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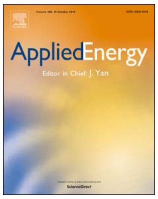

# The novel perovskite-type Ni-doped $Sr_{0.92}Y_{0.08}TiO_3$ as a reforming biogas ($CH_4$ + $CO_2$) for $H_2$ production

Byeong Wan Kwon[a], Joo Hyeng Oh[a], Ghun Sik Kim[a], Sung Pil Yoon[a,b], Jonghee Han[a], Suk Woo Nam[a,b], Hyung Chul Ham[a,b,*]

[a] Fuel Cell Research Center, Korea Institute of Science and Technology (KIST), Hwarang-ro 14-gil, Seongbuk-gu, Seoul 02792, Republic of Korea
[b] Division of Energy & Environment Technology, KIST School, Korea University of Science and Technology (UST), Seoul 02792, Republic of Korea

## HIGHLIGHTS

- The novel Ni-doped $Sr_{0.92}Y_{0.08}TiO_3$ was prepared via Pechini Method.
- The novel Ni-doped $Sr_{0.92}Y_{0.08}TiO_3$ was activated under $N_2$ or reduction condition.
- The $N_2$-activated catalyst showed the better activity than the $H_2$-activated case.
- The 5 mol% Ni-doped $Sr_{0.92}Y_{0.08}TiO_3$ catalyst showed excellent long-term stability.

## ARTICLE INFO

*Keywords:*
Biogas
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Ni-doped $Sr_{0.92}Y_{0.08}TiO_3$ perovskite catalyst and activating catalysts

## ABSTRACT

In this study, novel perovskite-type $Sr_{0.92}Y_{0.08}TiO_3$-based catalysts were investigated for hydrogen production by the dry reforming of biogas (comprising $CH_4$ and $CO_2$). Ni-doped $Sr_{0.92}Y_{0.08}TiO_3$ catalysts with improved catalytic activity were grown using the Pechini method. The prepared catalysts were characterized using X-ray diffraction to check for impurities introduced in the perovskite structure by doping method. The reforming of methane over perovskite-based catalysts has been extensively investigated; however, detailed understanding of the activating catalytic sites under different conditions is still lacking. To understand the details of the activating catalyst mechanism, transmission electron microscopy, temperature-programed reduction, X-ray photoelectron spectroscopic (XPS) analysis were performed under different activating conditions. XPS analysis of 5 mol% Ni-doped $Sr_{0.92}Y_{0.08}TiO_3$ revealed that the $H_2$-activated catalyst lost active lattice oxygen sites and Ni sites due to formation of Ni hydroxide. Thus, the $H_2$-activated catalyst has lower catalytic activity than the $N_2$-activated one.

## 1. Introduction

The demands for clean and environment-friendly energy and fuels have increased rapidly as a part of worldwide efforts to reduce global warming. Many researchers have attempted to develop more efficient and more economically viable processes for producing fuels. Biogas, mainly comprising $CO_2$ and $CH_4$, is produced from anaerobic decomposition of biomass like trees, sugarcane, corn, and various kinds of seeds [1–5]. Reforming of methane has been reported to be a promising method to generate fuel like syngas containing $H_2$ and CO. Reforming techniques include steam reforming (SR), dry reforming (DR), partial oxidation (PO), and autothermal reforming (AR) [1,2,6–11], among which dry reforming of methane (DRM) has attracted considerable interest because it produces high-purity syngas containing little $CO_2$. Furthermore, DRM is an eco-friendly technology because it uses two main green-house gases to produce syngas [1,2]. Ni-based catalysts have usually been used in reforming processes. However, the conventional Ni-based catalysts for DRM tend to be deactivated due to carbon formation physically blocking the active sites of the catalyst. Similar to coking, sulfur-containing compounds such as hydrogen sulfide and benzothiophene, present in bio-gas can also deactivate the catalyst by forming nickel sulfide on the catalyst surface [6–9].

