



# Methane decomposition into CO<sub>x</sub> free hydrogen and multiwalled carbon nanotubes over ceria, zirconia and lanthana supported nickel catalysts prepared via a facile solid state citrate fusion method



Manoj Pudukudy<sup>a,\*</sup>, Zahira Yaakob<sup>a</sup>, Mohd Sobri Takriff<sup>b</sup>

<sup>a</sup> Department of Chemical and Process Engineering, Faculty of Engineering and Built Environment, Universiti Kebangsaan Malaysia, UKM, Bangi 43600, Selangor, Malaysia

<sup>b</sup> Research Center for Sustainable Process Technology (CESPRO), Faculty of Engineering and Built Environment, Universiti Kebangsaan Malaysia, UKM, Bangi 43600, Selangor, Malaysia

## ARTICLE INFO

### Article history:

Received 24 June 2016

Received in revised form 28 July 2016

Accepted 5 August 2016

### Keywords:

Methane cracking

Solid state citrate fusion

Rare earth supports

Nickel

Hydrogen

Multiwalled carbon nanotubes

## ABSTRACT

Methane decomposition is the most effective route for the simultaneous production of CO<sub>x</sub>-free hydrogen and nanocarbon. In this work, a set of porous ceria, zirconia and lanthana supported nickel catalysts were successfully synthesized via a facile solid state citrate fusion method and used for the thermocatalytic decomposition of undiluted methane for the first time. The catalysts were completely characterized for their crystalline, structural, textural and reduction properties and correlated to their catalytic performance. The active phase of fresh catalysts was found to be NiO in the CeO<sub>2</sub> and ZrO<sub>2</sub> supported catalysts whereas the formation of lanthanum nickel oxide solid solution was observed in the Ni/La<sub>2</sub>O<sub>3</sub> catalyst. Various attractive porous morphologies of the fresh catalysts were confirmed by scanning electron microscopic studies. All of the catalysts exhibited high catalytic activity and stability for methane decomposition. The yield of hydrogen and carbon increased significantly with increasing the reaction temperature from 600 °C to 700 °C. A maximum initial hydrogen yield of 62%, 61% and 58% and a final carbon yield of 1360 wt%, 1159 wt% and 1576 wt% was achieved over ceria, zirconia and lanthana supported catalysts respectively, at 700 °C. The surface area of the catalysts could not have any significant effect on the catalytic efficiency and it was fully depended on the metal support interaction. The Ni/La<sub>2</sub>O<sub>3</sub> catalyst showed high catalytic stability than ceria and zirconia supported catalysts due to the enhanced surface dispersion of finely crystallized Ni nanoparticles on the lanthana matrix aroused by the reduction of lanthanum nickel oxide. Moreover, bulk deposition of highly uniform multiwalled carbon nanotubes with high graphitization degree ( $I_D/I_G = 0.95$ ) with different diameters depending on the Ni crystalline size was observed over the catalysts.

© 2016 Elsevier Ltd. All rights reserved.

## 1. Introduction

In recent years, hydrogen is considered to be an efficient source of clean energy [1]. Currently, the large scale production of hydrogen is executed by the steam reforming or partial oxidation of natural gas [2]. However, the simultaneous production of highly toxic greenhouse gases such as CO and CO<sub>2</sub> makes the process less effective, while considering the environmental issues like increased global warming and acid rain [3]. Methane decomposition is an alternative process for the production of pure hydrogen, where the production of greenhouse gases is completely avoided.

In this reaction, methane is directly converted into CO<sub>x</sub> free hydrogen and nanocarbon under anaerobic conditions [4]. For the non-catalytic decomposition reaction, high reaction temperatures of approximately 1200 °C are needed to crack the methane molecules [5]. However, the use of carbonaceous and metallic catalysts was reported to lower the reaction temperatures significantly [6]. Moreover, the nanocarbon deposited after reaction, mainly in the filamentous forms such as fibers or nanotubes, is of great importance in current nanoscience due to their exclusive electrical, chemical and mechanical properties [7]. Graphene is the other form of carbon obtained via this process.

