



ELSEVIER

Available online at [www.sciencedirect.com](http://www.sciencedirect.com)

ScienceDirect

journal homepage: [www.elsevier.com/locate/ijhe](http://www.elsevier.com/locate/ijhe)

## Ni–Co catalyst derived from layered double hydroxides for dry reforming of methane

Xiaoqing Zhang<sup>a</sup>, Chunhui Yang<sup>a</sup>, Yanping Zhang<sup>a</sup>, Yan Xu<sup>a</sup>,  
Shuyong Shang<sup>b,\*</sup>, Yongxiang Yin<sup>a,\*</sup>

<sup>a</sup> School of Chemical Engineering, Sichuan University, Chengdu 610065, PR China

<sup>b</sup> Institute for Chemical Engineering Technology, Yibin University, Yibin 644000, PR China

### ARTICLE INFO

#### Article history:

Received 6 December 2014

Received in revised form

7 June 2015

Accepted 18 September 2015

Available online xxx

#### Keywords:

LDH precursor

Ni–Co bimetallic catalyst

In-situ urea precipitation

Dry reforming of methane

Carbon deposition

### ABSTRACT

Ni/Co monometallic and bimetallic layered double hydroxides (LDH) were in-situ synthesized on the surface of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> by urea precipitation method. Then they were decomposed and reduced by H<sub>2</sub>/Ar atmospheric plasma jet at 400 °C for 15 min to become into catalysts. The LDH precursors were verified by XRD, SEM, FT-IR and Raman, while the catalysts were characterized by N<sub>2</sub> adsorption-desorption, XRD, TEM and H<sub>2</sub>-TPR. After that their catalytic activity and stability were evaluated in dry reforming of methane (DRM) reaction. Both Ni and 2Ni–1Co showed better catalytic performance than other catalysts. Finally, the weight and species of carbon deposition on spent catalyst were tested by TG-DTA analysis. The deposition of inert carbon was the main reason for deactivation of catalysts in DRM. Moreover, a highly uniform dispersion and small particle size of active component are achieved by in situ co-precipitation method, and  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> provided large specific surface area for these Ni/Co catalysts.

Copyright © 2015, Hydrogen Energy Publications, LLC. Published by Elsevier Ltd. All rights reserved.

### Introduction

Syngas plays an important role in chemical engineering since it is an intermediate for synthesizing various chemicals, such as methanol, dimethyl and synthetic gasoline. Dry reforming of methane,  $\text{CO}_2 + \text{CH}_4 = 2\text{CO} + 2\text{H}_2$ , is one of effective ways to produce syngas with carbon dioxides. It has been widely investigated in the present years because of significant features as follows: (1) makes use of natural gas resources with high CO<sub>2</sub> content, avoiding the expensive and intricate gas separation process, (2) offers the additional advantages to

convert greenhouse gas CO<sub>2</sub> and CH<sub>4</sub> into valuable chemicals, (3) is an efficient way to use of biogas from urban organic waste, a renewable resource containing methane (40–70%) and carbon dioxide (30–60%).

Many research results have verified that the Ni and Co catalysts exhibit promising catalytic performance for DRM due to their high activity and economics. Compared with the metals of Rh, Ru and Pt, Ni or Co catalyst is much cheaper and more suitable for industrial application. So for bimetallic systems, Ni–Co bimetallic catalysts were extensively studied due to their highly catalytic properties. Zhang J et al. [1] reported that Ni–Co bimetallic catalyst exhibited superior

\* Corresponding author. Tel.: +0086 13348865689.

\*\* Corresponding author. Tel.: +0086 13518216536.

E-mail addresses: [ssyandmlitcdj@163.com](mailto:ssyandmlitcdj@163.com) (S. Shang), [hyyx0675@sina.com](mailto:hyyx0675@sina.com) (Y. Yin).

<http://dx.doi.org/10.1016/j.ijhydene.2015.09.150>

0360-3199/Copyright © 2015, Hydrogen Energy Publications, LLC. Published by Elsevier Ltd. All rights reserved.

catalytic performance on activity and stability than other Ni–Me combinations, because the synergy between Ni and Co had greatly improved the catalytic properties and impeded the carbon formation. San-José-Alonso D et al. [2] found that Co rich catalyst presented good performance during DRM, but it should be improved to hinder carbon deposition. Nader Rahemi et al. [3] introduced plasma technology in synthesis and pretreatment of Ni–Co bimetallic catalyst, and proved that plasma had optimized catalysts' structure and endowed them excellent performance. In addition, Xu, Junke et al. [4], Aldashukurova [5], Zhu, Jianqiang [6] and Djinovic, P [7] et al. also reported that bimetallic catalyst of Ni–Co had great tolerance to coke formation resulted from the synergetic effects, highly dispersed active metal and strong metal-support interactions.

Layered double hydroxides (LDH) are lamellar metal hydroxides which composed of cation main layers and anion interlayer as shown in Fig. 1. The general formula of LDH can be expressed as  $[M_{1-x}^{2+} M_x^{3+} (\text{OH})_2]^{x+} (\text{A}^{n-})_{x/n} \cdot m\text{H}_2\text{O}$ , where  $M^{2+}$  and  $M^{3+}$  represent divalent and trivalent cations, respectively. And  $\text{A}^{n-}$  denotes as the anion of valence "n", the value of "x" is the mole ratio of  $M^{3+}/(M^{2+} + M^{3+})$ . The identities of  $M^{2+}$ ,  $M^{3+}$ , x and  $\text{A}^{n-}$  may vary over a wide range, therefore various layer structure with different physicochemical properties can be prepared by LDH synthesis method [8–10]. Because LDH has natural active component dispersion and appropriate alkalinity, as well as forming oxide with homogeneous mesoporous texture and proper specific surface area after volatilizing  $\text{CO}_3^{2-}$ ,  $\text{NO}_3^-$  and crystal water by calcinations, it is considered as a desirable catalyst precursor material [11–13].

