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Highly porous monolith/TiO_2 supported Cu, Cu-Ni, Ru, and Pt catalysts in methanol steam reforming process for H_2 generation

Pooya Tahay[a], Yasin Khani[a], Mohammad Jabari[a], Farzad Bahadoran[b,*], Nasser Safari[a,*]

[a] Department of Chemistry, Shahid Beheshti University, Evin, 1983963113 Tehran, Iran
[b] Gas Research Division, Research Institute of Petroleum Industry, West Blvd. of Azadi Sport complex, 1485733111, Tehran, Iran

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ABSTRACT

A comprehensive investigation on the steam reforming of methanol (SRM) process using a microstructure monolith in conjunction with a synthesized nanostructure of TiO_2 is presented. The surface of the designed monolith/TiO_2 structure was coated with copper, copper/nickel, ruthenium, and platinum as the catalyst. The prepared catalysts were then characterized with FE-SEM, AFM, BET surface area measurement, FT-IR, far-infrared, temperature programmed reduction (TPR), and X-ray diffraction (XRD). The obtained results show that in this process, the designed Monolith/TiO_2 structure has a remarkable impact on methanol conversion (99%) and carbon monoxide selectivity (5%). These results are interpreted by the high surface area and superb mass transfer in this micro/nano engineered structure. These results also indicated that the catalyst activity and dispersion are influenced by the metal-support interaction, which is more pronounced in the TiO_2 supports. The ruthenium catalyst presented the highest conversion and selectivity for this process. However, the economically viable property of the Cu-Ni catalyst supposes it as an alternative for the noble ruthenium catalyst.

1. Introduction

The environmental pollution as a result of fossil fuels is a global major concern. It is essential to find and replace these sources of energy with novel and green sources. Producing energy with fuel cells is one of the most promising procedures to make green energy [1,2]. Although preparing energy with these cells is environmentally friendly, this preparation requires hydrogen as a fuel [3]. Hydrogen is an explosive gas, and its storage and transportation have proven to be dangerous.

In-situ preparation of the hydrogen is one of the approaches that can be used to solve the mentioned storage and transportation problems. With this intention, steam reforming of methanol (SRM) is the preferred method for in-situ hydrogen production [4]. An advantage of the SRM method is that it has the highest efficiency to hydrogen production compared to other methods [5]. Furthermore, by having only one carbon in the methanol structure, the process temperature is lower in comparison with other reforming processes such as the ethanol reforming process (400 °C) [6]. This is due to the lack of the strong C—C bond in methanol. The methanol steam reforming reaction can be considered as follows:

$$CH_3OH + H_2O \leftrightarrow CO_2 + 3H_2 \quad (1)$$

$$CH_3OH \leftrightarrow CO + 2H_2 \quad (2)$$

$$CO + H_2O \leftrightarrow CO_2 + H_2 \quad (3)$$

The product mixture consists of hydrogen, carbon dioxide and small amounts of carbon monoxide along with unreacted water and methanol. Since the formed hydrogen is to be used in fuel cells, carbon monoxide formation must obviously be negligible, as carbon monoxide can deactivate the anode in low temperature fuel cells [7]. Therefore, the property and selectivity of the catalyst in the SRM process must be improved in order to obtain a desirable fuel cell feed.

Generally, methanol reforming catalysts can be summarized in two different classes: a) copper based class [8,9] and b) group 8–10 metal based class [10,11] catalysts. The copper-based catalysts are the conventional catalysts used in this process due to their higher activity. However, these catalysts have pyrophoric characteristics and are deactivated by thermal sintering. In comparison with the copper based catalysts, group 8–10 metal catalysts have been introduced as stable and selective catalysts with lower methanol conversion [11].

