Promoting effect of noble metals addition on activity and resistance to carbon deposition in oxidative steam reforming of methane over NiO–MgO solid solution

Mohammad Nurunnabi [a], Ken-ichiro Fujimoto [b], Kimihito Suzuki [b], Baitao Li [a], Shigeru Kado [a], Kimio Kunimori [a], Keiichi Tomishige [a,*]

[a] *Institute of Materials Science, University of Tsukuba, 1-1-1, Tennodai, Tsukuba, Ibaraki 305-8573, Japan*
[b] *Advanced Technology Research Laboratories, Nippon Steel Corporation, 20-1, Shintomi, Futtsu, Chiba 293-8511, Japan*

Abstract

Additive effects of noble metals such as Rh, Pt and Pd on NiO–MgO solid solution in oxidative steam reforming of methane under atmospheric pressure and pressurized condition were investigated. In the reaction under atmospheric pressure, $Ni_{0.2}Mg_{0.8}O$ lost the reforming activity due to catalyst oxidation; however, the addition of small amount of noble metals enhanced the activity drastically, especially at low W/F condition (0.13 g h/mol). From the reaction tests under pressurized conditions, the noble metal addition was also effective to the inhibition of carbon deposition. In terms of the promotion in catalyst activity and inhibition of carbon deposition, Rh was the most effective component even when the additive amount of Rh was as low as 0.035%.

1. Introduction

Oxidative steam reforming of hydrocarbons, where oxygen is introduced to the catalyst bed together with reforming agents like steam, is one of the promising methods for the production of hydrogen or synthesis gas [1]. However, when conventional steam reforming Ni catalyst is applied to the oxidative steam reforming of methane, severe catalyst deactivation has often been observed, and this is because active Ni species can be oxidized with oxygen [2–6]. Therefore, catalyst development is needed. It has been known that noble metal catalysts are effective to the oxidative steam reforming of methane [2,7–9]; however noble metals have problems in the cost and limited availability. Therefore, Ni catalysts modified with small amount of noble metals have been attempted. Another problem in

oxidative steam reforming of methane is carbon deposition, which is a common problem in conventional steam and dry reforming of methane and hydrocarbons [10–12]. It has been reported that NiO–MgO solid solution catalysts exhibited high resistance to carbon deposition in steam and dry reforming of methane [13–16]. Therefore, we adopt NiO–MgO solid solution as Ni catalysts for oxidative steam reforming of methane, and the additive effect of noble metals such as Rh, Pt and Pd is investigated. Especially, in order to estimate the resistance to carbon deposition, oxidative steam reforming of methane is also performed under pressurized condition (1.0 MPa).

2. Experimental

2.1. Catalyst preparation

$Ni_{0.2}Mg_{0.8}O$ solid solution was prepared by the solid reaction method from NiO (Wako Pure Chemical

Industries Ltd. Japan) and MgO (UBE Material Industries Ltd. Japan). The mixture of NiO with MgO was calcined in air at 1423 K for 12 h. The formation of $Ni_{0.2}Mg_{0.8}O$ solid solution was identified by X-ray diffraction (XRD). After the calcination, the BET surface area of $Ni_{0.2}Mg_{0.8}O$ was determined to be 2.6 m^2/g. As a reference, MgO was calcined at the same temperature and the BET surface area of MgO was determined to be 5.7 m^2/g. The loading of Rh, Pt or Pd on $Ni_{0.2}Mg_{0.8}O$ and MgO was performed by the impregnation of $Ni_{0.2}Mg_{0.8}O$ and MgO with the aqueous solutions of $Rh(NO_3)_3$ (N.E. Chemcat Corp. Japan), $Pt(NO_2)_2(NH_3)_2$ (N.E. Chemcat Corp. Japan), or $Pd(NO_3)_2$ (N.E. Chemcat Corp. Japan), respectively. After removal of the solvent by heating, the catalysts were dried overnight at 383 K and then calcined in air at 773 K for 3 h. The loading amounts of Rh, Pt and Pd were in the range between 0.02 and 0.5 mass%. Before use, all of these catalysts were pressed (500 kgf/cm^2) into disks and then crushed to 60–100 mesh particles.

