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Effect of the grain diameter of Ni-based catalysts on their catalytic properties in the thermocatalytic decomposition of methanol

Marta Michalska-Domańska [a, b, *], Jerzy Bystrzycki [b, †], Bartłomiej Jankiewicz [a], Zbigniew Bojar [b]

[a] Institute of Optoelectronics, Military University of Technology, Kaliskiego 2 Str., 00-908 Warsaw, Poland
[b] Faculty of Advanced Technology and Chemistry, Military University of Technology, Kaliskiego 2 Str., 00-908 Warsaw, Poland

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ABSTRACT

The influence of grain size on the catalytic activity of Ni-based solid-state catalysts in the thermocatalytic decomposition of methanol was investigated. The carbon deposit, obtained during the catalytic activity and stability tests, was analyzed in detail by scanning electron microscopy (SEM), Brunauer–Emmett–Teller analysis (BET), and X-ray diffraction (XRD). It was found that the Ni_3Al catalyst with a bigger grain diameter exhibits higher catalytic activity and stability in a methanol decomposition reaction. The reason for the differences in the catalytic activity and stability of solid-state catalysts depending on the grain diameter of the catalyst was proposed. At the tops of the obtained nanotubes/nanofibres, one can see Ni nanoparticles in all investigated Ni_3Al thin foils with every tested grain size.

1. Introduction

Nowadays, environmentally friendly energy sources are very important because fossil fuel resources are dwindling rapidly and the environment is being polluted by increased industrial emissions. From this point of view, the hydrogen economy has a good chance for expansion and, in the future, can replace traditional fossil fuel energy. Hydrogen is a natural, renewable energy source, which is widely available in the world in the form of many commonly occurring chemicals (including biomass, biogas, natural gas or hydrocarbons). On an industrial scale, hydrogen is currently produced by the methane steam reforming method (SMR) [1–6], but methanol is also widely considered by researchers as a hydrogen resource [7–11]. The advantages of using methanol instead of methane are its availability, relatively low toxicity and ease of storage, transport and usage [12]. The production of hydrogen generally requires chemical reactions carried out at an elevated temperature and suitable catalysts, depending on the source of hydrogen [13]. Traditionally, in thermocatalytic decomposition reactions, transition metals from group VIII of the periodic table of elements are used as catalysts (e.g., Ni, Fe, and Co) [14–18]. Ni-based catalysts exhibit extremely high catalytic activity in methanol decomposition and promote the production of carbon nanostructures (mainly carbon nanotubes) [19]. This can be considered a disadvantage (because of the gradual "poisoning" of catalysts) or as an advantage (because of the production of CNTs as a by-product, which can be used in other reactions, such as composite fabrication) [2,20,21,47].

At present, in the majority of industrial processes, the catalysts are used in the form of a powder. However,

* Corresponding author. Institute of Optoelectronics, Military University of Technology, Kaliskiego 2 Str., 00-908 Warsaw, Poland.
E-mail addresses: marta.michalska@wat.edu.pl, mrk.michalski@gmail.com (M. Michalska-Domańska).
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solid-state catalysts are also well known [22–24] and have the same advantages in relation to powder catalysts: they do not require a carrier, it is possible to give them all kinds of shapes (e.g., a honeycomb structure), they are not subjected to erosion during the reaction and there is also no alignment problem in this case. One of the Ni-based, solid-state catalysts is Ni_3Al [33], which belongs to multifunctional materials, combining properties of both the constructional and functional materials. They are resistant to oxidation and corrosion, have a relatively low density and a relatively high melting point, and are relatively easy to form [25–30]. According to the literature, Ni_3Al intermetallic thin foils exhibit catalytic properties in hydrocarbon decomposition reactions [31–37]. Based on the literature, the relatively high temperature of maximal hydrocarbon conversion is the main disadvantage of this material.

In the case of powder catalysts, the size of the catalytic particles or support particles is a very important factor determining the catalytic activity [20,21,38,40]. It is expected that the smaller particles of powder catalysts increase the surface of the metal and thereby activity should increase [39]. Chen et al. found that the support particle size has significant influences on the physicochemical properties and catalytic activity of the resulting $Ni/A1_2O_3$ catalyst, but little influence on the selectivity of *p*-nitrophenol hydrogenation. Additionally, at a comparable amount of Ni loading, the catalytic activity of $Ni/A1_2O_3$, prepared with alumina support of smaller particle size, was lower [40]. Matsumura et al. proved that the small nickel particles are disadvantageous in the methanol decomposition reaction. It was found that catalytic activity does not simply relate to the Ni surface area of the sample, but it depends on the amounts of carbon monoxide and hydrogen strongly adsorbed on the catalyst's surface [21]. They believed that catalytic activity in methanol decomposition depended on the Ni particles' size and, for particle dimensions from 60 to 100 nm, the catalysts were most effective [21]. Takenaka et al. found that the type of support had an influence on the size of supported Ni and because of this on their catalytic properties [20]. Moreover, the method of preparing the catalyst is important and significantly affects their catalytic properties [20,36–38]. So far, the impact of grain diameter on their catalytic properties in solid-state catalysts has been not tested.