A number of Ni, Co and Fe based metallic catalysts were reported for methane decomposition [8]. Among these metals, Ni is identified as the most active metal for methane decomposition due to its exclusive 3d-orbital structures [9]. However, the catalytic performance of bare Ni is related to several parameters

\* Corresponding author at: Department of Chemical and Process Engineering, Faculty of Engineering and Built Environment, Universiti Kebangsaan Malaysia, UKM, Bangi 43600, Selangor, Malaysia.

E-mail addresses: [manojpudukudy@gmail.com](mailto:manojpudukudy@gmail.com), [manojmscp@gmail.com](mailto:manojmscp@gmail.com) (M. Pudukudy).

as reviewed by Li et al. [10]. For an instance, it is reported that the activity of bare nickel catalysts is quite low at lower reaction temperatures and at high temperatures, due to the sintering and encapsulation of nickel by the nanocarbon, a faster deactivation of the catalyst was observed with a low catalytic stability. To improve the efficiency of nickel catalysts at moderate operating temperatures, several support materials were used during the synthesis of catalysts [11]. The use of a support material was already reported to promote the fine surface dispersion of metallic particles on the support and thereby increases the catalytic stability with high methane conversion and carbon yield [12]. Moreover, the textural properties of the support materials were effective to tune the surface chemistry, crystallinity and electronic characters of the metal particles via a migration effect as reported previously [13,14]. The commonly used catalyst supports for nickel in methane decomposition reaction are silica, alumina, titania, zeolites, magnesium aluminates, magnesia and so on [15–17]. Moreover, an appropriate metal-support interaction must be also considered before the selection of the catalyst supports. In addition to support, the catalytic activity of the catalyst mainly depends on the method of its synthesis [18].

A number of works was engrossed on the preparation of supported metal catalysts. Impregnation, deposition-precipitation, co-precipitation, solid state fusion, mechano-chemical activation and sol gel are the mainly used catalyst preparation methods in methane decomposition [19]. Eventhough many of the aforesaid methods are very effective for the development of improved catalytic properties; the solid state fusion is much more attractive since it is the most simple and one pot dry method for the preparation of catalysts with tunable properties such as fine metal dispersion and a proper metal support interaction [20]. Moreover, it devoid many complex and time consuming steps associated with the conventional wet synthesis methods such as washing, filtration, and drying.

Thus a combination of the solid state fusion method and use of rarely studied support materials like ceria, zirconia and lanthana for nickel catalysts is highly interesting in the methane decomposition catalysis. So far, there are only limited reports available for methane decomposition using rare earth metal oxides such as ceria and lanthana and transition metal oxide zirconia as the catalyst supports [21]. Ceria as a support material in methane decomposition is highly credited because of its ability to promote the metal dispersion and also the metal support interaction. Li et al. [22] studied methane decomposition over 10%Ni/CeO<sub>2</sub> catalysts prepared by different methods. As per their report, at a reaction temperature of 500 °C, the catalyst prepared by the impregnation and deposition-precipitation methods showed high hydrogen yield compared to the catalyst prepared by the co-precipitation method. This is attributed to the strong metal support interaction found in the coprecipitated catalyst, due to the formation of a Ni-O-Ce solid solution. Tang et al. [23] reported a set of Fe loaded CeO<sub>2</sub> catalysts for methane decomposition. According to their study, a catalyst with the composition of 60 wt% Fe<sub>2</sub>O<sub>3</sub> and 40 wt% CeO<sub>2</sub> showed the highest catalytic activity in terms of hydrogen yield. However, due to the chemical interaction of deposited nanocarbon with the lattice oxygen of ceria, small amounts of CO<sub>x</sub> were detected in the product gas. Odier et al. [24] also reported the same, over Pt/CeO<sub>2</sub> catalyst. However, an improved hydrogen formation was observed over the catalyst, due to the spillover effect of noble metals.

Zirconia supported catalysts are very rarely reported for methane decomposition. Kogler et al. [25] studied methane decomposition over zirconia, yttria-stabilized zirconia, and yttria catalysts, under dry and steam reforming conditions for the deposition of nanocarbon. They stated that the nanoparticulate zirconia is able to catalyze the growth of single and multiwalled carbon nanotubes via the chemical vapour deposition of methane.

