

Self-activation and self-regenerative activity of trace Rh-doped Ni/Mg(Al)O catalysts in steam reforming of methane

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Abstract

Ni/Mg(Al)O catalyst doped with trace amounts of Rh was tested in steam reforming of methane and the catalytic behavior was compared with the Ru-doped catalyst. Rh-doped Ni/Mg(Al)O catalyst showed a self-activation without any reduction treatment due to the ability for hydrogen production by C–H bond cleavage. Such production led to the reduction of lattice Ni²⁺ in Mg(Al,Ni)O periclase to metallic Ni by hydrogen-spillover. The Rh-doped Ni/Mg(Al)O catalyst showed also a self-regenerative activity during a daily start-up and shut-down (DSS) operation of steam reforming of methane. NiRh alloy was formed in the surface layer of metallic Ni particles and Rh was located more profoundly in the particles than Ru in NiRu alloy on the Ru-doped catalyst. The Rh-doping exhibited a prominent performance, whilst the Ru-doping resulted in neither self-activation nor stable activity in the DSS operation. Although the catalyst deactivation took place by the Ni⁰ oxidation into the lattice Ni²⁺ in Mg(Al,Ni)O periclase, trace Rh assisted the regeneration of the active metallic Ni from the lattice Ni²⁺ by hydrogen-spillover. Even metallic Ni particles that had been strongly sintered on the Rh-Ni/Mg(Al)O catalyst by steaming at 900 °C were re-dispersed during the DSS operation, resulting in high and stable activity. The self-regeneration of the Rh-doped Ni/Mg(Al)O catalyst has been achieved by continuous rebirth of active Ni metal particles due to reversible reduction–oxidation between the metallic Ni on the surface and the lattice Ni²⁺ in Mg(Ni,Al)O periclase, i.e., oxidative incorporation of surface Ni⁰ into the lattice Ni²⁺ of Mg(Al,Ni)O and reductive migration of the lattice Ni²⁺ to the surface Ni⁰ by hydrogen-spillover.

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1. Introduction

Steam reforming of hydrocarbons, especially of methane, has been developed and is still the largest and generally the most economical way to make hydrogen [1]. In hydrogen production for polymer electrolyte fuel cells (PEFC), the temperature varied frequently by daily start-up and shut-down (DSS) operation for domestic use in contrast to a large-scale use of reformers in the industry under stationary operating conditions. Between shut-down and start-up in the DSS operation, the catalyst bed in the reformer is purged by steam for securing the safety. Thus, each catalyst must be able to

tolerate to multiple cycles under such unusual transient conditions without deterioration.

We have reported that Ni/Mg(Al)O catalyst derived from hydrotalcite(HT)-like compounds produced highly dispersed and stable Ni metal particles on the surface [2–7], which showed high and stable activity in the stationary steam reforming and oxidative reforming of methane [4,5]. However, the Ni/Mg(Al)O catalysts were quickly deactivated due to the oxidation of Ni metal by steam when they were applied in the DSS operation of steam reforming of methane (SRM) [8]. A doping of trace noble metals on the Ni/Mg(Al)O catalysts has effectively suppressed the Ni oxidation during the DSS operation [9,10]. A similar approach has been taken for Rh-Ni/Mg(Al)O catalysts in the stationary partial oxidation or autothermal SRM [11,12] and Ru-Ni/Mg(Al)O catalysts in the dry reforming of methane [13]. The behaviors of MgO- or Al₂O₃-supported Ni catalysts in the stationary

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autothermal SRM were also improved by doping Rh, Pt or Pd [14–17]. The addition of Pt, Ir or Ru on the Ni/ γ -Al₂O₃ or Ni/MgAl₂O₄ catalyst resulted in an increase in metal surface area; moreover, the catalysts obtained were self-activated in the reforming reaction without pre-reduction treatment [18–20].

The author has found that trace Ru-doping was effective for suppressing the deactivation of the Ni/Mg(Al)O catalyst in the DSS SRM [9,10]. Moreover, a self-regenerative activity has been found on the trace Ru-doped Ni/Mg(Al)O catalyst [21]. In the present research, the effect of Rh-doping on the activity of the Ni/Mg(Al)O catalyst has been studied and compared with that of Ru-doping for self-activation and self-regeneration of active metallic Ni particles.

