



Superior catalytic behavior of trace Pt-doped Ni/Mg(Al)O in methane reforming under daily start-up and shut-down operation

Dalin Li^a, Kazufumi Nishida^a, Yingying Zhan^a, Tetsuya Shishido^b, Yasunori Oumi^a, Tsuneji Sano^a, Katsuomi Takehira^{a,*}

^a Department of Chemistry and Chemical Engineering, Graduate School of Engineering, Hiroshima University, Kagamiyama 1-4-1, Higashi-Hiroshima 739-8527, Japan

^b Department of Molecular Engineering, Graduate School of Engineering, Kyoto University, Katsura 1, Nishikyo-ku, Kyoto 615-8510, Japan

ARTICLE INFO

Article history:

Received 7 May 2008

Received in revised form 7 August 2008

Accepted 18 August 2008

Available online 26 August 2008

Keywords:

CH₄ reforming

Self-activation

Self-regeneration

Ni/Mg(Al)O catalyst

Pt doping

Daily start-up and shut-down operation

ABSTRACT

Doping effects of Pt and Ru on Ni/Mg(Al)O catalysts were compared in daily start-up and shut-down operations of steam reforming of CH₄. Trace Pt-doped catalyst showed better behavior than trace Ru-doped catalyst; the former was self-activated but the latter was not, although both exhibited self-regenerative activity. Moreover, the former exhibited sustainable activity, although the latter was quickly passivated, in the autothermal reforming of CH₄. Formation of Pt–Ni alloy on the surface of fine Ni metal particles on the catalysts was suggested by EXAFS analyses. CH₄ was dissociatively activated to form hydrogen on Pt, assisted by adsorbed O or OH species, leading to the self-activation via Ni reduction by hydrogen spillover from Pt. The self-regeneration of the Pt–Ni/Mg(Al)O catalysts can be achieved by the continuous rebirth of active Ni metal species via reversible reduction–oxidation between Ni⁰ and Ni²⁺ in/on Mg(Ni,Al)O periclase assisted by the hydrogen spillover.

© 2008 Published by Elsevier B.V.

1. Introduction

Steam reforming (SR) of hydrocarbons, especially of CH₄, is the most widespread and generally the most economical way to make hydrogen [1]. This process still requires further advancement in the preparation of low cost catalysts with high sustainability. Hydrogen production for polymer electrolyte fuel cells (PEFCs) is a research area of urgent importance in addressing global warming. In contrast to the reformers in large-scale industry processes under stationary operating conditions, the temperature varies frequently due to daily start-up and shut-down (DSS) operations for hydrogen production of PEFCs in domestic use. Between shut-down and start-up in the DSS operation, the catalyst bed in the reformer is purged by steam or air to enhance safety. Thus, a catalyst must be able to tolerate multiple cycles under such unusual transient conditions without deterioration.

We previously reported that Ni/Mg(Al)O catalyst derived from hydrotalcite (HT)-like compounds produced highly dispersed and stable Ni metal particles on the surface [2–4] and were successfully applied in SR and oxidative SR of CH₄ [2,3]. Deactivations of Ni-

loaded catalysts were reported to be caused by coking, sintering or oxidation of the active metal species [5,6]. Ni metal can be oxidized not only by gaseous oxygen, but also even in the presence of steam. The Ni/Mg(Al)O catalysts were quickly deactivated due to the oxidation of Ni metal by both oxygen gas and steam when applied in the DSS operation of SR of CH₄ [7].

Recently, we reported that the doping of trace noble metals on the Ni/Mg(Al)O catalysts was effective for suppressing the Ni oxidation during the DSS operation [8,9]. The Ni/Mg(Al)O catalysts doped with traces of noble metals exhibited high and sustainable activity in the DSS SR of CH₄ [9] and partial oxidation (PO) of propane to synthesis gas [10]. Moreover, we have reported an excellent catalytic behavior, that is, self-regenerative activity of the Ni/Mg(Al)O catalyst doped with trace Ru during the DSS SR of CH₄ [11]. However, the Ru-doped Ni/Mg(Al)O catalyst could not be self-activated in SR of CH₄ and, moreover, was not sustainable enough when it was used in autothermal steam reforming (ATSR) of CH₄, resulting in a drastic deterioration in the catalytic activity. In the present paper, we report both self-activation and self-regenerative activity of trace Pt-doped Mg(Ni,Al)O catalyst. We also report its sustainable activity not only in DSS SR but also in ATSR of CH₄. The effects of Pt doping on such catalytic behavior have been carefully investigated and compared with those of Ru doping [11].

