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Highly stable and active Ni-mesoporous alumina catalysts for dry reforming of methane

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ABSTRACT

Nanostructured Ni-incorporated mesoporous alumina (MAL) materials with different Ni loading (7, 10 and 15 wt %) were prepared by a template assisted hydrothermal synthesis method and tested as catalysts for CO₂ reforming of methane under different conditions (nickel loading, gas hourly space velocity (GHSV), reaction temperature and time-on-stream (TOS)). The most active catalyst tested (Ni(10 wt%)-MAL) showed a very high stability over 200 h compared to a Ni(10 wt%)/ γ -Al₂O₃ prepared using a co-precipitation method which had a significant loss in activity after only ~4 h of testing. The high stability of the Ni-MAL materials prepared by the template assisted method was due to the Ni nanoparticles in these catalysts being highly stable towards migration/sintering under the reaction conditions used (800 °C, 52,000 mL h⁻¹ g⁻¹). The low susceptibility of the Ni nanoparticles in these catalysts to migration/sintering was most likely due to a strong Ni-support interaction and/or active metal particles being confined to the mesoporous channels of the support. The Ni-MAL catalysts also had significantly lower amounts of carbon deposited compared to the catalyst prepared using the co-precipitation method.

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1. Introduction

Recently there has been renewed attention in CO₂ (dry) reforming of methane (Eq. (1)), due to potential environmental benefits of utilising CO₂ and an increase in demand for syngas (H₂/CO). Syngas is primarily produced from a catalytic steam reforming process where the resulting H₂/CO product ratio is higher than the ratio required for down-stream methanol and hydrocarbon conversion processes [1,2]. Dry reforming of methane can however produce syngas with an H₂/CO ratio close to unity, making it an ideal feed for the Fischer Tropsch reaction and for highly selective syntheses of a wide range of chemical compounds such as formaldehyde, acetic acid,

dimethyl ether, methyl tert-butyl ether, olefins and liquid hydrocarbons [3].

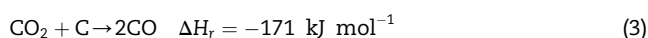
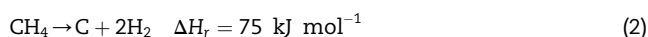
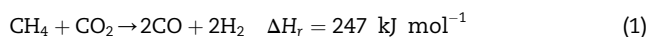
Dry reforming of methane has been extensively studied on supported group VIII metal catalysts [4–8]. Both noble metals (e.g. Ru, Rh, Pt, Pd) and non-noble metals (e.g. Ni, Fe, Co) have been found to be catalytically active towards this reaction [9]. Although noble metal based catalysts are usually highly active, and experience low carbon deposition [10–12], they have the drawbacks of high cost and limited availability hence there has been significant interest in the development of cheaper non-noble metal based catalysts. Of the non-noble metal based catalysts Ni based catalysts in particular have received a significant amount of interest due to the promising

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activity and selectivity that has been achieved [13–16]. The main drawback experienced with nickel based catalysts however is their propensity to produce significant quantities of carbon, which in turn significantly reduces their stability over time.

It has recently been reported that both the amount and type of carbon deposited from methane decomposition (Eq. (2)) during the dry reforming reaction will influence the activity/stability of Ni based catalysts [17]. Several researchers have shown that there are four main forms of carbon deposited, C α , C β , C γ and inactive; namely amorphous, filamentous, graphitic carbon and bulk carbon [18–22]. It has been reported that of these carbon types, amorphous carbon is the most active, being consumed rapidly by the Boudard reaction (Eq. (3)), whilst it is proposed that filamentous and graphitic carbon do not block active sites, but are consumed at a lesser rate than amorphous carbon. It is proposed that bulk carbon causes a rapid loss of activity through physical coverage of the active sites and that this carbon is not consumed in the Boudard reaction [21].



Strategies to improve the activity of Ni-based catalysts and to prevent the deposition of inactive carbon (and hence improve the lifetime of Ni-based catalysts) have focused on preparing catalysts with optimum metal dispersion/particle size and good support-metal interaction. Methods to achieve the aforementioned for Ni-based catalysts have mostly involved adding dopants and/or investigating the influence of different support materials.

