Carbon produced by the catalytic decomposition of methane on nickel: Carbon yields and carbon structure as a function of catalyst properties

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A B S T R A C T

The interplay of carbon quantity, carbon type, methane decomposition activity and catalyst deactivation by deposited carbon are all important aspects to be considered in assessing the practical use of the catalytic methane decomposition route, using nickel/titania catalysts.

Increasing the nickel loading from 7% to 20% in Ni/TiO$_2$ increased methane decomposition conversion but the activities and carbon yields per unit Ni fell as the nickel content increased. The carbon produced on high Ni-loaded samples is more graphitic in nature. Filaments of carbon are the main products and the diameter increases as the Ni particle size on the catalyst increases, which, in turn, increasing at higher Ni loadings. Studies of binary supports on the activity of nickel demonstrated that not all systems led to improved catalyst performance. But, in these systems, factors such as metal-support interaction are also important. Introduction of copper to the supported nickel system exerts an effect on the morphology of the carbon nanostructures produced but other aspects are little affected.

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1. Introduction

The production of CO$_x$-free hydrogen from methane is an attractive prospect for utilizing natural gas. Catalytic decomposition has been well studied but the basic ground rules regarding the connection between catalytic properties and the yield or quantity and structure or quality of the carbon formed are yet to be established. The present paper addresses this issue. The carbon characteristics are of fundamental importance in that they will largely dictate the uses, if any, to which the carbon can be put. Given the huge quantities of carbon coproduced in this process, thoughts turn naturally to very large scale uses, one of which would involve direct carbon fuel cell (DCFC)-based (Munnings et al., 2014; Giddey et al., 2012) conversion to carbon dioxide. This would make the methane conversion to electrical energy less CO$_x$-free but, given that the efficiency of the DCFC promises to be very high (Munnings et al.,

2014), much higher than that of the hydrogen PEMFC (polymeric electrolyte membrane fuel cell), the overall conversion via splitting and processing the hydrogen and carbon via the two fuel cell paths should be overall much more efficient than direct gas combustion.

Previous studies on methane conversion using supported metal catalysts have been reported. For example, Avdeeva et al. (2002a) studied the effect of iron (Fe) and bimetallic compositions of Fe and copper (Cu) on methane decomposition. Methane conversion was however low (<7% for a 50% Fe/Al$_2$O$_3$ at 625 °C). Ermakova et al. (2001) also investigated the production of carbon from methane decomposition using Fe supported on SiO$_2$, Al$_2$O$_3$, ZrO$_2$, and TiO$_2$. The reported carbon yield was however low (the highest being 45 g/g$_{Fe}$ for Fe/SiO$_2$). One other metal catalyst that has been widely investigated for the decomposition of methane is nickel (Baker et al., 1987). Matsumura and Nakamo (2004) studied the effect of supports such as silica; γ-alumina and zirconia on the activity of nickel for steam reforming of methane where it was observed that type of support had an influence on the activity of nickel. In their study, zirconia showed the highest activity. However, this is not an appropriate route to solid carbon as the carbon is lost either as CO$_2$ or CO. The effect of a mixture of Ni and NiO on

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methane conversion was reported by Couttenye et al. (2005). In their study, nickel acetate dispersed on either silica or cordierite was thermally decomposed to produce a mixture of Ni and NiO. Results showed an average 14% methane conversion for a period of 6 h after which the conversion steadily declined. Italiano et al. (2009) also studied the decomposition of methane in a structured multilayer reactor at different temperatures (773–873 K). The reactor employed a silica cloth impregnated with nickel with magnesia as a promoter. Conversion was low and the catalysts quickly deactivated at high temperatures. Several attempts to find a suitable catalyst and conditions that could convert methane to CO_x-free hydrogen have been made but most of these catalysts are either not sufficiently active or they easily become deactivated. These low conversions and rapid deactivation have prompted further efforts. Interest in the decomposition of methane remains high, however, in view of the potential role it could play in sustainable energy production via low-carbon routes (Pudukudy et al., 2014, 2015a, 2015b, 2015c, Pudukudy and Yaakob, 2015; Shen and Lua, 2015). What is now needed are higher mileage catalysts or more continuous decomposition systems with, if possible, continuous carbon recovery.

A mixture of supports (typically binary oxides) could improve on the action of single-component supports thereby improving the activities of the supported metals (Fierro, 2005a; Doolin et al., 1994a). For example, Aghababazadeh et al. (2006) reported the synthesis of CNTs from methane using an $Fe/Al_2O_3.SiO_2$ system. Since some of the commonly used supports for the synthesis of MWCNTs include calcium carbonate (Couteau et al., 2003; Mhlanga et al., 2009), alumina (An and Lim, 2002 and silica (Engel-Herbert et al., 2007) an investigation into the combined effect of using titania-silica, titania-alumina and silica-alumina was carried out in the present work.