* Corresponding author. Tel.: +81 824 24 6488; fax: +81 824 24 6488.

E-mail address: takehira@hiroshima-u.ac.jp (K. Takehira).

2. Experimental

2.1. Catalyst preparation

Ni-loaded Mg(Al)O catalyst with the Mg/Ni/Al atomic ratio of 2.5/0.5/1 was prepared by co-precipitation as described previously [2–4]; Mg_{2.5}(Ni_{0.5})–Al HT-like precursor, in which a part of Mg²⁺ in Mg–Al HT was replaced by Ni²⁺, was prepared by co-precipitation of the nitrates of metal components. An aqueous solution containing the nitrates of Mg²⁺, Ni²⁺ and Al³⁺ was added slowly into an aqueous solution of sodium carbonate at room temperature and at pH 10.0. After the solution was aged at 60 °C for 12 h, the precipitate was washed with de-ionized water and dried in air at 100 °C. The Mg_{2.5}(Ni_{0.5})–Al HT-like precursor was calcined in a muffle furnace in a static air atmosphere by increasing the temperature from ambient temperature to 850 °C at a rate of 0.83 °C min⁻¹ and maintaining it at 900 °C for 5 h, to form Mg_{2.5}(Al,Ni_{0.5})O periclase as the precursor of Ni_{0.5}/Mg_{2.5}(Al)O catalyst. The periclase materials were obtained as powders, and the Ni loading was found to be 16.0 wt% by inductively coupled plasma spectroscopy analyses after the calcination at 850 °C.

Pt, Rh or Ru doping was done by adopting a “memory effect” of Mg(Ni)–Al HT [8]; a 1.0 g portion of Mg_{2.5}(Al,Ni_{0.5})O periclase powders was dipped in an aqueous solution of Pt(II), Rh(III) or Ru(III) nitrate for 1 h at room temperature, followed by drying in air at 100 °C. A prescribed amount of Pt(II), Rh(III) or Ru(III) nitrate was dissolved in 5 ml of de-ionized water. Mg(Ni)–Al HT was reconstituted from Mg_{2.5}(Ni_{0.5},Al)O periclase during the dipping due to a “memory effect.” During this reconstitution, both Pt and Ru were physically trapped, whereas Rh(III) was chemically replaced at the Al(III) sites, in the layered structure of the HT [12]. The sample was finally calcined at 850 °C for 5 h and the precursors of Pt-, Rh- or Ru-doped Ni_{0.5}/Mg_{2.5}(Al)O catalysts were obtained. The precursor powder was pressed to a disc, crushed roughly, and sieved to the particle sizes of 0.36–0.60 mm in a diameter and used in the reforming reactions.

As a control, 13.5 wt% Ni/γ-Al₂O₃ catalyst was prepared by the incipient wetness method using γ-Al₂O₃ (JRC-ALO8) and an aqueous solution of Ni(II) nitrate, followed by calcination at 850 °C for 5 h.

2.2. Characterization of catalyst

The structures of the catalysts were studied by using powder X-ray diffraction (XRD), transmission electron microscopy (TEM), X-ray absorption (XANES and EXAFS), inductively coupled plasma optical emission spectrometry (ICP), temperature programmed reduction (TPR), temperature programmed oxidation (TPO), and N₂ and H₂ adsorption.

XRD was recorded on a Mac Science MX18XHF-SRA powder diffractometer with mono-chromatized Cu Kα radiation (λ = 0.154 nm) at 40 kV and 30 mA. The diffraction pattern was identified through comparison with those included in the JCPDS (Joint Committee of Powder Diffraction Standards) database. The size of Ni metal particles on the catalyst was calculated from Scherrer's equation: $d = K\lambda/\beta \cos \theta$; β, full width at half maximum; K = 0.94 and λ = 1.5405 Å.

TEM images were obtained on a FE-TEM Hitachi HF-2200 instrument. The samples were crushed to fine powders, dispersed in heptane using supersonic waves, and deposited on a Cu TEM grid with a holey carbon film.

