



Fabrication of a regenerable Ni supported NiO-MgO catalyst for methane steam reforming by exsolution

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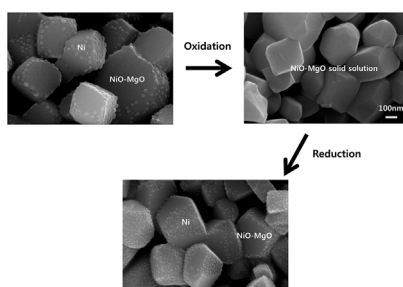
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HIGHLIGHTS

- Ni nanoparticles supported on NiO-MgO solid solution were synthesized by exsolution.
- The growth of Ni nanoparticles depended on the homogeneity of the solid solution.
- The catalytic activity was not to be degraded appreciably for 1000 h of operation.
- The metallic nickel moved reversibly to and out of the parent solid solution.

GRAPHICAL ABSTRACT



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ABSTRACT

Nickel nanoparticles supported on a NiO-MgO solid solution are fabricated using the exsolution process. Upon reduction, the nickel nanoparticles are exsolved from a $\text{Ni}_{0.4}\text{Mg}_{0.6}\text{O}$ solid solution powder. From the results obtained from transition electron microscopy (TEM) and temperature programmed reduction (TPR) measurements, it is concluded that the size and dispersion state of the nickel nanoparticles strongly depend on the homogeneity of the parent solid solution. Sintering the parent solid solution powder at a high temperature results in a homogeneous solid solution, which leads to a decreased reducibility of the nickel ions and, consequently, well-distributed Ni nanoparticles are successfully obtained. The metallic nickel moves reversibly to and out of the parent solid solution in response to a specific atmospheric condition. The methane steam reforming over the as-synthesized nickel nanoparticles are evaluated and appreciable degradation (1000 h) of the catalytic activity is not found for the catalyst sample that is sintered at 1000 °C followed by subsequent reduction to 800 °C.

1. Introduction

There are two important issues to consider when designing a catalyst for industrial use; one is the catalytic activity and its associated selectivity, determined directly by its bulk and surface chemical

composition, microstructure or morphology, and phase composition [1]. The other is the thermal and mechanical stability which ensures the successful implementation when used in catalytic systems [2,3]. Various preparation methods have previously been studied and implemented for creating efficient catalytic materials with potential

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commercial applications. The blending (precipitation) and mounting (infiltration) methods are the most common traditional processes used to prepare catalytic materials [2].

The infiltration or impregnation method is widely employed in the preparation of metal-supported oxide catalysts and consists of catalytic nanoparticles dispersed on the surfaces of a porous oxide support. However, it is difficult to control the size, distribution, and anchorage of the catalyst nanoparticles using this method [4]. In addition, the infiltration method can be a time-consuming and costly process [5]. Catalytic materials can also be obtained by blending the proper reagent from a liquid medium with precipitating agents. The precipitate is transformed into the catalyst in subsequent calcination processes.

Exsolution is a new type of blending technique currently being studied by various researchers [6–9]. In exsolution, the catalytically active species - for example, metal ions - are incorporated into the crystal structure of the oxide support and, upon reduction, cationic metals are precipitated as metallic nanoparticles, effectively coating the surface of the oxide support. The finer and homogeneously dispersed catalytic nanoparticles can be fabricated using exsolution. In comparison with the infiltration process, the time-consuming multiple deposition steps are not required in the exsolution process. Another interesting feature observed in the catalytic system prepared by exsolution is that the metallic nanoparticles move back onto the oxide support in a reversible manner during redox cycles [6,10,11]. This suggests that the exsolved nanoparticles can be regenerated via simple redox cycles.

NiO-MgO and its related oxide systems have been extensively studied due to their excellent catalytic activity in the methane reforming process and in the hydrogenation of nitriles derived from metallic catalyst with basic properties [12–15]. Normally, the NiO-MgO materials are prepared by impregnating MgO with an aqueous solution of nickel precursors - typically nickel nitrates - followed by reduction under a hydrogen atmosphere. In addition, they can be prepared by reducing a NiO-MgO solid solution powder. Since exsolution strongly depends on the composition and thermal history - for example, following calcination and reduction of the solid solution powder -, control of the size, its content, and distribution of the exsolved nickel nanoparticles are important research topics that need to be addressed.

In this study, the NiO-MgO solid solution powder was synthesized using aqueous solutions of metal nitrates and Ni/MgO catalyst powder were prepared from the solid solution powder by the exsolution technique. We investigated the effect of various parameters such as reduction temperature and time for the growth of the nickel nanoparticles from the parent solid solution powder. In particular, we focused on the sintering temperature for the solid solution powder to control the *in situ* growth of nickel nanoparticles. In addition, the catalytic activity in the methane steam reforming reaction was investigated using the synthesized exsolved nickel nanoparticles supported on the NiO-MgO solid solution powder.

