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Multicomponent Ni-CeO_2 nanocatalysts for syngas production from CO_2/CH_4 mixtures

E. le Saché[a], J.L Santos[b], T.J. Smith[a], M.A. Centeno[b], H. Arellano-Garcia[a], J.A. Odriozola[b], T.R. Reina[a,*]

[a] Department of Chemical and Process Engineering, Faculty of Engineering and Physical Sciences, University of Surrey, Guildford, UK
[b] Departamento de Química Inorgánica e Instituto de Ciencias de Materiales de Sevilla. Centro mixto US-CSIC Avda. Américo Vespucio 49, 41092 Seville, Spain

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ABSTRACT

The dry reforming of methane with CO_2 is a common route to transform CO_2/CH_4 mixtures into added value syngas. Ni based catalysts are highly active for this goal but suffer from deactivation, as such promoters need to be introduced to counteract this, and improve performance. In this study, mono- and bi-metallic formulations based on 10 wt.% Ni/CeO_2-Al_2O_3 are explored and compared to a reference 10 wt.% Ni/γ-Al_2O_3. The effect of Sn and Pt as promoters of Ni/CeO_2-Al_2O_3 was also investigated. The formulation promoted with Sn looked especially promising, showing CO_2 conversions stabilising at 65% after highs of 95%. Its increased performance is attributed to the additional dispersion Sn promotion causes. Changes in the reaction conditions (space velocity and temperature) cement this idea, with the Ni-Sn/CeAl material performing superiorly to the mono-metallic material, showing less deactivation. However, in the long run it is noted that the mono-metallic Ni/CeAl performs better. As such the application is key when deciding which catalyst to employ in the dry reforming process.

1. Introduction

Carbon dioxide is one of the major issues facing the world currently, the adverse effects on the environment that CO_2 emissions cause are well documented and are causing global concern; with the year 2014 seeing 35.7 billion tonnes of CO_2 produced from fossil fuel combustion and industrial processes alone [1]. However, industry is taking major steps to help mitigate these effects, by capturing a proportion of the CO_2 being produced each year. The array of technology used to capture CO_2 is large, including absorption in liquids [2] and adsorption on solids [3], which can be implemented either pre- or post-combustion depending on the application. The scheme to reduce atmospheric carbon emissions via capture is part of a worldwide initiative, with the captured carbon being stored by geological, mineralisation or oceanic means. Nevertheless, a lot of progress needs to be made within this field before it becomes a truly viable option [4,5].

An alternative solution can be employed instead of storage, namely the chemical upgrading of CO_2 to fuels and chemicals. In addition to the depletion of CO_2 emissions, extra motivation is provided by the generation of value-added products [6].

Among the different alternatives for CO_2 utilisation, the dry reforming of methane (DRM, Eq. (1)) is a promising route and has the added benefit of utilising methane which has a global warming potential 25 times that of CO_2 [7]:

$$CH_4 + CO_2 \rightleftharpoons 2CO + 2H_2 \quad (1)$$

$$\Delta H_{298K} = +247\,kJ/mol$$

$$\Delta G_{298K} = +170\,kJ/mol$$

This route leads to the production of syngas (H_2 and CO) [8], which is a highly useful and valuable intermediary. It can be used as a precursor in chemical processes, such as methanol production and the Fischer-Tropsch Synthesis (FTS) to create long chain hydrocarbons (e.g. diesel) [9].

Besides natural gas, there are several different sources of methane that can be utilised to coincide with the theme of fossil fuel and emissions awareness. For instance, biogas produced by the anaerobic digestion of organic matter is also the dominant mechanism for producing landfill gas; the main constituent of which is biogas. Both have roughly equal concentrations of methane and carbon dioxide [8].

However, the dry reforming operational conditions impose some challenges to develop this technology. For instance, due to the endothermic nature of the reaction and the high stability of the reactants (methane and carbon dioxide), high temperatures and suitable catalysts are needed to achieve optimal conversions and selectivity to syngas. Unfortunately, high temperatures also cause catalyst deactivation. This

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* Corresponding author.
E-mail address: t.ramirezreina@surrey.ac.uk (T.R. Reina).

