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Catalytic evaluation of nickel nanoparticles in methane steam reforming

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ARTICLE INFO

Article history:

Received 30 June 2016

Received in revised form

26 August 2016

Accepted 27 August 2016

Available online xxx

Keywords:

Methane steam reforming

Hydrogen production

Ni nanoparticles

Coke deposition

ABSTRACT

Development of a highly efficient and coke-resistant, nickel nanoparticles (Ni.NPs) based catalyst in the steam reformation reaction of methane is reported. The catalyst was prepared by dispersing Ni-nanoparticles over silica functionalized alumina support. The synthesized samples were characterized by a combination of analytical techniques of X-ray diffraction (XRD), nitrogen physisorption (BET surface area), X-ray photoelectron spectroscopy (XPS), temperature programmed reduction (H₂-TPR) and temperature programmed oxidation (TPO).

Characterization results revealed that functionalization of alumina resulted in improved physicochemical properties of Ni-nanoparticles catalyst compared to the conventional nickel based catalysts. More importantly, a clear improvement on the catalytic hydrogen production and resistance to coke was observed. At all temperature studied Ni.NPs catalyst exhibited high methane conversions which reached to 100% at 750 °C. Also, the Ni.NPs catalysts exhibited high H₂ selectivity and excellent thermal stability.

The functionalization of alumina with silica improved the dispersion of Ni nanoparticles and prevented sintering and aggregation. Ni.NPs catalyst exhibited stable catalytic activities for a period of 48 h where no carbon deposition was evidenced neither by TPO nor XPS techniques. Contrary to Ni.NPs the conventional nickel catalyst suffered from severe deactivation due to deposition of filamentous carbon on the surface.

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Introduction

Steam reforming of methane is a well-established industrial catalytic process which deals with the conversion of natural gas into synthesis gas (syngas) or hydrogen which are subsequently transformed into higher value chemicals [1,2]. Methane steam reforming process is a first step in converting natural gas into syngas which can subsequently be converted

to various valuable products such as petroleum, diesel, methanol and ammonia [3,4]. Moreover steam reforming processes also are the main source of hydrogen and hence important in emerging hydrogen economy [5–7]. As shown in equations (1)–(3), steam reforming of methane consists of two reversible chemical reactions 1 and 2. Reaction 1 is strongly endothermic reaction whereas 2, the water gas shift reaction (WGS) is moderately exothermic [8–10]. The overall product of the reaction consists of a mixture of carbon monoxide, carbon

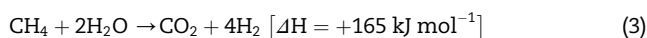
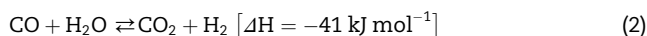
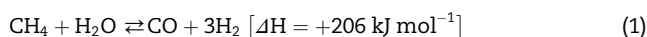
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<http://dx.doi.org/10.1016/j.ijhydene.2016.08.200>

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dioxide, hydrogen, unconsumed methane and steam. The product distribution is governed by various factors such as the type and temperature of the reactor, the operating pressure and the composition of the feed gas.



Steam reforming of methane is catalyzed by various transition metals belong to groups 8–10 such as Ni, Co, Ru, Rh, Pd, Pt, etc [9,11,12]. However due to its activity, ready availability and low cost, Ni-based catalysts are generally the preferred choices for industrial applications [13–15]. It is generally accepted that methane is activated on the surface of Ni⁰ resulting in CH_x species which in turn reacts with –OH groups either adsorbed on nickel or on a support surfaces [16].

For an efficient production of hydrogen or syngas mixture, design of an efficient catalyst with high catalytic performances is very crucial. A major factor of deactivation of methane steam reforming catalysts is the deposition of carbon in different forms such as carbonaceous and filamentous carbon [17,18]. The deposited carbon then either may encapsulate the Ni active surface or diffuse inside the catalyst active phase and hence resulting in reduction of the activity and altering the fluid dynamics of the reactor [19–21].