Ni K-edge, Ru K-edge and Pt L₃-edge XAFS spectra were measured at the BL01B1 station of the SPring-8 with the approval of the Japan Synchrotron Radiation Research Institute (JASRI) (proposal 2006A1217). The storage ring was operated at 8 GeV with a ring

current of 98–100 mA. A double mirror system was used to avoid higher harmonics in the X-ray beam. A Si(1 1 1) single crystal was used to obtain a monochromatic X-ray beam. Ni K-edge XAFS spectra were measured in transmission mode by using two ion chambers filled with N₂ (I₀) and 25% Ar diluted with N₂ (I). Ru K-edge XAFS spectra were measured in transmission and fluorescence modes using ion chambers [50% Ar diluted with N₂ (I₀) and 75% Ar diluted with Kr (I)] and a Lytle detector (100% Kr), respectively. Pt L₃-edge XAFS spectra were measured in transmission and fluorescence modes using ion chambers [15% Ar diluted with N₂ (I₀) and 50% Ar diluted with N₂ (I)] and a Lytle detector (100% Kr), respectively. Analyses of EXAFS data were performed using the REX2000 program (Version: 2.5.7; Rigaku Corp.). For EXAFS analyses, the oscillation was first extracted from EXAFS data using a spline-smoothing method [13]. The oscillation was normalized by an edge height ca. 50 eV higher than the adsorption edge. For the curve-fitting analysis, the empirical phase shift and amplitude functions for the Ni–Ni, Ru–Ru and Pt–Pt bonds were extracted from data for Ni and Pt foils and Ru metal powder, respectively. Theoretical functions for the Ru–Ni, Pt–Ni, Ni–O and Ru–O bonds were calculated using the FEFF8.2 program [14]. The 0.50 wt% Ru- or Pt-doped Ni_{0.5}/Mg_{2.5}(Al)O sample was used for this measurement in order to guarantee the accuracy of the analytical results.

ICP measurements were performed with a Seiko SPS 7700. The content of each metal component was determined after the sample was completely dissolved using diluted hydrochloric acid and a small amount of hydrofluoric acid.

TPR of the catalyst were performed at a heating rate of 10 °C min⁻¹ using a H₂/Ar (5/95 ml min⁻¹) mixed gas as reducing gas after passing through a 13× molecular sieve trap to remove water. A U-shaped quartz tube reactor (6 mm i.d.) equipped with a thermal conductivity detector for monitoring H₂ consumption was used. Before the TPR measurements, the sample was calcined at 300 °C for 2 h in an O₂/Ar (10/40 ml min⁻¹) mixed gas.

TPO experiments were performed on the catalyst after the steaming at 900 °C for 10 h, followed by the stationary SR of CH₄ at 700 °C for 3 h, from room temperature to 900 °C at a heating rate of 2.5 °C min⁻¹ in an O₂/N₂ (5/20 ml min⁻¹) mixed gas. The amount of coke formed on the catalyst was estimated from the amount of CO₂ formed during the TPO experiment. No CO was detected during TPO.

The N₂ adsorption (–196 °C) study was conducted to examine the BET surface area of the samples after the calcination. The measurement was carried out on a Bell-Japan Belsorp-mini. The samples were pretreated in N₂ at 200 °C for 10 h before the measurements were obtained.

Ni dispersion was determined by static equilibrium adsorption of H₂ at ambient temperature using the pulse method. A 50-mg catalyst sample was reduced at 900 °C in a H₂/N₂ (5/20 ml min⁻¹) mixed gas for 1 h, and this reduced catalyst was used for the measurement. During the pulse experiment, the amount of H₂ was monitored by a TCD gas chromatograph. Uptake of H₂ at monolayer coverage of the Ni species was used to estimate Ni metal dispersion and particle size. The equation used to calculate dispersion was:

$$\%D = 1.17 \frac{X}{Wf} \quad (1)$$

where X is H₂ uptake in μmol g⁻¹ of catalyst, W is the weight percent of nickel, and f is the fraction of nickel reduced to the metal, assumed to be 80% for the HT-derived catalysts [9] and 100% for the impregnated catalyst. The average crystallite diameters, d, were calculated from %D, assuming spherical metal crystallites [15]:

$$d = \frac{971}{\%D} \quad (2)$$

Download English Version:

<https://daneshyari.com/en/article/43298>

Download Persian Version:

<https://daneshyari.com/article/43298>

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