Wolfbeisser et al. [26] reported a Ni/ZrO<sub>2</sub> catalyst and its Cu promoted one for methane decomposition. As per their report, both of the catalysts showed high activity and stability for methane decomposition. Moreover, an activation process was occurring in methane between 377 °C and 462 °C range, resulting in an irreversible modification of the catalytic activity of the NiCu system towards Ni-like behaviour. The rapid increase catalytic activity was due to the increased concentration of nickel on the surface of the zirconia support. Moreover, the Cu promotion increased the coke resistance capacity of the Ni/ZrO<sub>2</sub> catalyst [27]. Kurasawa et al. [28] reported methane decomposition over Ni/ZrO<sub>2</sub> catalysts synthesized via a glycothermal method and reported that a highest carbon yield was obtained for the zirconia supported catalyst compared to other support materials. Multiwalled carbon nanotubes with the diameters of ~30 nm were formed over the Ni/ZrO<sub>2</sub> catalysts via methane decomposition.

Lanthana based perovskite catalysts were also reported for methane decomposition. This is based on the fact that the reduction of perovskites produces nanosized metal species, which keeps an appropriate metal support interaction and thereby enhances the efficiency of the catalyst in terms of hydrogen and carbon yield. Liu et al. [29] studied methane decomposition over Fe nanoparticles obtained by the reduction of LaFeO<sub>3</sub> perovskites and stated that bulk amounts of single walled carbon nanotubes with a narrow diameter distribution of 0.8–1.8 nm were formed over the catalysts. The growth of SWCNTs over the aforesaid catalyst was due to the deposition of highly uniform and closely distributed Fe nanoparticles on the lanthana matrix. Chen et al. [30] reported lanthana supported NiCo bimetallic catalysts for methane decomposition. According to them, a high catalytic activity was obtained for the bimetallic catalysts without any pre-reduction steps. Kuras et al. [31] studied methane decomposition over nickel-lanthana perovskites and reported an improved catalytic activity for the production of multiwalled carbon nanotubes at high temperatures, irrespective of the time for catalyst reduction and temperatures. According to them, the aforementioned parameters do not have any effect on the nickel particle size on the lanthana support. Gallego et al. [32] reported a LaNiO<sub>3</sub> perovskite prepared by the self-combustion method for methane decomposition at 600 °C and 700 °C. The stated that the catalysts exhibited high catalytic stability for the production of hydrogen and multiwalled carbon nanotubes, even after a long duration of time on stream of 1320 min at 700 °C. Rivas et al. [33] reported methane decomposition over a nickel catalyst obtained by the activation of LaNiO<sub>3</sub> perovskite. The high catalytic stability of the nickel catalyst was due to the surface stabilization of nanosized NiO together with its fine dispersion on the lanthana matrix, which further reduced the sintering of nickel particles. Cunha et al. [34] reported an improved catalytic stability of the Fe/La<sub>2</sub>O<sub>3</sub> catalyst for methane decomposition. They stated that, as a textural promoter, lanthana has the ability to tune the surface area of the catalyst effectively and acts like an electronic promoter. Recently Maneerung et al. [35] reported Ni, Co and Fe based bimetallic lanthana perovskites as catalyst precursors for methane decomposition and reported that the LaNi<sub>0.8</sub>Fe<sub>0.2</sub>O<sub>3</sub> and LaNi<sub>0.8</sub>Co<sub>0.2</sub>O<sub>3</sub> perovskites showed high catalytic performance in terms of hydrogen and carbon yield. Both chain and tube-like carbon nanofilaments were deposited over the catalysts after methane decomposition.

However, in this manuscript, a set of ceria, zirconia and lanthana supported nickel catalysts were prepared via a facile solid state fusion method using citric acid as the surfactant, and characterized for their crystalline, structural, morphological and textural and redox properties. The catalysts were also successfully used for the thermocatalytic decomposition of undiluted methane at moderate reaction temperatures of 600 °C, 650 °C and 700 °C without any diminishing effect for a period of 360 min of time on the

Download English Version:

<https://daneshyari.com/en/article/7160054>

Download Persian Version:

<https://daneshyari.com/article/7160054>

[Daneshyari.com](https://daneshyari.com)