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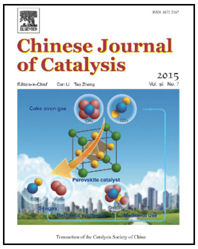

Article

Synthesis, characterization, and catalytic performance of $La_{0.6}Sr_{0.4}Ni_xCo_{1-x}O_3$ perovskite catalysts in dry reforming of coke oven gas

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ABSTRACT

The dry reforming of coke oven gas (COG) to produce syngas was performed over $La_{0.6}Sr_{0.4}Ni_xCo_{1-x}O_3$ catalysts in a fixed-bed reactor at 800 °C. These perovskite-type oxides were synthesized using a sol-gel method and characterized using X-ray diffraction (XRD), N_2 adsorption-desorption, temperature-programmed reduction of H_2, scanning electron microscopy, transmission electron microscopy, and thermogravimetry-differential scanning calorimetry. XRD results showed that the $La_{0.6}Sr_{0.4}Ni_xCo_{1-x}O_3$ perovskite-type oxides formed quaternary solid solutions. The effects of the degree of Ni substitution (x) and the catalyst calcination temperature on the dry reforming of COG were investigated. XRD analysis of the tested catalysts showed the formation of Ni^0, Co^0, and $La_2O_2CO_3$, of which the latter is the main active phase responsible for the high activity and stability, and the suppression of coke formation under severe reaction conditions. COG rich in H_2 can also reduce the formation of carbon deposits by inhibiting CH_4 decomposition.

1. Introduction

Synthesis gas is an important feedstock for the petrochemical industry, and consists mainly of H_2 and CO. It is widely produced from natural gas (CH_4) and is used in a diverse range of industrial processes [1,2]. The established techniques for producing syngas are effective, and depend on the different characteristics of the CH_4 reforming reactions [3,4] such as steam reforming, dry reforming, and partial oxidation reforming [5]. Among these natural reforming processes, in terms of global warming and growing energy needs, dry reforming or CO_2 reforming of CH_4 ($CH_4 + CO_2 \rightarrow 2CO + 2H_2$) has been shown to have significant environmental and economic advantages, because two harmful greenhouse gases are converted to green H_2. This process is stimulating increasing interest, because it produces syngas with a low H_2/CO ratio, which is preferable for liquid hydrocarbon production in the Fischer-Tropsch reaction [6–8].

Most current studies in this field concentrate on CO_2 reforming of CH_4 from natural gas, but other CH_4 sources are also appropriate for the reaction [9]. One such alternative is coke oven gas (COG), which is a by-product of coke production from coal in the steel industry [10,11]. The composition of COG is typically H_2 (~58%–60%), CH_4 (~23%–27%), CO (~5%–8%),

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and CO_2 (less than 3%). Only a small fraction of the COG can be used as fuel in the coking plant; the rest is generally burnt off or even discharged into the atmosphere [12]. The environmental impact is large, because of the substantial greenhouse gas emissions [13,14]. Much attention has therefore been given to the CO_2 reforming of COG, which can provide a more sustainable solution for the transformation of this highly energetic gas and minimization of CO_2 concentration [15]. The most significant feature of this alternative is the production of syngas with a H_2/CO ratio close to 2, the ideal proportion for methanol synthesis, without any conditioning stages. Another interesting characteristic of CO_2 reforming of COG is that the energy required for this endothermic reaction can be provided by the blast furnace, which produces a large volume of exhaust gas [16]. Furthermore, CO_2 reforming of COG is a catalysed reaction for which the rapid deactivation of the catalyst caused by carbon deposition is a serious problem [17]. The development of catalysts with high activities and stabilities, and which inhibit carbon formation during the reforming reaction, is therefore important.

In recent decades, noble-metal-based catalysts have been reported to be less sensitive to coking than Ni-based catalysts. However, Ni-based catalysts still warrant investigation, because their low cost and high availability make them more affordable in commercial processes [18,19]. In this respect, one strategy is to introduce Ni and/or Co in a defined structure or solid solution. Perovskite-type oxides (ABO_3) with a well-defined structure have interesting redox properties and are accessible, enabling them to acquire very highly dispersed nanoscale metallic particles under a reducing atmosphere; this promotes the catalytic activity and diminishes coke formation [20,21]. Another advantage of perovskite-type oxides is the wide range of possible substitutions of A and/or B cations, enabling combination of elements with different oxidation states [22].

