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Catalytic performance of Ni–Al nanoparticles fabricated by arc plasma evaporation for methanol decomposition

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ABSTRACT

The catalytic properties of Ni-25 at% Al (Ni₂₅Al) nanoparticles fabricated by arc plasma evaporation toward methanol decomposition were studied at temperatures ranging from 513 to 753 K. The Ni₂₅Al nanoparticles showed much higher activity than gas atomized Ni₂₅Al powders. They showed a high degree of selectivity for methanol decomposition into H₂ and CO. Side reactions such as methanation and water-gas shift reaction were suppressed to a high temperature of 673 K, which is hardly achieved for common Ni catalysts. Detailed characterization of the Ni₂₅Al nanoparticles showed that they were composed of Ni, Ni₃Al, and Al₂O₃ phases with Ni and Al oxides on the surface of the Ni and Ni₃Al phases. The Ni oxides were reduced to Ni phase by a hydrogen reduction prior to methanol decomposition, while the Al oxides remained unchanged. It is supposed that the Ni phase provided the active sites for methanol decomposition, and the Ni₃Al and Al₂O₃ phases acted as supports for the Ni phase. Probably the Ni₃Al and Al₂O₃ phases provided good resistance to agglomeration of the Ni phase during the reaction, which might contribute to maintain the high catalytic performance of the nanoparticles for methanol decomposition. Copyright © 2014, Hydrogen Energy Publications, LLC. Published by Elsevier Ltd. All rights reserved.

Introduction

Bimetallic catalysts with nanosized particles have received considerable interest as the catalysts for environmental cleanup, including for cleaning automotive and industrial exhaust gases, and for energy production involving fuel cells [1–3]. Bimetallic nanoparticles are commonly synthesized by wet chemical processes, such as the chemical reduction of

metal salts. However, it is not easy to ensure the homogeneity and crystallinity of the nanoparticles when fabricated through such methods. This is because wet chemical processes involve low temperatures, and thus, the degree of alloying of the constituent metallic elements is often limited. In contrast to wet chemical processes, thermal plasma-based ones involve the evaporation of the constituent metals at temperatures higher than 10,000 K, followed by the rapid condensation of the gas phases [4–6]. It is, therefore, to be expected that the

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degree of alloying would be higher during thermal plasma-based synthesis processes and that these processes would lead to the formation of homogenous, high-crystallinity alloys and intermetallic phases. So far, a number of thermal plasma-based processes have been developed. Among them, the vacuum arc plasma evaporation (VAPE) method is commonly used for the deposition of thin films [7,8] and the fabrication of pure metal and intermetallic nanoparticles [9,10].

It has been reported that the formation of intermetallic compounds was important for obtaining good catalytic properties [3,11,12]. In the Ni–Al system, there exist several intermetallic compounds, namely, NiAl₃, Ni₂Al₃, NiAl, and Ni₃Al. Among these, NiAl and Ni₃Al are known to be promising high-temperature structural materials owing to their excellent strength at high temperatures and resistance to corrosion and oxidation [13–15]. We recently reported that Ni₃Al powders have a catalytic potential for methanol decomposition and methane steam reforming [16–20]. The Ni₃Al powders used as catalysts had been fabricated by either mechanical milling or a gas atomization process. Since the size of the Ni₃Al particles had been relatively large (their diameter was greater than several micrometers) and their specific surface area had been low, surface pretreatments had been necessary to enhance the catalytic activities of the powders. In our previous reports we alternatively attempted to fabricate Ni₃Al nanoparticles using the VAPE method [21,22]. The fabricated nanoparticles were not in a Ni₃Al single phase, but composed of Ni, Ni₃Al, and a small amount of NiAl, with Al₂O₃ and NiO phases formed on their surfaces. We found that the nanoparticles exhibited high catalytic activities for CO oxidation, and their activities were comparable to that of Pt-based catalysts [22].

