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Research Paper

CO and C₃H₈ oxidation activity of Pd/ZnO nanowires/cordierite catalystMehmet Şen^a, A. Osman Emiroğlu^{b,*}, M. Bahattin Çelik^c^a Department of Automotive Technology, AIBU, 14900 Bolu, Turkey^b Department of Mechanical Engineering, AIBU, 14100 Bolu, Turkey^c Department of Automotive Engineering, Karabuk University, 78050 Karabuk, Turkey

HIGHLIGHTS

- The potential of using ZnO nanowires as monolith catalyst carrier was investigated.
- ZnO nanowire structures have greater effective porosity and more open surface area.
- CO and C₃H₈ oxidation activities of Pd/ZnO nanowires/cordierite were examined.
- ZnO nanowires are promising materials for the use as a catalyst wash-coat.

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ABSTRACT

Using nanowires grown on monolith cordierite as catalyst wash-coat is a new concept. ZnO nanowires array has different pore-region diffusion of reactants in the catalyst media because it can have greater effective porosity and average diffusion length scale than traditional catalyst carrier. Also, thickness of ZnO nanowires array is less than conventional wash coat. ZnO nanowires were grown on monolith cordierite channels, and Pd was impregnated on the nanowires. The catalyst structure was characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD), and atomic absorption spectrometry (AAS). The activity performance of Pd/ZnO nanowires catalyst for C₃H₈ and CO was examined under lean, stoichiometric and rich conditions. T50 was achieved under stoichiometric condition of gas mixture for C₃H₈ and CO at 400 °C and 235 °C, respectively.

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1. Introduction

Regulations of the stringent exhaust emissions require extremely active and durable catalysts. Despite the improvements in the engine and combustion technology, it is not possible to remove the exhaust emissions without using catalysts in a satisfactory manner. Three-way catalysts (TWC) are extensively used to reduce the amounts of carbon monoxide (CO), unburned hydrocarbons (HC) and nitrogen oxides (NO_x) in the automotive exhaust emissions [1,2]. Today, most of the catalytic converters used in automobiles consist of a honeycomb monolithic substrate made of ceramic materials with high melting temperatures. Cordierite is the most common of these ceramic materials.

In the catalytic process, there exists a direct relationship between the number of the reactant molecules converted to products in a given time and the number of catalytic sites available to the reactants.

Therefore, it is common to maximize the number of active sites by dispersing the catalytic particles onto a high surface area carrier such as Al₂O₃, SiO₂, TiO₂, La₂O₃, ZrO₂, and CeO₂. γ-Al₂O₃ is the most widespread carrier used in catalysis, in particular, for environmental applications. Usually, the carriers themselves are not catalytically active for the specific reaction in question. However, they are essential to the promotion of the activity and selectivity and the maintenance of the overall stability and durability of the catalyst [1]. In order for the shape and size of zinc oxide (ZnO) to be easily controlled in a variety of structures, nanorods, nanowires, nanotubes and the other morphology of ZnO crystals can be synthesized [3,4]. There are many studies showing the synthesis of ZnO on different supports [5–7]. Using the hydrothermal method, the synthesis of nanowires on large surfaces can be accomplished uniformly at low temperatures [5,6,8]. Hydrothermal synthesis of nanowires has the following two stages of seeding and growth [6,9,10].

Pt, Pd and Rh (platinum-group elements; PGEs) are the active components for the reduction of exhaust emissions. Among them, Pd is frequently used in many industrial catalytic processes, especially in the removal of motor vehicle emissions at low temperatures

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since it has important functions such as high redox properties and oxidation activity [11,12]. Due to the high sintering resistance of Pd on ZnO, heat resistance of Pd/ZnO is better than any other alternative active metal species at high reaction temperatures [13]. Furthermore, in hydrogen-rich environments, Pd/ZnO catalyst is highly active in the selective oxidation of CO [14,15].

The use of Pd/ZnO structures as catalysts is usually observed in MSR (methanol steam reforming) applications [16–18]. In most of these studies, ZnO was used in powder form. Danwittayakul and Dutta [16] investigated catalytic activity of Pd-doped ZnO nanowires grown on cordierite in MSR and reported that as the aspect ratio was high, ZnO nanowires had higher surface area, and thus became more active in MSR reaction. Also, Baker et al. [19,20] synthesized ZnO nanowires on the single-crystal Si-wafer, using hydrothermal method, examined propane (C_3H_8) oxidation activity of the catalysts prepared by coating with Pt and Pd by sputter-coating, and reported that nanowires array increased the performance of the catalyst because it increased the surface distribution of the active points. Guo et al. [21] reported that thermal and mechanical resistances of ZnO nanowires grown on monolith cordierite are very high, and the amount of active metal used in nanowires was 10–40 times less than the conventional powder catalyst.

The aim of this study is to investigate the potential of ZnO nanowire structures to be used as monolith catalyst carrier. ZnO nanowires are different from the ordinary carrier construction applied to customary catalytic processes. ZnO nanowires have different pore-region diffusion of reactants in the catalyst media because they can have greater effective porosity, more open surface area and average diffusion path than the conventional catalyst carrier as illustrated in Fig. 1.