2.2. Catalytic reaction

Oxidative steam reforming of methane was carried out in a fixed bed flow reaction system under the atmospheric pressure and pressurized conditions. The reactor was similar type to that reported previously [4]. A quartz tube (inner diameter, 4.4 mm $\varnothing$) inside a stainless steel tube (inner diameter, 7.4 mm $\varnothing$) was used as the reactor, and the quartz tube was sealed by the silicon rubber gasket. At the outlet of the catalyst bed, the reaction temperature was monitored by the thermocouple, which was inserted into a thin quartz tube (thermowell). Catalyst reduction was carried out by hydrogen flow under atmospheric pressure at 1073 K for 0.5 h in each experiment. For a comparison, the activity test was also carried out on the catalysts without the reduction pretreatment. The partial pressure ratio of reactants was $CH_4/H_2O/O_2 = 2/1.5/1$. CH_4 was introduced to the reactor through the thin quartz tube, whose outlet was located just before the quartz wool. H_2O and O_2 were introduced into the reactor outside the CH_4 feeding tube, where H_2O was supplied by using the microfeeder. The total pressure was 0.1–1.0 MPa, and 0.03 g catalyst was used for each experiment. The length of the catalyst bed was about 4 mm. Contact time W/F (W = catalyst weight/g and F = total flow rate of the introduced gases/mol/h) was in the range of 0.13–1.2 g h/mol. The effluent gas was analyzed with an FID gas chromatograph (GC) (column packing: Gaskuropack 54) equipped with a methanator for CH_4, CO and CO_2. The C-containing production in the gas phase is CO and CO_2. TCD-GC (column packing: Molecular Sieve 13X) was used for H_2 analysis. An ice bath was set up between the reactor exit and a sampling port in order to remove water from the effluent gas for GC analysis. Methane conversion and CO selectivity in oxidative steam reforming of methane was calculated as described below:

Methane conversion (%)
$$= (C_{CO} + C_{CO_2})/(C_{CH_4} + C_{CO} + C_{CO_2}) \times 100$$
CO selectivity (%) $= C_{CO}/(C_{CO} + C_{CO_2}) \times 100$

C: concentration of each component in the effluent gas. In the results under pressurized conditions, the deposited carbon on the catalyst surface was observed as described below. Even in these cases, the formation rate of $CO + CO_2$ was almost balanced with the conversion rate of methane. This indicates that the deposition rate of carbon was so small and this can be lower than the error of GC-analysis.

2.3. Measurement of deposited carbon amount

Thermogravimetric analysis (TGA) for the estimation of carbon amount was carried out by using Shimadzu DTG-60 apparatus. After the catalytic reaction, about 0.01 g catalyst from the catalyst bed was used. TGA profile was measured under air flowing (20 ml/min) at the heating rate of 15 K/min. Exothermic weight loss was observed at the temperature range between 750 and 1000 K. This can be assigned to the combustion of deposited carbon [13]. It is possible to estimate the amount of carbon deposition on the basis of this weight loss. The detection limit of carbon amount in this method is approximately 0.1%. The obtained results below this detection limit are shown as "not detected (n.d.)".

2.4. Catalyst characterization

The reducibility of the catalysts was characterized by a temperature-programmed reduction (TPR) technique. Before the TPR measurement, the samples (about 0.05 g) were heated at 773 K for 0.5 h (heating rate 10 K/min) under He gas flow of 30 ml/min in order to remove any adsorbed species such as CO_2. After the sample was cooled down to room temperature under He flowing, the reactor was heated again from room temperature to 1123 K for 0.5 h at a heating rate of 10 K/min in a 5% H_2/Ar mixture gas flow of 30 ml/min. The temperature was measured by using a thermocouple located in the catalyst bed. The effluent gas was analyzed using TCD-GC.

Each chemisorption experiment was carried out in a high-vacuum system by a volumetric method. Before adsorption of H_2, the catalysts were treated in H_2 at 1073 K for 0.5 h in a fixed-bed reactor. After this pretreatment, the sample was transferred to the cell for adsorption measurements under air atmosphere. Before each measurement, H_2 pretreatment at 773 K was carried out for 0.5 h in the cell. After evacuation at 773 K, the sample was cooled down to room temperature. The irreversible amount of H_2 adsorption was determined at room temperature. The adsorption gas pressure was about 2.63 kPa. The sample weight was about 0.25 g. The dead volume of the apparatus was 63.5 cm^3.