As well-known, hydrogen is a clean and efficient energy source for fuel cells. Hydrogen is commonly produced over Cu and Ni catalysts through catalytic decomposition or steam reforming of methanol [23–27], but more efficient new catalysts are still continuously needed. In this study, we report the catalytic properties of the Ni–Al nanoparticles toward hydrogen production from methanol decomposition. The activity is discussed on the basis of detailed characteristics of the nanoparticles before and after the reaction obtained from synchrotron X-ray powder diffraction (SXR) analysis, transmission electron microscope (TEM) analysis, and temperature-programmed reduction (TPR) analysis.

Experimental

Catalyst preparation

An ingot with the stoichiometric composition of Ni₃Al (Ni-25 at% Al) was prepared by arc melting. Then, the Ni–Al (Ni25Al) nanoparticles were fabricated from the ingot using the VAPE method, which has been described elsewhere [12,22]. First, the work chamber in the VAPE system was evacuated to about 2.5×10^{-3} Pa, and then high-purity argon gas (99.999%) was introduced to the pressure between 1 and 50 Pa. The electric power for the arc plasma evaporation was 3 kW ($U = 20$ V, $I = 150$ A). The fabricated nanoparticles were passivated with a mixture gas of argon and air before they

were taken out from the work chamber in order to prevent them from igniting.

Catalytic performance

Experiments on the catalytic hydrogen production from methanol were carried out in a conventional fixed-bed flow reactor, as described in the previous report [28,29]. The amount of Ni₂₅Al nanoparticle sample set in the reactor was 0.04 g. Prior to the reaction, the sample was reduced at 773 K for 1 h in flowing H₂ (30 ml min⁻¹) unlike the case for CO oxidation [22]. This reduction temperature was determined from the results of a temperature-programmed reduction (TPR) measurement carried out at a heating rate of 10 K min⁻¹ from room temperature to 1173 K in a stream of H₂ diluted with Ar (4 vol% H₂; total flow rate, 50 ml min⁻¹). The H₂ consumption in TPR measurement was calibrated with pure NiO powder (99.9%, Kojundo Chemical Lab. Co. Ltd.).

After the hydrogen reduction, a nitrogen flow was introduced to flush the H₂, and the temperature was decreased to 513 K. Subsequently, pure methanol was introduced into the reactor at a liquid hourly space velocity (LHSV) of 60 h⁻¹ (defined as the volume of methanol in the liquid phase passed over each unit volume of catalyst per hour) using a plunger pump together with the N₂ carrier gas (30 ml min⁻¹). The reaction temperature was increased in stages from 513 to 793 K at intervals of 40 K. The outlet gas composition, including the gasified H₂O and CH₃OH contents, was analyzed after holding for 0.5 h at each temperature using two on-line gas chromatographs (GC) equipped with thermal conductivity detectors (GL Science, GC323). After the GC measurement, H₂O and CH₃OH were removed from the effluent gas by a cold trap, and the total flow rate of the outlet gases was measured with a soap bobber meter. The production rate of each product *i*, R_i , was calculated using the following equation:

$$R_i = (C_i \times F_i) / M \quad (1)$$

where C_i is the volume fraction of the gaseous product *i* in the outlet gas, excluding the CH₃OH and H₂O, F_i is the total flow rate of the outlet gas (mol min⁻¹), and M is the weight of the catalyst (g). The production rate of H₂O was calculated from ratio of the volume fraction of H₂ to that of gasified H₂O in the outlet gas.

For comparison, the same methanol decomposition test was carried out over an atomized Ni₃Al (Ni-25at%Al) powder sample (Kojundo Chemical Co., Ltd.) which was fabricated using conventional argon gas atomizing method. The particle size of the atomized powder was between 75 and 150 μm, and the BET specific surface area was 0.1 m²/g.

Catalyst characterization

Since Ni₃Al and Ni phases have cubic crystal structures with close lattice constants, SXR measurements were performed using a high-resolution X-ray powder diffractometer with a large-radius imaging-plate camera at the BL15XU beam-line in SPring-8 [30,31]. The wavelength of the incident X-ray beam was 0.065297 nm, which is the Nb K absorption edge.

The surface area of the nanoparticles was determined from the amount of nitrogen adsorption on the powder using the

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