The physicochemical properties and the extent of interaction between Ni active sites and support also play a crucial role in the complex chemistry of Ni supported catalysts [22]. In order to overcome the problem associated with carbon deposition on the catalysts surface several research attempts have been investigated. For example metal oxides possessing high oxygen mobilities such as ceria (CeO₂), and zirconia (ZrO₂), are believed to facilitate the oxidation of coke deposits and have been widely studied [23]. However the high oxygen mobilities resulted in oxidation of metallic Ni⁰ and led to a considerable loss in catalytic performance. Various precious metals such as platinum, rhenium, palladium and iridium have also been employed as promoters to provide active sites for coke oxidation [24]. However due to use of precious metals the practical applicability of these catalysts is undesirable. Alloying Ni with comparatively less expensive metals such as cobalt, manganese, tin, molybdenum and copper have also been reported [25]. This method also doesn't seem to be practically applicable as alloying of Ni may decrease the active sites as well as reduce the domain size of Ni and the resultant species are responsible for coke formation.

It is generally accepted that coke formation on Ni occurs either because of methane cracking or the Boudourad reaction [26]. Large and aggregated particles of nickel have a lower proportion of surface exposed Ni atoms and hence become more vulnerable to the deposition of various species of carbon. By contrast smaller domains of nickel have been reported to assist suppression of coke deposition [22,27]. It is evident from this discussion that carbon deposition and steam reformation of methane are structure sensitive in nature and the particle size of Ni has an important role in the steam reforming of methane. Smaller and stable particles are

advantageous in many ways for example; Ni small particles provide a large metal active surface area and hence improve the catalytic activities. Besides; other aspects concerning the Ni particle size are vital e.g., smaller Ni particles are known to possess more surface defects e.g. kinks and steps and hence results in larger catalytic turn over frequencies than larger Ni crystals. Bengaard and co-workers [28] reported that smaller crystals of nickel possess more open surfaces. Since carbon formation is a structure sensitive reaction and does not proceed if the particle size of nickel is below a critical size, and hence smaller Ni particles have been reported to more resistant to coking [29]. Borowiecki [30] reported that during the steam reforming of butane, compared to smaller particle of nickel larger particles were more susceptible to carbon deposition. The author has explained a correlation between the metal particle size and the rate of carbon deposition. It has also been reported by Holmen et al. that nickel particle size not only influence coking rates but also the ability of initiation, nucleation of carbon nano-particles which may happen as a result of methane decomposition [31]. Their results indicated that rate of coke formation was lower on smaller nickel particles as the initiation of carbon deposition might have been difficult.

The above discussion shows that the development of coke resistant and stable Ni-based catalysts for methane steam reforming still remains a key factor and a challenging topic for researchers. Ni nanoparticles exhibit higher activity in methane reformation reaction but under crucial reformation reactions conditions, it typically experience deactivation. In the present work, our synthetic approach was aimed to stabilize nickel nanoparticles at high operating temperatures by dispersing them over surface of silica (SiO₂) functionalized alumina (Al₂O₃). We attempted to achieve a strong interfacial interaction between layer of silica moieties on the surface of alumina and Ni nanoparticles. The synthesis and characterization of these catalysts, as well as their catalytic activity in methane steam reformation reactions, in general, and hydrogen production in particular is presented. The results are benchmarked to a conventional Ni catalyst.

Experimental and procedures

Catalyst synthesis

A set of two nickel based catalysts with a total Ni metal loading of 5wt% were synthesized. In order to provide an anchor and better dispersion for the Ni particles, surface of alumina (SASOL) was modified with 10wt% SiO₂. For the surface modification and functionalization, alumina was pre-calcined at 900 °C for five hours at a heating and cooling rate of 1 °C/min, followed by refluxing in the required amounts of triethoxysilane (Aldrich, ≥97.5%) and acetone (Fluka, >99%) for one hour at 110 °C. The solvent was then evaporated in a rotary evaporator. The residue was then dried at 110 °C and calcined at 900 °C for 3 h with 1 °C and –1 °C heating and cooling rates respectively.

Nickel nanoparticles (Ni.NPs) based catalyst supported over functionalized alumina (denoted as Ni.NPs) with a 5wt% of Ni.NPs was prepared with the procedure as follows.

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