$\Delta H^{\circ}_{298K} = +220\ \text{kJ/mol} \tag{7}$$

The catalysts required for the combination of SR and DRM are also expected to show high resistance to the coke formation and should have high mechanical strength [5–8]. Moreover, the active metal should be able to undergo oxy-reduction cycles without getting over oxidized. Most of the reported catalysts for this combination reaction are based on transition metals like Pt, Ru, Rh and Ni deposited on several supports [9–13]. Compared to precious metals, based on cost and availability, nickel based catalyst are preferable for industrial applications. Hence, developing a commercially viable catalyst, which is resistant to deactivation is the motivation in the synthesis of Ruddlesden-Popper (RP) type layered perovskite $Sr_{n+1}Ti_{n-x}Ni_xO_{3n+1}$ type oxides and their evaluation for SR, DRM and the combined reforming reactions.

Perovskites phases are well known for their applications as magnetic materials, semiconductors, room temperature super conductors, ferroelectrics, dielectrics, piezoelectric and as catalysts. The A_2BO_4 type compounds and ABO_3 compounds are end members of homologous series of Ruddlesden Popper (RP) type phases given by the general formulae $A_{n+1}B_nO_{3n+1}$ or $AO(ABO_3)_n$. where n2D layers of BO_6 corner sharing octahedra are joined along the stacking direction and separated by rock-salt AO layers along the crystallographic c-axis [14,15]. These RP phases exhibit interesting physical and catalytic properties [16], where A is the rare earth and/or alkaline earth ion and B is the transition metal ion in RP phases. Schematic presentation of strontium titanate RP phases are shown in Fig. S1.

For the first time, here we report the synthesis of strontium titanate RP phases using citrate gel method, both in presence and absence of Ni. A comparative investigation of catalytic properties as a function of mixed valence at B site and dimensionality of the structured oxide has been carried out. The RP phases of $Sr_2Ti_{1-x}Ni_xO_{4-\delta}$ (n = 1) phase and the higher-order of Ruddlesden-Popper phases (RP) $Sr_{n+1}Ti_{n-x}Ni_xO_{3n+1}$ (n = 2, 3 and ∞), has been undertaken to determine their activity in the reforming of CH_4 reaction using steam and CO_2.

2. Experimental

2.1. Catalyst synthesis

Synthesis of Ruddlesden Popper (RP) type oxide phases of $Sr_{n+1}Ti_nO_{3n+1}$ and $Sr_{n+1}Ti_{n-x}Ni_xO_{3n+1}$ (n = 1, 2, 3 and ∞) perovskites was carried out by citrate gel method [17]. Required quantities of $Sr(NO_3)_2$, $Ni(NO_3)_2{\cdot}6H_2O$ and $Ti[O(CH_3)_3CH_3]_4$ were dissolved in minimum required water and mixed together. This solution was added drop wise to the citric acid under vigorous stirring at 80 °C in a fume hood. The molar ratio of citric acid to nitrate salts was 3:1. The solution was heated under stirring, till most of the water is evaporated to form a gel. The gel was heated at 180 °C for 12 h to obtain spongy material. This fluffy material was powdered and calcined in air flow at 750 °C for 6 h to obtain RP phases.

Nickel susbstituted RP phases are designated based on their compositions as $Sr_2Ti_{0.7}Ni_{0.3}O_4$ (n_1), $Sr_3Ti_{1.5}Ni_{0.5}O_7$ (n_2), $Sr_4Ti_{2.3}Ni_{0.7}O_{10}$ (n_3) and $SrTi_{0.8}Ni_{0.2}O_3$ (n_∞).

2.2. Characterization

Powder X-Ray diffraction pattern of the materials were collected using PANalytical X'pert Pro diffractometer equipped with an X'celerator solid-state detector. Nickel filtered Cu Kα (λ = 1.5418 Å, 40 kV, 30 mA) was used to collect the data using a flat holder in Bragg-Brentano geometry. The XRD patterns were recorded in 2θ range of 10–90° in 0.02° steps. Rietveld refinement of XRD patterns were carried out by means of GSAS code.

The Brunauer-Emmett-Teller (BET) surface area of the samples was measured by nitrogen sorption at liquid nitrogen temperature (−196 °C) using Quantachrome Autosorb iQ instrument. Prior to N_2 adsorption, the samples were degassed at 300 °C for 3 h to remove residual moisture and trapped volatiles in the sample.

Active metal dispersion and surface area of Ni was determined by means of CO chemisorption using Quantachrome Autosorb-iQ. Before measurement, samples were reduced in-situ in hydrogen stream at 500 °C for 2 h and cooled to 40 °C in vacuum. Following this, the CO adsorption isotherms, both physisorption and chemisorption were obtained. Chemisorbed CO uptakes were determined by extrapolating the linear portion of the chemisorbed isotherm to zero pressure. The dispersion of Ni was calculated with the assumption that the stoichiometry of CO to Ni (surface) is equal to 2.

X-ray photoelectron spectroscopy (XPS) investigations were conducted using VG Scienta's R3000HP analyzer spectrometer, equipped with a concentric hemispherical analyzer. Al Kα monochromator MX 650 X-ray source was used for excitation, by maintaining the chamber pressure at 3×10^{-9} mbar. Sample was mounted on a sample holder in a preparation chamber, which was transferred to an analyzing chamber after reaching the targeted vacuum. The binding energy (BE) was calibrated with reference to the C 1s value of a carbon (285.0 eV) on the surface of the sample.

Temperature programmed reduction (TPR) profiles were obtained using Micromeritics Autochem 2920 system, equipped with TCD detector. Freshly calcined samples were heated to 400 °C in 5% O_2-He gas mixture (30 ml min^{-1}) at a heating rate of 5 °C min^{-1}. Following this heat treatment for 1 h, the sample was cooled