Many strategies have achieved to improve the catalyst stability and activity in chemical process. Micro-engineering of reactors is one of these strategies, [12] which decreases the equipment dimensions, sizes, weights, and increases mass transfer properties. Monolithic structures are micro-engineered reactors, which consists of many parallel channels separated by thin walls. These structures are noble alternatives for the

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* Corresponding authors.
E-mail addresses: bahadoranf@ripi.ir (F. Bahadoran), n-safari@sbu.ac.ir (N. Safari).

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usually fixed bed reactors. Traditional fixed bed reactors have many disadvantages, which are attributed to the inappropriate distribution of current flow, mass transport resistance, and pressure drop problems [13]. For instance, 90% of dispersed catalyst is not used in these reactors because of the unsuitable mass transfer. Monolith reactors, however, overcome the above difficulties by losing the pressure drop due to their open front structure and connected channels. Mass transfer is appropriate in these systems [14] and efficiency is raised because of the appropriate contact of the reactants and catalyst [15,16].

Change of catalyst support can alter the physical and chemical properties of the catalyst and is another strategy to improve the stability and activity of the catalyst [11,17–20]. The catalyst supports must have acceptable physical stability due to the harsh environment of the reforming reactions. The support should also present suitable physical properties such as high surface area, porosity, and pore size in order to increase the loading capacity of the support and accessibility of the catalyst on itself. Alumina is a common support for catalyst in the SRM reaction, while both coke formation [21] and catalyst aggregation [22] are appreciated disadvantages in this support. These two effects have an undesirable impact on the activity of the catalyst by decreasing the catalyst active site. Consequently, in order to achieve a catalyst with high stability, activity, and endurance against coke formation, modification of alumina or design of new supports are in progress [23].

TiO_2 is a low cost, nontoxic, thermal, and chemically stable metal oxide using in many catalytic processes [24,25]. In addition, by changing the particle sizes and morphology of TiO_2 nanoparticles, one is able to fine-tune the surface area [26,27], pores size, and pores volume [28–30] of the TiO_2 support. In the past two decades, significant efforts have been devoted to the synthesis of TiO_2 support with such properties, due to its importance in many fields of science such as material and energy science [31–34]. For example, Barbe et al. [35] found a method for the preparation of TiO_2 nanoparticles film with high porosity and surface area, which was used in the solar cells modules. These properties play important roles in the steam reforming process both by increasing the metals active area and raising the substances diffusion in the catalyst support [36–38]. Kuila et al. [39] used a synthesized TiO_2 support for reforming methanol in a fixed-bed reactor. They found that due to the large surface area of the support, the degree of distribution, and activity of immobilized catalyst was raised.

Alternatively, TiO_2 has shown temperature dependent interaction with metals (especially a strong metal-support interaction is reported with the noble metals) [40,41]. As a result, by changing the temperature one is able to control the catalyst properties [42] when TiO_2 is used as the catalyst support. For instance, the chemisorption of hydrogen and carbon monoxide on the surface of the metal catalyst can be controlled with this interaction [43,44]. Nichele et al. [45] found that the metal-support interaction in the nickel-TiO_2 catalyst plays a crucial role in the steam reforming reactions. Another advantage of the metal support interaction is the prevention of metal particles aggregation at the SRM reaction temperature. This aggregation affectedly reduces the catalyst activity by diminishing the catalyst surface area.

In spite of the remarkable advantages of conjunct monolith structure with TiO_2 nanoparticle film as catalyst support in the methanol reforming process, no systematic studies have reported on this reaction by monolith/TiO_2 support. For this reason, four different metal catalysts, including Cu, Cu-Ni, Pt, and Ru were deposited on the surface of monolith/TiO_2 supports, which were used as catalysts in the SRM reaction. In order to provide a comprehensive understanding of catalysts activities and their relations to the structure of the prepared support advanced characterization methods such as FESEM, AFM, XRD, BET, FT-IR, TPR, and GC were performed.