A number of researchers have conducted studies on the influence of dopants and/or support materials on the activity and stability of Ni-based catalysts in an attempt to develop improved catalysts for the dry reforming reaction and to gain a better understanding of the properties of Ni based catalysts that influence activity and stability (particularly carbon deposition). Hou et al studied the influence of doping MgO into mesoporous Ni/Al₂O₃ prepared by a co precipitation method and found that this led to significantly improved activity and stability compared to that obtained using the undoped catalyst [22]. Junke et al investigated dry reforming using La doped Ni–Al₂O₃ catalysts and reported that the addition of La limited carbon deposition to mostly active forms, hence reducing the formation of non-active filamentous and bulk carbon [18]. Junke et al reported the aforementioned results were achieved due to the added La assisting in limiting the Ni particle size to less than 15 nm. Montoya et al reported that CeO limits active metal/support interaction when used as a dopant, hence causing an ease of reducibility of the catalyst and resulting in high dispersion of small active Ni particles, which show less carbon deposition over time and a greater overall activity [23].

Research on the influence of support materials for Ni based catalysts has shown that certain high surface area supports can be effective in increasing Ni dispersion and thermal stability, hence decreasing the deactivation over time of the

catalysts due to sintering and migration effects [11]. Within the dry reforming reaction a very high selectivity towards H₂ was reported when nickel was supported on MCM-41 mesoporous materials, which was superior to that of Ni/SiO₂ catalysts and comparable to the performance of highly active Ru/SiO₂ catalysts [24]. Nickel-alumina aero-gel high surface area catalysts tend to show higher activity than SiO₂ supported catalysts due to an increased surface area support [25,26]. Wei et al [27–29] investigated Ni catalysts supported on nano-sized supports ZrO₂, MgO and γ -Al₂O₃ supports and found that the material showed high thermal stability and had strong anti-carbon properties due to high preparative control resulting in well dispersed active metal sites which interacted to a strong degree with the support structure. The incorporation of active metals directly into the framework of mesoporous molecular sieves has been shown to combine the benefit of a high surface area support, and the availability of highly distributed active metal sites to the reaction being studied [30].

In this study, we have investigated the dry reforming of methane over a range of conditions using a monometallic Ni/mesoporous alumina catalyst prepared using a relatively new template based method. Most of the Ni supported alumina catalysts that have been used for catalysing dry reforming of methane to date have been prepared by co precipitation or wet impregnation methods. The aforementioned catalysts (that did not contain additives) have however been reported to be unstable because the Ni nanoparticles did not interact with the support sufficiently to minimise sintering at the required high temperatures, forming larger particles on the outer surface of the material resulting in less active carbon types which hindered the reaction. The template based method used in this study to prepare Ni/mesoporous alumina catalysts was selected due to claims that this method leads to the production of a highly ordered, thermally stable support structure containing active Ni particles within the micropore channels that have a reduced likelihood of sintering at high temperatures [31]. An improved understanding of the influence of catalyst preparation methods/catalyst-support structure for Ni based dry reforming catalysts is important for understanding the role of these factors in catalytic activity and carbon deposition.

2. Experimental

2.1. Materials

Polyethyleneoxide-polypropyleneoxide-polyethyleneoxide Pluronic P123 was obtained from BASF; γ -Al₂O₃, nickel nitrate was obtained from Merck; and aluminium isopropoxide (Al(OPrⁱ)₃) was purchased from Aldrich Chemical Co.

2.2. Catalyst synthesis

A mesoporous alumina containing Ni (Ni(7 wt%)-MAI) was synthesized using a template assisted method [22] with modifications. In a typical synthesis of Ni(7 wt%)-MAI, 4.0 g of Pluronic P123 was dissolved in 30 ml of ethanol under stirring at room temperature, before 8.0 g of Al(OPrⁱ)₃ was added to the solution. Nickel precursor solution was made separately by dissolving 0.896 g of Ni(NO₃)₂·6H₂O in 10 ml ethanol and 6 ml

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