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can be via sintering of the active metal phase, or by the promotion of side reactions forming solid carbon [8,10]. This carbon then deposits on the catalyst, blocking the active phase [11]. This deposition can proceed by the Boudouard reaction (BR, Eq. (2)), methane decomposition (Eq. (3)) and CO reduction (Eq. (4)):

$$2CO \rightleftharpoons C(s) + CO_2 \tag{2}$$

$$CH_4 \rightleftharpoons C(s) + 2H_2 \tag{3}$$

$$CO + H_2 \rightleftharpoons C(s) + H_2O \tag{4}$$

Methane decomposition especially is known to occur on Ni particles. Carbon remains adsorbed on the metal particles preventing access to the active metallic phase and thus decreasing the catalytic performance [12]. Carbon formation is favored by larger Nickel particles, therefore when sintering occurs during the reaction it enhances carbon deposition. Thus sintering has a double effect on the catalyst activity: first the active surface decreases altering the catalytic activity and second carbon formation is more favored on bigger particles leading to a faster deactivation of the catalyst [8,11].

Hence an effective dry reforming catalyst must be resistant to sintering as well the formation of (hard) carbon upon its surface. Concurrently, it must be relatively inexpensive and produce optimal conversions, such that it can realistically be employed in medium and large-scale applications.

Traditionally, Ni based materials are the state of the art catalysts for reforming reactions, [8,13–16,12] and for the dry reforming in particular [8,10,17]. Nevertheless, Ni is highly prone to nucleate carbonaceous deposits and to undergo sintering, resulting in severe activity depletion [17–19]. In response to these drawbacks a great deal of work in the last decade have been focused on the application of precious metal based catalysts, for reforming reactions [20]. Catalysts based on Rh [21–23], Ru [24,25] Pt [20,26,27] among others systems can outperform Ni and overcome partially or completely the stability issues. However, their cost makes them unviable for a realistic application.

Alternatively, Ni based materials can be promoted, reducing the impact of sintering and coking and improving the overall performance. Recently, Pastor-Perez et al demonstrated that a multicomponent catalyst based on Ni-CeO_2 is a good choice for glycerol reforming [28]. The introduction of CeO_2 in the catalysts formulation reduces the acidity and increases the oxygen mobility of the support [27,29], both factors helping to avoid carbon deposition. In addition, bimetallic combinations i.e. Ni-Fe, Ni-Co, Ni-Sn [19,30], Ni-Pt [20,26,31,32] have been studied, showing in some cases very promising results. In particular, Ni-Sn materials have proven to be of interest towards reforming reactions [30,33,34]. Similarly to carbon, tin contains p electrons in its outer shell close to a stable s-orbital. When carbon is present the 3d electrons of nickel interact with the 2p electrons of carbon to form nickel carbide. The presence of tin would favours the interaction of Sn p orbitals with Ni 3d electrons, thereby reducing the chance of nickel carbide formation as a coke precursor [12]. However, in large amounts tin inhibits reactant conversions. Hou et. al. studied the effect of tin addition on coke formation and the catalytic activity of Ni/α-Al_2O_3 for DRM and found that a Sn/Ni molar ratio of 0.02 was the optimum trade-off between the loss of activity and the prevention of coke formation [19]. On the other hand, the promotion of Ni catalysts with low amounts of noble metal is also of interest: a low cost Ni catalyst would benefit from the C-resistance and enhanced activity of a noble metal. Ni-Pt catalysts showed promising results with Pt loadings as low as 0.3 wt% [20,26]. The introduction of Pt was found to ease the reduction of NiO, to better disperse Ni particles and help achieving smaller Ni particles [20,32,31].

In summary, the promoter can be included in the metallic phase, in the support or in both, leading to multicomponent materials with enhanced catalytic features.