2. Experimental

2.1. Materials and methods

All solvents, titanium isopropoxide (TIP), α-terpinol, acetic acid, nitric acid, $Ni(NO_3)_2{\cdot}6H_2O$, $Cu(NO_3)_2{\cdot}3H_2O$, $Ru(N=O)(NO_3)_3$ and $H_2PtCl_6{\cdot}6H_2O$ were purchased from Merck and used without further purification. Ethyl cellulose (5–15 mPas at 5% in toluene: ethanol 80:20) were purchased from Aldrich and used without further purification. Ultra-Sonication (Sonics VC-750) and centrifugation (Sigma 3–18 ks) were performed with the indicated instruments. The $H_2Pt(OH)_6$ was synthesized with a previously reported method [46]. The monoliths used in this work were extruded cordierite with a square-channeled shape (400 cells/in.^{2}) from Corning Company.

X-ray analyses were conducted by XRD to identify the crystal structure using a model INEL EQUINOX 3000 X–ray diffractometer with Cu Kα radiation ($\lambda = 0.15406$ nm) in the 2θ range of 5°–110°. The surface area, pore volume and pore diameters were estimated with the BET (Brunauer-Emmett Teller) method from nitrogen adsorption-desorption isotherms. The data were obtained at −196 °C on a constant–volume adsorption apparatus (Micromeritics TriStar II 3020). Prior to the adsorption-desorption measurements, all samples were degassed at 200 °C in N_2 flow for 3 h. Temperature programmed reduction (TPR) profiles of the catalysts were recorded using a Micromeritics TPR/TPD 2900 unit which employs a thermal conductivity detector (TCD). FE-SEM analysis was carried out to determine morphology and particle size using a field emission electronic microscope (FESEM), ZEISS, SIGMA Series. Atomic force microscope (AFM) was performed in a DPN 5000, working in the non-contact mode with standard silicon tips. All samples had been washed and cleaned by DI water before AFM images were taken. FT-IR and far infrared spectroscopy were performed by a Thermo Nicolet Nexus 870 FTIR ESP FT-IR Spectrometer. The viscosity was measured by Viscometer Fungilab model Alpha at 1 rpm. The catalyst stability test was performed with ultrasonic (Bandelin type DK 255 P) in ethanol for 15 min.

2.2. TiO_2 Nanoparticles and slurry preparation

TiO_2 nanoparticles were synthesized by using a previously reported method [47]. 30 g of TIP was mixed with 6.3 g acetic acid for 10 min. The precursor was transferred into a solution of 150 ml water and 2.1 ml nitric acid while it was strongly stirred. After 30 min, the temperature was slowly increased to 80 °C and refluxed for 4 h. The solution was poured into a 250 ml autoclave and was heated at 200 °C for 12 h. After cooling, 1.5 ml nitric acid was added to the dispersing of the agglomerated TiO_2 nanoparticles. After sonication, the resultant colloidal solution was dried at 85 °C for 10 h.

TiO_2 slurry was prepared using a modified method which has previously been reported [47]. 3 g of the synthesized TiO_2 was mixed with 3 ml of water and was grounded in a porcelain mortar. After 10 min of mixing, 30 ml methanol was slowly added into the mixture. This mixture was transferred to a beaker with 80 ml of methanol and sonicated for 15 min. 12 g of α-terpinol was added to the mixture and further sonicated for 15 min. In the next step, a 10% solution of ethyl cellulose in ethanol was added to the previous blend and the resulted mixture was sonicated for 15 min. Finally, the mixture was concentrated with a rotary evaporator to the most appropriate viscosity (320–370 cP) for wash coating.

2.3. Preparation of monolith/ TiO_2/metal catalyst

The procedure for the preparation of Monolith/TiO_2/metal catalyst is illustrated in Fig. 1. The first step is the preparation of the monolith/TiO_2 support by injection of TiO_2 slurry into the monolith channels, then removing the excess slurry by passing air through the monolith channels. After that, the prepared structure was dried for 15 min at