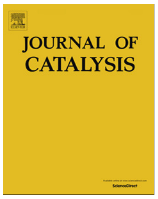
Journal of Catalysis 358 (2018) 168–178

Contents lists available at ScienceDirect

Journal of Catalysis

journal homepage: www.elsevier.com/locate/jcat



$LaFe_{0.9}Ni_{0.1}O_3$ perovskite catalyst with enhanced activity and coke-resistance for dry reforming of ethane

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ARTICLE INFO

Article history:
Received 7 August 2017
Revised 6 December 2017
Accepted 10 December 2017

Keywords:
Perovskite
Dry reforming
Coke-resistance
Oxygen vacancy
CO_2

ABSTRACT

A $LaFe_{0.9}Ni_{0.1}O_3$ perovskite catalyst was evaluated for dry reforming of ethane (DRE), with two conventional oxide supported Ni catalysts (Ni/La_2O_3 and $NiFe/La_2O_3$) being used as references. $LaFe_{0.9}Ni_{0.1}O_3$ showed the best activity and high coke-/sintering-resistance. TEM, TGA, and Raman characterizations confirmed that the deactivation of Ni/La_2O_3 was owing to the growth of Ni particles and the accumulation of coke, although the formation of $La_2O_2CO_3$ was able to remove part of the coke during the reaction. The introduction of Fe-related species inhibited the coke formation while decreased the activity due to the loss of active sites. A portion of Ni ions in the perovskite lattice could be reduced to form highly dispersed and stable Ni nanoparticles on the surface during the reaction and oxygen vacancies were left in the perovskite lattice. Pulse reactor studies revealed that the oxygen vacancies in the perovskite could facilitate the activation and dissociation of CO_2 to form CO and reactive oxygen species. Moreover, C_2H_6 was activated with the assistance of oxygen from the surface or subsurface of $LaFe_{0.9}Ni_{0.1}O_3$ to form CO, rather than directly dissociated to surface carbon species as observed over Ni/La_2O_3.

1. Introduction

The reduction of CO_2 emissions has attracted worldwide attention due to the global warming and ocean acidification effects [1–4]. The discoveries of abundant shale gas offer the possibility of catalytic converting CO_2 into CO using light alkanes from shale gas. Dry reforming of methane (DRM) has been widely investigated because it can convert CH_4 and CO_2 into syngas (CO and H_2), which can be used as feedstock to produce chemicals and fuels by the Fischer-Tropsch and methanol synthesis processes [5–8]. However, the DRM process is highly energy-consuming and the catalysts usually suffer from the sintering of active sites and coke formation due to the high operating temperatures [6,9,10]. On the other hand, ethane is the second-largest component (typically ~ 10 wt%) of shale gas after methane. It is an alternative way to convert CO_2 to syngas via the dry reforming of ethane (DRE) process as follows:

$$C_2H_6 + 2CO_2 \rightarrow 4CO + 3H_2(\Delta H^{\circ}_{298K} = 428.1\ \text{kJ mol}^{-1})$$

The DRE reaction can reach $\Delta G < 0$ at a temperature that is approximately 100 K lower than that of the DRM, which could potentially reduce the operating cost and catalyst deactivation [9].

Ni-based catalysts have been extensively explored for dry reforming of alkanes using CO_2 with the advantages of considerable catalytic activity and lower cost compared to precious metal catalysts [11–16]. However, catalyst deactivation due to metal sintering and coke formation still limits their practical industrial applications [17]. For Ni-based catalysts, several methods are employed to overcome the drawbacks: (i) alloying Ni with other metals such as Pt, Co, and Fe [7,10,18–21]; (ii) using functional supports or promoters (K and Na, etc.) to assist the removal of coke [11,22]; and (iii) increasing the extent of metal-support interactions [4,23].