In the solid state, grain boundaries represent rapid diffusion paths in the materials [41,42], so it was expected that the smaller the grain, the bigger the catalytic activity. In this work, Ni_3Al thin foils with different average grain diameters were used in catalytic tests in the methanol decomposition reaction. The catalysts were prepared by a new method [43], as compared to the methods developed by other researchers [25–28,33,44,45]. In this paper, the explanation of the grain diameter effect on the catalytic properties of Ni_3Al thin foils in thermocatalytic methanol decomposition has been attempted.

2. Experimental

The Ni_3Al intermetallic alloys with a composition of 77.54Ni-22.1Al-0.26Zr-0.1B (at %) was induction-melted from pure elements in high purity argon and then cast into a shell mold. The as-cast ingot was cut into sheets using a fraction saw. The thin foils of Ni_3Al were obtained by cold rolling at room temperature to 95% of thickness reduction without intermediate annealing. The cold deformed alloy was then subjected to recrystallization annealing at different temperatures and times in an argon atmosphere to obtain desirable average grain diameters: for about 30 μm, it was 5.5 h at 1100 °C; for about 5 μm, it was 1 h at 900 °C. Additional information about the fabrication process has been described previously [43]. Before the catalytic tests, the Ni_3Al foil was mechanically polished (up to the thickness of approximately 50 μm) and degreased in acetone.

Methanol decomposition assays were carried out in the fixed-bed reactor with high-purity Ar as a carrier gas. The flow rate of the pure methanol feed was 0.006 dm^3/h and the flow rate of the carrier gas was three dm^3/h. The methanol was put into the reactor system at a constant rate using an infusion pump. The feed rate of the inert gas was controlled by an electronic flow controller purchased from BetaErg provided with two drivers: a low-bandwidth (0.0015–0.3 ml/min) and high-bandwidth (0.3–12 dm^3/min). At first, methanol changes to gas at 100 °C in the low-temperature reactor, and next, in the high-temperature reactor, the proper decomposition reaction occurs.

The intermetallic phase was tested in a temperature range of 100–600 °C, where the temperature was increased by 100 °C and was maintained constant for 1 h. Ni_3Al with for the 5 μm grain diameter, the tested temperature range was extended to 700 °C. Around the temperature of maximal methanol conversion, the measuring points were concentrated: in the temperature range 450 °C–650 °C, the temperature increased by 50 °C and was held constant for 1 h. Temperature control in the reactors was done using electronic controllers connected with thermocouples. In the temperature of maximal methanol conversion, isothermal catalytic tests were conducted for 17 h. The analysis of the gaseous products of reactions was performed on-line by using a gas chromatograph Clarus 500 coupled with a mass spectrometer Clarus 560S purchased from Perkin Elmer.

The surface morphology of thin foils before reactions were observed using a field-emission scanning electron microscope FE-SEM (FEI, Quanta 3DFEG) equipped with an electron backscatter diffraction (EBSD) and EDS detector. The solid products of the reactions were also analysed by using a Quanta 3DFEG.

The specific surface area of the obtained nanostructures was measured by the Brunauer–Emmett–Teller method (S_{BET}) using a Micromeritics Accelerated Surface Area and Porosimetry System (ASAP 2020, Micromeritics) at 77 K with Kr as the adsorption gas, in the range of relative pressures from 0.08 to 0.45. All the samples were outgassed in a vacuum for 2 h at 200 °C before the analysis. The mass of solid products formed during the methanol decomposition reactions was determined by a Radwag analytical laboratory balance AS 60/C/2 with an accuracy of 0.01 mg.

The phase structure of the surfaces of the intermetallic catalysts and the solid products was examined by X-ray diffraction using a Rigaku Ultima IV diffractometer with Co Kα radiation (λ=1.78897 Å) and operating parameters of 40 mA and 40 kV with a scanning speed of 1°/min with step

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