Valderrama et al. [23] used the B-site-substituted perovskite-type oxide $LaNi_{1-x}Co_xO_3$ as a catalyst precursor for the dry reforming of CH_4. Ni^0, Co^0, and $La_2O_2CO_3$ were formed in catalytic tests, and gave high activities and stabilities. Sutthiumpor et al. [24] found that a small amount of Sr with a promotional doping element in the A site gave a better catalytic performance, because of the presence of surface oxygen species.

However, there have been few studies of B-site-substituted perovskite-type oxides with a fixed A-site doping content. The main objective of this study was therefore to investigate the activities and stabilities of quaternary solid solutions, $La_{0.6}Sr_{0.4}Ni_xCo_{1-x}O_3$, as catalysts for CO_2 reforming of COG in a fixed-bed reactor. The effect of calcination temperature on the catalytic performance was also studied.

2. Experimental

2.1. Catalyst preparation

$La_{0.6}Sr_{0.4}Ni_xCo_{1-x}O_3$ quaternary perovskite-type oxides were prepared using a sol-gel method. Stoichiometric quantities of $La(NO_3)_3·6H_2O$, $Sr(NO_3)_2$, $Ni(NO_3)_2·6H_2O$, and $Co(NO_3)_2·6H_2O$ were mixed and dissolved in the required amount of deionized water. Ethylenediaminetetraacetic acid (EDTA) and citric acid (CA) were added to the aqueous solution as complexing agents, in appropriate molar ratios (all metal ions/EDTA/CA = 1:1:1.5) [25,26], and the pH was adjusted to 7–8 by ammonia titration. The resulting solution was stirred at near 100 °C with an electromagnetic agitator until evaporation of water had reduced the solution to a hyaloid gel. This gel was dried overnight at 120 °C, and calcined in air for 6 h, after heating to 850 °C at a rate of 5 °C/min.

2.2. Sample characterization

The phase compositions and internal structures of the catalysts before and after reaction were identified by X-ray diffraction (XRD), using a Rigaku D/Max-2200 X-ray diffractometer. The scans (2θ) were conducted over the range 10° to 90° at a rate of 6°/min, using Cu K_α radiation (40 kV, 40 mA).

The surface areas and pore sizes of the solids were measured by N_2 adsorption-desorption at −196 °C, using a Micromeritics ASAP 2010 adsorption meter; the samples (0.1–0.2 g) were degassed for 2 h at 200 °C before measurement.

Temperature-programmed reduction (TPR) studies were performed using a Micromeritics AutoChem II 2920 instrument equipped with a thermal conductivity detector (TCD) under a flow of a reducing H_2 mixture. Samples (0.1 g) of fine catalyst were placed in a quartz-tube reactor of radius 5 mm, heated to 200 °C, and purged at constant temperature in an Ar atmosphere. A mixture of 5% H_2 in Ar was then passed through the reaction tube at a flow rate of 30 mL/min; the temperature was increased to 1000 °C at 10 °C/min. The effluent gas was monitored by the TCD to detect variations in the H_2 concentration, which indicate the possible compositions of subproducts.

The morphologies and elemental compositions of the catalysts, and metal dispersion and carbon deposition on the catalysts after the reaction were determined using field-emission scanning electronic microscopy (FE-SEM; JEOL JSM-6700F) and transmission electron microscopy (TEM; JEOL JEM 200CX).

Thermogravimetry-differential scanning calorimetry (TG-DSC) was performed, using a thermal analyser (NETZSCH STA 449 F3), to measure the amount of deposited carbon on the catalyst after reaction. In the TG-DSC process, a sample (20 mg) was exposed to a gas mixture consisting of 10% O_2 in N_2 at a flow rate of 40 mL/min, while the temperature was raised from ambient to 900 °C at a rate of 10 °C/min.

Temperature-programmed hydrogenation (TPH) was also performed using the Micromeritics AutoChem II 2920. A sample (50 mg) of each tested catalyst was placed in a quartz tube and heated to 950 °C at a rate of 10 °C/min under 10% H_2 in Ar. The TPH tail gas was tested using a microreactor-mass spectrometer (Hiden Analytical, Catlab).

2.3. Dry reforming of COG

Catalytic activity tests were performed at atmospheric pressure in a 6-mm internal diameter quartz-tube reactor installed in a fixed-bed continuous flow system, as we have pre-