Several groups have studied alternate catalytic materials to overcome the problems of conventional Ni-based catalysts. The studies conducted in this field have focused on low-cost materials with key features like high reforming activity, coking resistance, and sulfur tolerance. Perovskite materials (typical formula = $ABO_3$) have been widely investigated due to their inherent oxygen mobility that suppresses coke formation and sulfur poisoning. Perovskite structures consist of large 12-coordinated cations at the A site and small 6-

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* Corresponding author at: Fuel Cell Research Center, Korea Institute of Science and Technology (KIST), Hwarang-ro 14-gil, Seongbuk-gu, Seoul 02792, Republic of Korea.
*E-mail address:* hchahm@kist.re.kr (H.C. Ham).

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coordinated cations at the B site. Properties of perovskite-type oxides e.g. their ferromagnetic or ferroelectric properties, can easily be controlled by doping at the A or B sites in $ABO_3$ [12–18].

$SrTiO_3$ exhibits the typical chemical formula of the perovskite structure and provides high thermal stability under both oxidizing and reducing conditions [15–17]. When a small amount of $Y^{3+}$ is substituted for $Sr^{2+}$ in $SrTiO_3$ (known as Y-doped $SrTiO_3$, or SYT), its mixed ionic and electronic conductivities (MIEC) are increased [15,16]. However, SYT still has a low methane reforming activity. For instance, our previous study [15,16] using SYT displays a $CH_4$ conversion of 15% at 750 °C. The catalytic activity of SYT can be enhanced by the addition of a small amount of other transition metals in the Ti lattice site (i.e. doping of SYT). In this study, we use Ni as the dopant to boost the DRM performance of SYT catalysts.

In the present study, the novel Ni-doped $Sr_{0.92}Y_{0\cdot08}TiO_3$ was investigated as a catalyst for $H_2$ production from dry reforming of biogas. The aims of this study are to evaluate the initial performance and the long-term stability of 5 mol% Ni-doped $Sr_{0.92}Y_{0.08}TiO_3$ catalyst under different conditions for activating the catalyst. To understand the role played by the different activation conditions, the tested catalysts were characterized using transmission electron microscopy (TEM) with energy-dispersive X-ray analysis (EDX), scanning electron microscopy (SEM) with energy-dispersive X-ray analysis (EDX), temperature-programmed reduction (TPR), X-ray photoelectron spectroscopy (XPS), Raman spectroscopy, and X-ray diffraction (XRD).

## 2. Materials and methods

### 2.1. Catalysts preparation and characterization

The doped perovskite catalysts were prepared herein via the Pechini method (Fig. 1), which is a type of sol-gel method based on intensive blending of positive ions in a solution, leading to controlled transformation of the solution into a polymer gel, followed by removing the polymer matrix and developing a highly homogeneous oxide precursor.

Yttrium nitrate [$Y(NO_3)_3\cdot H_2O$ (Aldrich)] and strontium nitrate [$Sr(NO_3)_3\cdot H_2O$(Aldrich)] were dissolved in deionized water. Titanium isopropoxide [$Ti(OCH(CH_3)_2)_4$ (Aldrich)] was dissolved in ethylene glycol for stabilization and nickel nitrate hexahydrate [$Ni(NO_3)_3\cdot 6H_2O$ (Junsei)] and 70 g of citric acid were dissolved together in deionized water; these solutions were mixed at 80 °C for 24 h. The obtained precipitate was dried at 110 °C and then subjected to calcination at 400 °C to eliminate the organic material. The prepared catalysts were further calcined at 650 °C for 5 h.