The use of promoters for methane decomposition has also been discussed. Reshetenko et al. (2003) used copper with Ni/alumina and attributed the promotion to a reduction in the extent of Ni sintering. Alternatively, facilitation of hydrogen spillover by copper was reported by Orlik and Shashkova (2008). In related work, platinum or iridium were used in methane autothermal reforming (Joelmir et al., 2004).

In this study, results of an investigation into methane decomposition using different Ni/TiO_2 at different loadings and temperature conditions are presented. TiO_2 was chosen as support because of its availability and its stability at the required operating temperatures. Although commercial TiO_2 was used, TiO_2 can be easily prepared in the laboratory and it can easily be separated from the carbon material. It should also be noted that some studies have been reported on the use of Ni in CH_4 decomposition, but using other supports (Al_2O_3, SiO_2). This study thus provides a possibility to compare the Ni/TiO_2 with other supported metals. Also studied is the effect of binary supports on the activity of Ni in methane conversion.

The yield of carbon is important in that conversion-time on stream behaviour normally follows a rectilinear curve in that steady conversion can be maintained for some time before carbon fouling of the solid catalyst surface causes a fairly precipitous fall in activity. Catalyst regeneration, or, more likely, catalyst reformulation would normally have to be considered. The fact that carbon yields per mass of metal catalyst are as high as sometimes seen is due partly to the carbon growth mechanism which involves the outward growth of filaments bearing catalytically active (nano) metal sites at the tip and partly due to the fact that some forms of carbon are themselves active in methane decomposition.

The carbon product typically displays a nanostructure, comprising both ordered and disordered forms of carbon. It is well known that Raman spectrometry can readily record the structure in

these terms. Backed-up by electron microscopy, useful characterization studies have been conducted based on the use of various catalysts to determine the basic carbon structure/carbon yield/catalyst properties relationship for methane decomposition.

In this paper we have tried to build on previous work by demonstrating in a single study the interplay between decomposition rate, carbon type formed, catalyst type and metal loading, where it is acknowledged that such interplay will largely determine the practical applicability of the methane decomposition route in the manner envisaged.

2. Experimental

Chemicals and reagents were obtained from Sigma-Aldrich. Titania (Degussa P25) was procured from Japan. All gases were sourced from Afrox.

2.1. Synthesis of catalysts

Catalysts are prepared by deposition-precipitation method or the incipient wetness impregnation method (Einh~iuser, 1997; Marabini et al., 1992; Bayraktar and Kugler, 2004; Ebitani and Hattori, 1991; Heidebrechta et al., 2008). The deposition method has the advantage of producing highly dispersed metal particles. The incipient wetness impregnation method is an easy and fast procedure for preparing supported metal catalysts with comparable activities (Ebitani and Hattori, 1991; Heidebrechta et al., 2008; Scholtenab et al., 1985). In this project, the incipient wetness impregnation method was used and a range of Ni/TiO_2 catalysts with nickel loadings of between 7 and 20% were prepared. A solution of known concentration of nickel precursor ($Ni(NO_3)_2 \cdot 6H_2O$) was prepared by dissolving a known amount of the nickel salt in approximately 15 ml distilled water and pouring this slowly (with mixing) onto a known amount of titania, followed by stirring for about 30 min at room temperature and where necessary, the excess water was evaporated by mild heating (approximately 50 °C) before drying overnight at 110 °C. After drying, the catalyst was calcined in air at 500 °C for 4 h using a heating rate of 5° C/min. After calcination, the catalyst was ground and sieved to 150 μm. Some studies were carried out using alumina as the support, and copper promoted nickel catalysts were also investigated. The catalyst compositions chosen were 7% Ni–1%Cu and 7%Ni–0.1%Cu for the copper containing samples. These catalysts were prepared by the incipient wetness impregnation of the support by $Cu(NO_3)_2 \cdot 3H_2O$ (99.5%, Merck) followed by drying (110 °C) and calcination (500 °C). For mixed supports 1:1 mechanical mixtures of the individual supports were rendered homogenous followed by impregnation with nickel nitrate solution. For copper-modified nickel on titania, co-impregnation of the support with both copper and nickel nitrate was carried out, followed by the treatments identical to those used for nickel only systems. Thermal and textural properties of the catalysts were studied using a thermogravimetric analyzer (TGA) and Brunauer-Emmett-Teller (BET) equipment respectively.

For electron microscopy (EM) studies, a small quantity of carbon material was dispersed in methanol (about 5 cm^3) using an ultrasonic bath for 10 min. A drop of the suspension was spread onto a holey carbon copper grid (200 mesh) and allowed to dry. The grid was then mounted onto the exchange rod and placed into the chamber of the TEM (JEOL 100S) for viewing. Carbon samples (from methane decomposition) were mounted on aluminium stubs with carbon tape as a support. The samples were then coated with gold palladium sputter in order to make the surface conductive. Viewing of the specimen was performed by mounting the sample into a SEM (JEOL, JSM-840 Scanning microscope).