In some previous work, catalysts derived from LDH had been investigated in DRM system. Katsuomi Takehira et al. [14] studied the auto thermal reforming of  $\text{CH}_4$  by Ni–Mg–Al LDH, higher catalytic activity were obtained by comparing with conventional catalyst prepared by impregnation method. Alak Bhattacharyya et al. [15] also synthesized hydrotalcite clay catalyst for DRM, and gained prospective excellent performances. Long H et al. [16] have carried out a Ni–Co bimetallic catalysts derived from LDH by co-precipitation for dry reforming of methane. However, so far many studies only focused on the catalysts derived from pure LDH materials. It has rarely reported that Ni–Co bimetallic catalyst derived from LDH which supported by some porous carriers, such as  $\text{Al}_2\text{O}_3$  and CNTs. These porous carriers could endow catalyst much better performance in reaction, especially for gas reaction. Meanwhile, they could enhance the thermal stability of

catalyst under high reaction temperature. These features are very favorable for industrial application of Ni–Co bimetallic catalyst. So in the present work, Ni–Co–LDH/ $\gamma\text{-Al}_2\text{O}_3$  has been prepared by in-situ co-precipitation method in urea solution. Ar/ $\text{H}_2$  atmospheric plasma jet was used to decompose and reduce the catalytic precursors. Moreover, a systematic evaluation of catalytic performance on Ni/Co monometallic and bimetallic catalysts has been carried out.

## Experiment and characterization

### Catalysts preparation

The Ni–Co–Al–LDH/ $\gamma\text{-Al}_2\text{O}_3$  (2Ni–1Co) was prepared by following steps: Firstly, 5 g  $\gamma\text{-Al}_2\text{O}_3$  supports were cleaned by atmospheric cold plasma jet and the average particle size of 40–60  $\mu\text{m}$ . Then impregnated with 40 ml aqueous solution of  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (1.0 mol/L),  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (0.5 mol/L) and urea (4 mol/L) with stirring at 50 °C for 2 h in three-necked, round-bottomed flask by oil bath. After that, removed the residual solution and raised the temperature of oil bath up to 120 °C. The sample was crystallized under this condition for 6 h and then washed with deionized water until the eluate was neutral. Then the sample was dried at 70 °C for 12 h, until that the preparation of Ni–Co–Al–LDH/ $\gamma\text{-Al}_2\text{O}_3$  (2Ni–1Co) was completed. The rest samples Co–Al, 2Co–1Ni, 1.5Co–1.5Ni and Ni–Al can be done in the same manner, only changed the molarities of  $\text{Ni}^{2+}$  and  $\text{Co}^{2+}$ . Finally these samples were taken as catalytic precursors. For catalytic activity test in DRM, this LDH/ $\gamma\text{-Al}_2\text{O}_3$  precursors need to be directly decomposed and reduced by  $\text{H}_2/\text{Ar}$  atmospheric cold plasma jet. And then they would become into catalysts, which were denoted as Co–LDH, 2Co–1Ni–LDH, 1.5Co–1.5Ni–LDH, 1Co–2Ni–LDH and Ni–LDH respectively.

The schematic of the atmospheric cold plasma jet is shown in Fig. 2. An inside copper stick is connected to the high voltage supply. The coaxial stainless steel crust serves as the grounded electrode. The mixture of  $\text{H}_2$  and Ar ( $\text{H}_2/\text{Ar} = 1:9$ ) with a flux of 0.6  $\text{m}^3/\text{h}$  is supplied as the plasma-forming gas. When the AC voltage (20 kHz, 600 V) is utilized, the plasma can be formed between the two electrodes and the jet ejected into catalyst bed. Profiting the hydrogen atoms in plasma, the decomposition and reduction of catalyst can be carried out in about 15 min simultaneously. The temperature of catalyst bed was measured by thermocouple, which maintained at 673 K during this process.

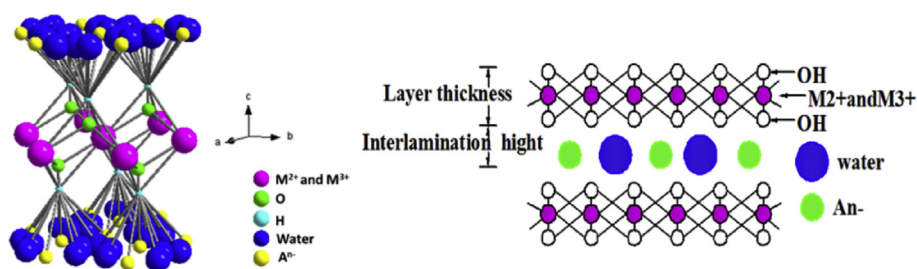


Fig. 1 – Schematic of LDHs structure.

Download English Version:

<https://daneshyari.com/en/article/7713240>

Download Persian Version:

<https://daneshyari.com/article/7713240>

[Daneshyari.com](https://daneshyari.com)