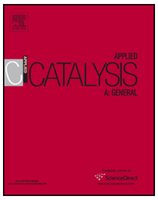
Applied Catalysis A: General 510 (2016) 216–226

Contents lists available at ScienceDirect

Applied Catalysis A: General

journal homepage: www.elsevier.com/locate/apcata



Metal-foam-structured Ni–Al_2O_3 catalysts: Wet chemical etching preparation and syngas methanation performance

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ARTICLE INFO

Article history:
Received 2 July 2015
Received in revised form 23 October 2015
Accepted 18 November 2015
Available online 29 November 2015

Keywords:
Structured catalyst
Syngas methanation
Foam
Enhanced heat transfer
CFD simulation

ABSTRACT

Production of substitute natural gas (SNG) by methanation of syngas generated from various carbon sources provides a promising route towards coal clean utilization and sustainable energy future. Monolithic Ni (or Cu, NiCu-alloy)-foam-structured Ni–Al_2O_3 catalysts were developed by a facile modified wet chemical etching method. The as-prepared catalysts were characterized by X-ray diffraction, scanning electron microscopy, inductively coupled plasma atomic emission spectrometry and H_2-temperature programmed reduction. Among these catalysts, Ni–Al_2O_3/Ni-foam has the most surface active Ni atoms and exhibits the best catalytic methanation performance, achieving 99.9% CO conversion with 90.0% methane selectivity and being stable for at least 1000 h for a feed gas of H_2/CO (3/1) at 330 °C and gas hourly space velocity (GHSV) of 5000 h^{-1}. Effects of reaction temperature, reaction pressure and GHSV are also investigated on the catalytic performance of Ni–Al_2O_3/Ni-foam for CO methanation. Computational fluid dynamics calculation and experimental measurement consistently show that such monolithic Ni–Al_2O_3/Ni-foam can dramatically reduce the "hotspot" temperature due to its high thermal conductivity. Moreover, the feasibility of our Ni–Al_2O_3/Ni-foam catalyst for co-methanation of a simulated feed gas from coal gasification is studied as well as CO_2 methanation in the presence of high CH_4 concentration. We anticipate that our present work might stimulate commercial exploitation of the new-generation structured catalyst and reactor technology for the strongly exothermic syngas methanation toward energy-efficient process for SNG production.

1. Introduction

With the depletion of petroleum reserves, combined with ever-increasing demand for clean and reliable energy supply, it is exigent to develop renewable and alternative energy sources [1,2]. Production of substitute natural gas (SNG) by methanation of syngas provides a promising way towards alternative and sustainable energy future, because syngas could be generated from various carbon sources (coal, biomass, municipal solid waste, and even coke oven gas *etc.*) [3,4], and the methanation process is highly efficient (*e.g.*, overall chemical efficiency of 65% or higher from wood to SNG) [5,6]. Especially for the countries with coal-predominant energy structure, it is particularly desirable to develop coal-to-SNG technology to achieve the clean and high-efficient coal utilization and meanwhile to prevent the serious pollution [3].

It is noted that syngas methanation is a strongly exothermic process ($CO + 3H_2 \rightarrow CH_4 + H_2O$, $\Delta H_{25\,^{\circ}C} = -206$ kJ mol^{-1}; $CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$, $\Delta H_{25\,^{\circ}C} = -165$ kJ mol^{-1}) and undesired hotspots often arise in the reactor bed, which makes the temperature-control difficult and even shortens the catalyst lifetime. Although various technologies (packed bed (PB) with small particles, fluidized bed and slurry bed) are proposed for solving the limitation of heat transfer, some other challenges arise simultaneously: PB with thin reactor tube and small enough particles could achieve uniform temperature distribution, but its large pressure drop will lead to the problems of poor stability and high energy consumption; fluidized bed improves heat transfer efficiency inside the reactor but suffers from low production efficiency, poor durability and high operation cost [7]; slurry bed obtains an isothermal temperature profile by introducing a liquid phase, while an additional mass transfer resistance between the gases and solid catalyst is also

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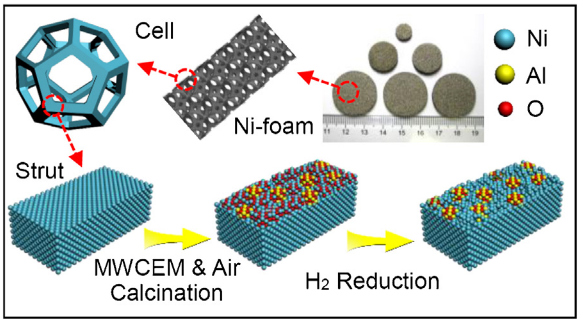
http://dx.doi.org/10.1016/j.apcata.2015.11.034

incurred. To date, large-scale implementation of syngas methanation to SNG is still based on a series of adiabatic fixed-bed reactors with inter-bed cooling and/or product gas recycling, which requires expensive high-temperature recycle compressor and leads to high energy consumption [8]. Thus, to develop an energy-efficient SNG process is particularly desirable and becomes the greatest source of inspiration for catalyst and/or reactor innovation. Various oxides supported Ni-based [4,9] and Ru-based [2,10] catalysts have been explored extensively for the methanation process. Nevertheless, most researches have been preferably focused on improving low-temperature activity and high-temperature anti-sintering property of the catalysts almost without shooting any glance at the consideration of heat transfer solutions. It should be minded that enhanced heat transfer would permit to avoid cascades of reactors and recycles as it is the case in actual SNG plant.