Recently, Kim et al. reported that when Fe was added into the $Ni/Mg_xAl_yO_z$ catalysts, Fe-Ni alloy formed and played the role as

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https://doi.org/10.1016/j.jcat.2017.12.012

the active phase for DRM [7]. In their studies, FeO_x was formed during the dry reforming process and it reacted with the coke via a redox mechanism to produce CO, resulting in a lower degree of coke deposition. In general, supports with acidity are more inclined to cause coke deposition. On the contrary, La_2O_3 is a basic support and can promote CO_2 adsorption, activation, and absorption due to the mild acidity of CO_2. Thus, using La_2O_3 as the functional support for Ni was widely reported [11,18,24]. These Ni/La_2O_3 catalysts were synthesized via typical loading methods, such as the impregnation method [11,18,24], or derived from the $LaNiO_3$ perovskite [25,26]. According to the literature [11], the activation of CO_2 occurred on the La_2O_3 support with the formation of $La_2O_2CO_3$ during the reaction. $La_2O_2CO_3$ could further react with carbon near the Ni nanoparticles to produce CO and regenerate La_2O_3. The strong metal-support interaction (SMSI) is another key factor that can influence the performance of Ni-based catalysts. For example, good comparisons have been made among Ni/CeO_2 catalysts for DRM, in which CeO_2 with different exposed facets were used as supports [23,27]. The catalyst with the strongest interaction between Ni and CeO_2 had the best stability compared to the other ones.

Perovskites with the ideal general formula of ABO_3 are known as versatile materials that allow different cations to be incorporated into their structures [25,28,29]. Unlike the $LaNiO_3$ perovskite that would be destroyed under reforming conditions, some other perovskites, such as $LaFeO_3$ and $SrTiO_3$, are rather stable to endure high temperatures even in a reductive atmosphere [30]. Ni ions could be located in the B sites of those stable perovskites and reduced to form surface nanoparticles in the reforming process. Generally, these Ni nanoparticles are firmly incorporated into their parent lattice, resulting in an SMSI effect [30–35]. Zubenko et al. synthesized Ni-doped lanthanum-iron perovskites for DRM and they attributed the decrease of coke formation to the SMSI effect [31]. Similar results and conclusions were also reached over the $La_{0.52}Sr_{0.28}Ni_{0.06}Ti_{0.94}O_3$ and several other Ni-perovskite catalysts [33,35]. However, to the best of our knowledge, the correlations between the catalytic performance (e.g., activity and stability) and structural properties (e.g., Ni nanoparticles and oxygen vacancies) are still unclear.

Herein, the catalytic performance of the $LaFe_{0.9}Ni_{0.1}O_3$ perovskite for the DRE reaction was studied and compared with the Ni/La_2O_3, $NiFe/La_2O_3$, and $LaFeO_3$ catalysts. The physical and chemical properties of the catalysts were characterized by various techniques. Moreover, pulse reactor studies were conducted to explore the effect of oxygen vacancies on the catalytic activity and the mechanism for coking resistance.

2. Experimental

2.1. Catalyst synthesis

The perovskites, $LaFe_{1-x}Ni_xO_3$ ($x = 0$ and 0.1), were prepared using a citrate method that was similar to the process reported in the literature [32], using $La(NO_3)_3 \cdot 6H_2O$ (99.9%, Alfa Aesar), $Fe(NO_3)_3 \cdot 9H_2O$ (99.99%, Sigma-Aldrich), $Ni(NO_3)_2 \cdot 6H_2O$ (99.999%, Sigma-Aldrich), and citric acid (99+%, Alfa Aesar). The nitrates with stoichiometric ratios were dissolved in deionized water. Then 10% excess citric acid over the number of ionic equivalents of cations was added to the solution. The resulting solution was evaporated at 363 K under vigorous stirring to get a gel. Then a spongy amorphous citrate precursor was obtained after the gel was dried at 383 K in an oven overnight. The citrate precursor was milled and calcined in static air at 573 K for 1 h to decompose the organics, then heated to 1023 K and held for 5 h to obtain the perovskite structure. The temperature ramping rate was 1 K min^{-1} in the calcination process.