2. Experimental procedure

A nickel magnesium oxide (NiO-MgO) solid solution powder with the general formula of $\text{Ni}_{0.4}\text{Mg}_{0.6}\text{O}$ was prepared by the co-precipitation method from nickel nitrate (> 99.0%, Aldrich), magnesium nitrate (> 99.0%, Aldrich) and potassium carbonate (> 99.0%, Aldrich). A green precipitate was obtained after adding the potassium carbonate into an aqueous solution of nickel and magnesium nitrates. The precipitate formed was filtered and washed using hot de-ionized water. The precipitate was then dried at 100 °C for 12 h and subsequently calcined at 800 °C for 5 h. The obtained powder was further heat-treated (sintered) at 800, 900, and 1000 °C for 3 h before being reduced (exsolved) under a hydrogen atmosphere at 700, 800, and 900 °C for various times.

The crystal structure of the NiO-MgO solid solution powders and the catalyst samples were analyzed by using X-ray diffraction (XRD, RU-

200 B, Rigaku Co., Ltd.) with Ni-filtered $\text{CuK}\alpha$ radiation. Temperature-programmed reduction (TPR) measurements were carried out in a quartz reactor using a 5% H_2/Ar mixture with the flow rate of 50 sccm. The heating rate was $10\text{ }^\circ\text{C}\cdot\text{min}^{-1}$ and the sample weight was 0.5 g. The microstructure was examined by field emission scanning electron microscopy (FE-SEM, JSM-6700 F, JEOL). Chemical mapping with EDS was performed using four integrated silicon-drift EDS detectors (ChemSTEMÔ technology) in the transmission electron microscope (Talos F200X, FEI) operated at 200 kV. The beam current used was 1.6 nA cm^{-2} since it gives higher count rates for X-ray signals in a shorter time.

Catalytic tests for the methane steam reforming reaction were performed using a combined system comprised of a conventional fixed-bed quartz reactor (8 mm in diameter) and an on-line micro-gas chromatography. 100 mg of $\text{Ni}_{0.4}\text{Mg}_{0.6}\text{O}$ solid solution powder was pelletized into a disk (5 mm diameter with 1.5 mm thickness) which were sintered at 800, 900, and 1000 °C for 3 h. The sintered disk sample was loaded into the middle of the reactor between two flocks of quartz wool. Before carrying out the methane steam reforming reaction, the catalyst samples were heated at 700 °C in a stream of Ar (100 sccm) and then reduced in a stream of H_2 (100 sccm) at 700, 800, and 900 °C for various times. The catalytic reaction was carried out at different temperatures using a mixture of 50 sccm of 10% CH_4 and 50 sccm of Ar that was introduced through the quartz reactor. Water vapor (10%) was added to the feed gas using a bubbler. After a reaction time of 30 min, the outlet gases were analyzed with an on-line micro-gas chromatography (GC, CP-4900, Varian). The micro-GC was equipped with PPQ and M5A columns, and a thermal conductivity detector (TCD). Experimental set-up for investigating the methane steam reforming reaction was shown in Figure S1 in Supplementary Materials.

3. Results and discussion

3.1. Analysis of catalysts

Fig. 1 shows the X-ray diffraction (XRD) patterns of the as-synthesized solid solution powder and the catalyst samples reduced at 700, 800, and 900 °C for 5 h. All diffraction peaks observed in the as-synthesized powder was assigned to $\text{Ni}_x\text{Mg}_{1-x}\text{O}$ ($x = 0.6$ and 0.5 ; JCPDS #34-0410 and #24-0712) with no peaks corresponding to the nickel oxide (NiO), magnesium oxide (MgO), or other unwanted secondary phases being observed in the spectra. This result indicated that the synthesized powder was a single-phase solid solution of NiO and MgO

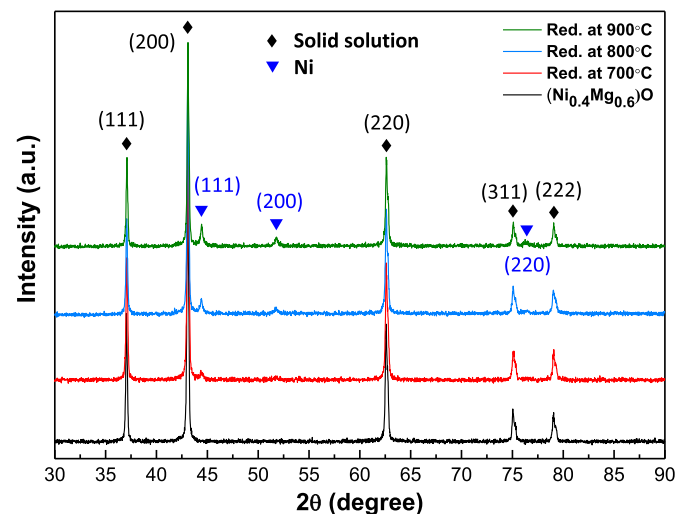


Fig. 1. XRD patterns of the parent solid solution powder and catalyst samples reduced at 700, 800, and 900 °C for 5 h. The catalyst samples were sintered at 1000 °C for 3 h before reduction.

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