Structured catalysts and catalytic reactors (SCRs), with inherent outstanding features such as low pressure drop, high surface area to volume and enhanced heat/mass transfer, have been attracting ever-growing interests in the heterogeneous catalysis [11–14]. Especially for the highly endo/exothermic reactions, for instance, high heat transfer can suppress the formation of cold- or hot-spots within the catalyst bed and thereby allow long service life and safe operations. Accordingly, substantial research efforts have been dedicated to developing novel microfibrous structured catalysts and catalyzed metallic heat exchangers for the applications in highly endo/exothermic reactions, such as nanoporous-gold/Al-fiber catalysts for methanol to methyl formate [15,16], metal-microfibrous entrapped catalysts (MFEC) for dry reforming of methane [17,18] and Fischer–Tropsch synthesis [19], stainless-steel-fiber@HZSM-5 core–shell catalysts for methanol-to-propylene (MTP) [20,21], Ni-fiber structured gold nanoparticle catalysts [22,23] for the gas-phase selective oxidation of alcohols, and precious metal catalysts supported on monoliths for coupling the strongly endothermic hydrocarbon steam reforming with the strongly exothermic combustion reaction [14]. Far beyond these, monolithic metal-foams are also highly attractive candidates for the fabrication of structured catalysts with benefits of low density, interconnected porous structure, favourable mass/heat transfer, low pressure drop and desired mechanical robustness [24,25]. In spite of these marked promising features, what to be most noteworthy is that the practical applications of these metal-foams in catalysis are severely restricted by their low surface area and unsatisfied catalytic functionalization. Practically, the integration of active components onto monolithic foams involves a dissatisfactory coating process which leads to ill-controlled physic-chemical structure of the coated-catalysts [25,26] as well as their poor adherence to foam-surface [13,27], and binder harmful contamination [28].

The aforementioned metal foams are opening an opportunity on the development of novel monolithic catalyst and reactor technology for the energy-efficient SNG process from syngas, but effective and efficient non-coating method for placing catalytic active sites onto the surface of metal-foam structures is particularly desirable and is still a significantly challenging area. Herein, we demonstrate a facile protocol for catalytically functionalizing the monolithic metal-foams (metal: Ni, Cu, or NiCu alloy) via a modified wet chemical etching (MWCE) method to directly create Ni–Al_2O_3 catalysts on their struts. Scheme 1 shows the fabrication strategy of the representative Ni–Al_2O_3/Ni-foam catalyst engineered from micro- to macro-scales. The representative Ni–Al_2O_3/Ni-foam catalyst not only exhibits comparable activity/selectivity to the commonly used Ni/Al_2O_3 catalyst, but also shows excellent stability, high permeability and enhanced heat transfer. Computational fluid dynamics (CFD) calculation and experimental measurement consistently show that the hotspot in such Ni-foam-structured catalyst bed is dramatically reduced benefiting from its high thermal conductivity.



Scheme 1. Schematic illustration of modified wet chemical etching method for the representative Ni-foam-structured Ni–Al_2O_3 catalyst fabrication.

2. Experimental

2.1. Catalyst preparation

The thin-sheet metal-foam-structured catalysts were fabricated on macro-scale using our MWCE method followed by thermal treatment activation. Such method was developed on the basis of wet chemical etching technique [29,30]. Metal-foam chips (100 pores per inch (PPI); 2 mm thickness, 16.0 mm or 23.6 mm diameter equal to the reactor inner diameter of quartz tube (16.0 mm) or stainless steel tube (23.6 mm) respectively) of nickel (Ni), copper (Cu) and cupronickel (CuNi-alloy, Cu 90 wt% and Ni 10 wt%) were obtained from their large parent sheets by laser cutting. These metal-foam chips were respectively immersed into the chemical etching solutions and held at 65 °C for 2 h. The chemical etching solution consisting of 1.0 mmol L^{-1} sodium dodecyl sulphate (SDS, $C_{12}H_{25}$-OSO_3Na), 0.2 mol L^{-1} acetic acid (CH_3COOH) and 0.3 mol L^{-1} aluminium nitrate ($Al(NO_3)_3$) was employed for the Ni- and CuNi-alloy foams, while such solution with nickel nitrate ($Ni(NO_3)_2$) adding to a concentration of 0.2 mol L^{-1} was utilized for the Cu-foam. All the chemicals were purchased from Sinopharm Chemical Reagent Co. Ltd., and directly used without further treatment. After wet chemical etching, the resulting foams were thoroughly washed using distilled water and dried overnight at 100 °C, followed by calcining in air for 2 h. The calcination temperature of 300 °C was used except for the Ni-foam, of which the calcination temperature was 550 °C. The corresponding catalysts are denoted as Ni–Al_2O_3/Cu-foam, Ni–Al_2O_3/CuNi-alloy-foam and Ni–Al_2O_3/Ni-foam, respectively.

For comparison, a reference catalyst Ni/Al_2O_3 was prepared using incipient wetness impregnation method by impregnating γ-Al_2O_3 (mesh of 60–80, purchased from Alfa Aesar with surface area of 247 $m^2\ g^{-1}$) with an aqueous solution of $Ni(NO_3)_2$ (appointed to 15 wt% NiO) followed by calcining in air at 550 °C for 2 h.

2.2. Catalyst characterizations

The foam-structured catalysts were characterized by scanning electron microscopy (SEM, Hitachi S-4800; Japan) equipped with an energy dispersive X-ray fluorescence spectrometer (EDX, Oxford; UK) and transmission electron microscopy (TEM, FEI-Tecnai G2 F30; USA). Specific surface area (SSA) was determined using standard Brunauer–Emmett–Teller (BET) theory based on N_2 adsorption isotherm obtained at −196 °C on a Belsorp max instrument (BEL; Japan). H_2 chemisorption was performed on a Quantachrome ChemBET 3000 (USA) chemisorption apparatus with a thermal conductivity detector (TCD) at room tempera-