Under these premises, the aim of this work is to develop advanced multicomponent catalysts for chemical CO_2 recycling via the dry reforming of methane. Following a sequential design strategy (going from the simplest Ni/Al_2O_3 to the most complex design Ni-Sn/CeO_2/Al_2O_3 or Ni-Pt/CeO_2/Al_2O_3) we have developed highly efficient materials for dry reforming, while revealing the key aspects for a successful catalyst design.

2. Experimental

2.1. Catalyst preparation

The Cerium promoted support was synthesized by impregnation of $Ce(NO_3)_2{\cdot}6H_2O$ (Sigma-Aldrich) on γ-Al_2O_3 (Sasol –SCFa-230) in order to obtain a 20 wt% loading of CeO_2. This support, named “CeAl” was calcined at 800 °C for 8 h. The different active phases were added by sequential wet impregnation starting with the impregnation of Ni using $Ni(NO_3)_2{\cdot}6H_2O$ (Sigma-Aldrich) and a calcination step of 800 °C for 4 h. The second impregnation involved either $H_2Cl_6Pt{\cdot}6H_2O$ (37.5%, Sigma-Aldrich) or $SnCl_2{\cdot}2H_2O$ (Sigma-Aldrich) and calcination at 800 °C for 4 hours. The metal loading of the catalysts was calculated to be 10 wt.% of Ni, 0.3 wt.% of Pt and 0.4 wt.% of Sn (molar Sn/Ni = 0.02). For sake of simplicity, oxygen is omitted in the selected nomenclature. The prepared catalysts are then called Ni/Al, Ni/CeAl, Ni-Sn/CeAl and Ni-Pt/CeAl.

2.2. Catalyst characterisation

X-ray diffraction (XRD) patterns were recorded on an X'Pert Pro PANalytical, using Cu Kα radiation (40 mA, 45 kV). The spectra were registered over a 2θ range between 10–90 °, with an angle increase of 0.05° every 160 s.

Temperature programmed reduction with hydrogen (H_2-TPR) analysis was carried out on the calcined catalyst in a U-shaped quartz reactor. A gas flow of 50 ml min^{-1} of 5% H_2 in an Ar atmosphere (Air Liquide) was utilised. A 50 mg catalyst sample was heated at a rate of 10 °C min^{-1} from room temperature to 900 °C. Utilising an on stream thermal conductivity detector (TCD) to monitor the hydrogen consumption.

The textural properties of the catalyst were analysed by N_2 adsorption-desorption experiments at −196 °C (liquid nitrogen temperature). The measurements were performed on a Micromeritics Tristar 22. With the samples being degassed for 2 h at 250 °C in vacuum, before the analysis.

Raman spectroscopy was performed on the used catalytic samples. With the measurements being taken on a Horiba Jobin Yvon dispersive microscope (HR800) with confocal aperture 1000 μm, using a laser spot diameter of 0.72 μm and spatial resolution of 360 nm. The microscope was equipped with a diffraction grating of 600 grooves/mm, and a CCD detector, using a green laser (λ = 532.14 nm, maximum power 20 mW) and a 100 × objective.

Scanning electron microscopy (SEM) analysis was performed on both the fresh and used samples in a vacuum. Utilising a JEOL 5400 microscope equipped with an EDS analyser (Oxford Link).

The temperature-programmed oxidation (TPO) was carried out in a U-shaped reactor under a total flow of 50 mL min^{-1} (5% O_2 in He) from room temperature to 900 °C with a heating rate of 10 °C min^{-1}. The formed products were analysed by mass spectrometry (MS) in a Pfeiffer vacuum mass spectrometer.

2.3. Catalytic tests

The catalytic behaviour of the prepared samples for the dry reforming of methane was carried out under atmospheric pressure in a continuous flow quartz tube reactor. The reactor set up is detailed in Fig. 1. For each catalyst screening reaction, 0.1 g (particle size 100–200 μm) of catalyst was supported upon a reactor bed of quartz wool. The catalyst was reduced in situ in a 100 mL/min flow containing