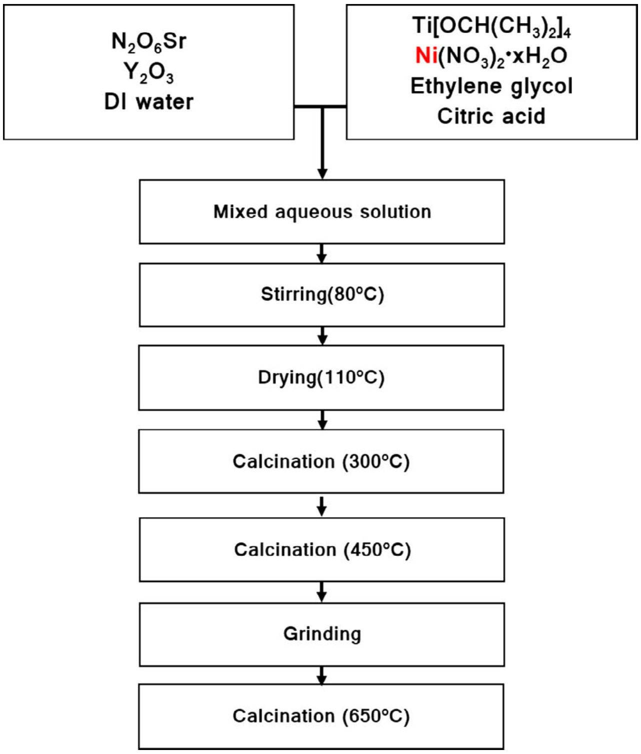

**Fig. 1.** Flow chart of the Pechini method.

The thus-prepared prepared catalysts were analyzed by an X-ray diffractometer (Rigaku RINT-5200 system). The reduced catalysts and samples after the reforming reaction were also tested by XRD analysis.

X-ray photoelectron spectra (XPS) were obtained using a PHI 5000 X-ray photoelectron spectrometer with a monochromated Al-Kα X-ray source.

The morphology of the catalyst surface after different activation treatments for the catalysts, was analyzed using transmission electron microscopy (TEM, FEI, Talos) and energy-dispersive X-ray spectroscopy for element mapping. Powdered samples were dispersed in methanol and were deposited on the copper TEM grid.

The morphology and amounts of coking formation on the catalyst surface after the reforming reaction were analyzed using scanning electron microscopy (FE-SEM, FEI, Inspect F) and energy-dispersive X-ray spectroscopy.

### 2.2. Catalytic activity test

The reforming testing compartment contains a co-axial quartz tube. The prepared doped perovskite catalysts were tested for DRM in a fixed-bed reactor with an outer diameter of 12.7 mm. The fuel was fed into the top of the tube, and the bottom acted as an exhaust line to the gas chromatograph (GC). The catalyst layer was placed into a tube-type furnace. The exit stream was cooled to 4 °C to remove water. The composition of the dry off-gas was measured by GC with a thermal conductivity detector (TCD) and two separated columns PLOT Q and MOLESIEVE (both 30 m in length), using He and Ar, respectively, as carrier gases to determine the concentrations of $H_2$, CO, $CO_2$, and $CH_4$. Prior to the activity test, one of the catalysts was treated to 750 °C under 100 mol% $N_2$ while the other was pre-reduced at 750 °C for 4 h under the flow of 15 mol% $H_2$ balanced with $N_2$. The DRM reaction was carried out under following conditions: catalyst loading = 0.2 g, temperature = 650–800 °C, pressure = 1 atm, $CO_2/CH_4$ molar ratios = 1/2, 1/1, and 2/1, with 50 vol% of $N_2$ balance gas and gas hourly space velocities (GHSVs) = 6000, 12,000, and 18,000 $h^{-1}$. The activities of the synthesized catalysts were evaluated in terms of methane conversion using the gas composition measured by GC.

## 3. Results and discussion

### 3.1. Effect of Ni concentration as-prepared catalysts

The crystal structures of the synthesized Ni-doped $Sr_{0.92}Y_{0.08}TiO_3$ with different Ni concentrations (1, 3, and 5 mol%) were analyzed using XRD spectroscopy. Fig. 2(a) shows that all the samples exhibit diffraction peaks (i.e. $2\theta = 22.76°$, 32.42°, 40.02°, 46.54°, 52.34°, 57.82°, 67.88°, and 77.28°) characteristic of $SrTiO_3$ and no peaks owing to impurities. This indicated that all the synthesized samples have perovskite structure with a homogeneous $SrTiO_3$ crystalline phase [16–18].

In comparison with Y-doped $SrTiO_3$, the relative peak intensities of the perovskite peaks decreased (i.e. the samples became progressively less crystalline) with increasing Ni concentration. The samples with higher Ni concentrations were primarily amorphous in nature, with a small degree of crystallinity [19,20].

To evaluate the deviation of $SrTiO_3$ from ideal cubic structure, the deviation from the ideal structure in perovskite oxides can be expressed by the following general equation: t (tolerance factor) = $(r_a + r_o)/\sqrt{2}$