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 following the previous work [2–7]; Mg_{2.5}(Ni_{0.5})-Al HT-like precursor was prepared by co-precipitation of the nitrates of Mg²⁺, Ni²⁺ and Al³⁺ at pH 10.0 at room temperature, followed by aging at 60 °C for 12 h. The precipitate was washed with de-ionized water and dried in air at 100 °C. The precursor was calcined in a static air atmosphere by increasing temperature from ambient temperature to 850 °C at a rate of 0.83 °C min⁻¹ and kept at 850 °C for 5 h. Powders of Mg_{2.5}(Al,Ni_{0.5})O periclase as the precursor of the Ni_{0.5}/Mg_{2.5}(Al)O catalyst were obtained and Ni loading was 16.0 wt% by inductively coupled plasma spectroscopy (ICP) analyses after the calcination at 850 °C.

Doping of Rh or Ru has been done by adopting a “memory effect” of Mg(Ni)-Al HT [9]; a 1.0 g portion of the powders of Mg_{2.5}(Al,Ni_{0.5})O periclase was dipped in an aqueous solution of Rh(III) or Ru(III) nitrate for 1 h at room temperature, followed by drying in air at 100 °C. A prescribed amount of Rh(III) or Ru(III) nitrate was dissolved in 5 ml of de-ionized water. During the dipping, followed by the drying treatments, Mg(Ni)-Al HT was reconstituted from Mg_{2.5}(Ni_{0.5},Al)O periclase due to the “memory effect” on the surface of catalyst particles. During the reconstitution, Rh or Ru was incorporated or physically trapped in the layered structure of the HT. The sample was finally calcined at 850 °C for 5 h to form the precursor of the Rh or Ru-Ni_{0.5}/Mg_{2.5}(Al)O catalysts. The powders of the precursors were pressed to a disc, crushed roughly and sieved to the particles of 0.36–0.60 mm in 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 (ALO8) and an aqueous solution of Ni(II) nitrate, followed by calcination at 850 °C for 5 h. Commercial Ni catalyst, FCR (12 wt% Ni/ α -Al₂O₃), was supplied from Süd-Chemie Catalysts Japan Inc. and was used also as a control. FCR as received was first crushed to fine powders, pressed to a disc, crushed roughly, sieved to the particles of 0.36–0.60 mm in diameter and used in the reforming reaction.

2.2. Characterization of catalyst

The structure of the catalysts was studied by using powder X-ray diffraction (XRD), transmission electron microscopy (TEM), X-ray absorption (XANES and EXAFS), ICP, temperature programmed reduction (TPR), temperature programmed oxidation (TPO) and N₂ and H₂ adsorption methods.

XRD was recorded on a Mac Science MX18XHF-SRA powder diffraction-meter with mono-chromatized Cu K α radiation ($\lambda = 0.154$ nm) at 40 kV and 30 mA. The diffraction pattern was identified by comparing with those included in the Joint Committee of Powder Diffraction Standards (JCPDS) data base. A particle size of Ni metal on the catalyst was calculated from the Scherrer equation: $d = K\lambda/\beta \cos \theta$, where β is the full width at half maximum, $K = 0.94$ and $\lambda = 1.5405$ Å.

TEM measurements were performed with a FE-TEM Hitachi HF-2200 instrument. The catalyst particles were dispersed in heptane under ultrasonic vibration, dipped up with a Cu micro grid and dried.

The Ni K-edge and Rh K-edge EXAFS were measured at the BL01B1 station of the SPring-8 with the approval of the Japan Synchrotron Radiation Research Institute (JASRI) (Proposal No. 2006B1217). 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 EXAFS spectra were measured in transmission mode by using two ion chambers filled with N₂ (I_0) and 25% Ar diluted with N₂ (I). Rh K-edge EXAFS spectra were measured in transmission and fluorescence modes by using ion chambers (100% Ar (I_0) and 75% Ar diluted with Kr (I)) and Lytle detector (100% Kr), respectively. Analyses of EXAFS data were performed using the REX2000 program (Version: 2.3.3; Rigaku Corp.). For EXAFS analyses, the oscillation was first extracted from EXAFS data using a spline smoothing method [22]. The oscillation was normalized by the edge height around 50 eV higher than the adsorption edge. For the curve-fitting analysis, the empirical phase shift and the amplitude functions for the Ni–Ni and Rh–Rh bonds were extracted from data for Ni and Rh foils. Theoretical functions for the Rh–Ni, Ni–O and Rh–O bonds were calculated using the FEFF8.2 program [23].

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 was 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 \times molecular sieve trap to remove water. A U-shaped quartz tube reactor (6 mm i.d.) equipped with a TCD for monitoring the H₂ consumption was used. Prior to the TPR measurements, the sample was calcined at 300 °C for 2 h in an O₂/Ar (10/40 ml min⁻¹) gas mixture.

The N₂ adsorption (–196 °C) study was used to examine the BET surface area of the samples after 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.

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