The green points in Fig. 1a and 1b represent the active metals on the carrier material surfaces. The red arrows, on the other hand, represent the diffusion path of the gasses to active areas. Fig. 1b shows that ZnO nanowires array has geometrically well-defined structure at nanometer scale, whereas in Fig. 1a the traditional catalyst carriers have a geometrically random construction though having materials with a similar chemical composition. Consequently, the exhaust emission gases can reach the active metals impregnated on nanowires easily which will have a positive effect on the catalyst activity. For this reason, using more effectively active regions will decrease the amount of precious metals required.

Another point is that the open frontal area (OFA) of the catalyst (in which the gas flows) is more because the ZnO nanowire coating thickness on cordierite is less when compared with the traditional carrier material coating thickness. This situation will cause less decrease in the exhaust pressure in vehicle applications, and therefore the loss in the power in the engine stemming from the decrease in the pressure will also decrease [22–24]. Another advantage of ZnO nanowire coating thickness being much less when compared with the alumina coating thickness is that the active metals are closer to the surface to allow the exhaust gases to reach

them. For this reason, this will decrease the reaction time of the reactants and the leaving time of the products from the catalyst because this will decrease the surface/sub-surface diffusion path lengths of the product gas molecules [1].

In this fundamental study, Pd was impregnated on the ZnO nanowire arrays grown on monolith cordierite, and its effects on CO and C_3H_8 oxidation have been examined.

2. Experimental procedure

2.1. Preparation of catalysts

The catalyst was prepared from 400 cells per square inch (cpsi) monolith cordierite ($2MgO.2Al_2O_3.5SiO_2$) substrates by cutting 1" in diameter to 1" in height. ZnO nanowires were grown on monolith cordierite using an aqueous solution technique followed by Greene et al. as summarized below [5,6].

Nanowire synthesis was carried out in the two stages: seeding and growth. For the seeding process, 5 mM solution was prepared by dissolving zinc acetate dihydrate ($Zn(Ac)_2.2H_2O$, 98%, Sigma-Aldrich) in ethanol (absolute, Merck). The catalyst was placed into 30 mL seed solution and was heated in the microwave oven at 70 W for 5 min. Then it was calcined by keeping it at 300 °C in muffle furnace for 30 min. For the growth process, 600 mL solution was prepared by 25 mM zinc nitrate hexa hydrate, ($Zn(NO_3)_2.6H_2O$, 99%, Sigma-Aldrich), 25 mM hexamethylenetetramine ($(CH_2)_6N_4$, 99%, Sigma-Aldrich) and 5 mM polyethyleneimine (50% H_2O , Fluka) dissolved in deionized water.

The catalyst was wrapped in aluminum silicate cotton and was placed in plastic measuring cylinder which was drilled at the bottom for circulation of growth solution. The catalyst in measuring cylinder was placed into beaker and the growth solution was added then heated for 3 h at 90 °C on a hot-plate. This process was repeated three times with refreshed growth solution. Circulating in a measuring cylinder of growth solution with a peristaltic pump was provided to carry the solution to the cordierite channel. Afterwards, the catalyst was washed with de-ionized water and calcined at 300 °C for 30 min.

The Pd/ZnO nanowires array catalyst was prepared by using the wetness impregnation method. All operations were carried out under atmospheric conditions. For this purpose, 1 mM Pd solution (30 mL) was prepared by dissolving $PdCl_2$ (99.9%, Sigma Aldrich) in ethanol. Impregnation process was carried out by dipping catalyst in Pd solution for one day at 55 °C. The catalyst was calcined at 450 °C for 4 h to remove chlorine compounds.

2.2. Characterizations of catalysts

A Jeol JSM-6390A model scanning electron microscopy (SEM) was used to evaluate the structure, size and distribution of nanowires. Composition quantification, crystallographic structure determination and crystallite size analysis of the ZnO nanowires were conducted by using a Rigaku model Multiflex X-Ray Diffractometer with Cu K- α radiation source. The size and morphology of the ZnO and Pd particles, and Pd distribution on nanowires were examined from micrographs obtained with a Jeol 2100 JEM High-Resolution transmission electron microscope (TEM). Amount of Pd in the catalyst was determined by using a Perkin Elmer Analyst 800 model atomic absorption spectroscopy (AAS).

2.3. Activity test of catalysts

Test system was constructed as in Fig. 2 to determine the capacity of oxidation of the catalyst.

The catalyst placed in the quartz glass tube was inserted in a Protherm model tubular furnace. Sent into the furnace were 99%

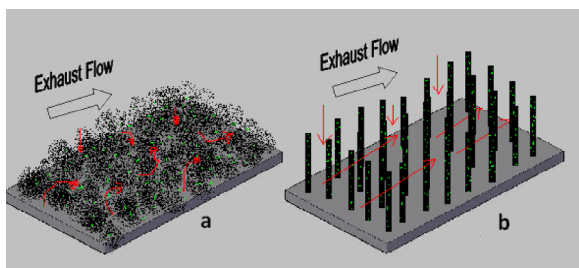


Fig. 1. Schematic model of (a) traditional random structure and (b) nano-array ordered form.

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