The Ni/La_2O_3 and $NiFe/La_2O_3$ catalysts were prepared by the wetness impregnation method. The La_2O_3 support was synthesized using the same procedure as mentioned above for perovskite synthesis. Then the metal salts were impregnated onto the support with excess water. The Ni content for all Ni-contained catalysts was 2.41 wt%, while the Fe loading amount for the $NiFe/La_2O_3$ catalyst was 2.29 wt%. After being dried at 383 K overnight, the supported catalysts were calcined at 723 K for 4 h.

2.2. Catalyst characterization

The *ex-situ* and *in-situ* high-resolution synchrotron X-ray diffraction (XRD) patterns with a wavelength of 0.24128 Å were collected at beamline 17-BM of advanced photon source (APS) at Argonne National Lab (ANL). For the *in-situ* experiments, an amorphous silica capillary containing catalysts was mounted to a flow cell setup, as described in detail in previous work [10,36]. During the measurement, a gaseous mixture of C_2H_6, CO_2, and He with a volume ratio of 1/1/2 (10 mL min^{-1} in total) was first passed through the capillary, aiming at detecting the structure evolution in reaction gases. The temperature was increased from 300 to 873 K at a rate of 20 K min^{-1} and then held at 873 K for 40 min. After that, C_2H_6 was cut off to leave CO_2 (2.5 mL min^{-1}) and He (7.5 mL min^{-1}) in the gas flow for 30 min. Then the gas was switched to H_2 (5.0 mL min^{-1}) and He (5.0 mL min^{-1}) for 30 min to test the stability of the structure in a stronger reductive environment.

The Brunauer-Emmett-Teller (BET) specific surface area was determined based on N_2 adsorption recorded at 77 K using an AMI-300ip (Altamira) instrument, which was equipped with a thermal conductivity detector (TCD). Prior to the N_2 adsorption, the catalysts were purged at 383 K in a He flow for 30 min to desorb the moisture and other gases adsorbed on the catalysts.

H_2 temperature-programmed reduction (TPR) experiments were performed using the AMI-300ip instrument. For each TPR experiment, approximately 50 mg catalyst was put into a U-shaped quartz tube and pretreated at 573 K for 30 min in a 10% O_2/He flow (50 mL min^{-1}). After the reactor being cooled down to 300 K a gas mixture of 10% H_2/Ar was introduced into the reactor at a flow rate of 50 mL min^{-1}. Then the TCD signal of hydrogen was continuously recorded while the sample was heated to 1273 K with a heating rate of 10 K min^{-1}.

Pulse CO chemisorption was also carried out on the Altamira AMI-300iP instrument to measure the amount of CO uptake on each catalyst. About 100 mg catalyst was used in each experiment and the catalyst was firstly reduced in a 10% H_2/Ar flow for 30 min at 873 K. Then the catalyst was purged in a He flow until the temperature was cooled down to 313 K. After the baseline became stable, the loop gas of 10% CO/He (590 μL) was pulsed by a He stream over the catalyst. The TCD signal was recorded until the peak area of CO became constant. The CO uptake values of the catalysts could provide a way to normalize different catalysts as reported in the literature [10,37].

The morphologies and Ni particle size of the catalysts were analyzed using a transmission electron microscopy (TEM; JEM-2100, JEOL) at a voltage of 200 kV. Specimens for TEM measurements were prepared by dispersing the samples ultrasonically in ethanol for 15 min. After that, a droplet was deposited on a lacey carbon TEM grid and allowed to dry.

Thermogravimetric analysis (TGA; Pyris Series-Diamond TG/DTA) for the spent catalysts was performed to investigate the coke deposition. The TGA experiments were conducted in a pure O_2 atmosphere with a flow rate of 200 mL min^{-1}. The temperature was ramped from 300 to 473 K and held for 70 min to remove the adsorbed water, and then heated to 1273 K with a heating rate of 10 K min^{-1}. Raman spectroscopy (Witec Alpha 300) equipped