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Development of a new bi-functional steam reforming/water-gas shift catalyst for production of hydrogen in a membrane reactor

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ABSTRACT

Two bi-functional catalysts were developed and experimentally tested at 550 °C and atmospheric pressure to determine the activity for both steam reforming of methane (SRM) and water-gas shift (WGS) reactions. The compositions of the catalysts are 0.8wt%Cu-3.0wt%Ni (CR1) and 2.4wt%Cu-1.5wt%Ni (CR2) supported on CeO_2–La_2O_3 (Ce/La = 2.33). The feed gases consist of CH_4/H_2O = 1:2.8 for SRM and CO/H_2O = 1:3 for WGS reaction. The catalysts used in this study have been more active for both reactions on an active site basis than their counterpart commercial catalysts. The CH_4 conversion rate increases by 128% over CR1 and by 36.7% over CR2 respectively, compared with that of the commercial reforming catalyst (RR) for SRM. Also, the CO conversion rate increases by a factor of 8.4 over CR1 and 3.7 over CR2 respectively, compared with that of the commercial high temperature water-gas shift catalyst (HT2) for WGS. The good dispersion of Cu and Ni species in the CeO_2–La_2O_3 support and their interaction with the support could contribute to their enhanced performance.
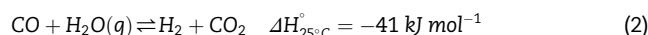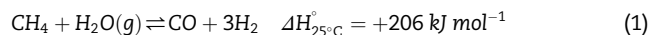
Introduction

Background

Hydrogen (H_2) is an important feedstock for use in ammonia synthesis and hydrocarbon processing, and recently, there has been an increasing demand for using H_2 in gas turbines and fuel-cells for power generation in both stationary and transport applications [1]. H_2 is mainly produced through steam reforming of hydrocarbons such as natural gas. Traditional steam methane reforming (SMR) has been performed over both commercial Al_2O_3 or $MgAl_2O_4$ supported Ni reforming catalysts operating in the temperature range 750–850 °C and with high H_2O/CH_4 molar ratios (2.8–3.5), making it an energy-intensive and expensive process. The SMR reaction can be described by the following equations:

$$CH_4 + H_2O(g) \rightleftharpoons CO + 3H_2 \quad \Delta H^{\circ}_{25°C} = +206 \; kJ \; mol^{-1} \quad (1)$$

$$CO + H_2O(g) \rightleftharpoons H_2 + CO_2 \quad \Delta H^{\circ}_{25°C} = -41 \; kJ \; mol^{-1} \quad (2)$$

where reaction (1) is the main reaction for SMR and reaction (2), the water-gas shift (WGS) reaction, is a secondary reaction that also occurs to a certain extent during reforming. The amount of CO produced via SMR is usually quite high (about
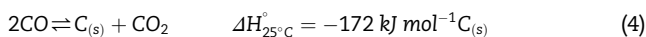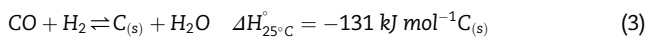
5% in the product gas), but it is affected by operating conditions such as reaction temperature, pressure and the CH_4/H_2O ratio. High CO concentration in the reforming product gas can cause carbon formation on the catalyst and reactor wall via the following reactions:

$$CO + H_2 \rightleftharpoons C_{(s)} + H_2O \quad \Delta H^{\circ}_{25^{\circ}C} = -131 \; kJ \; mol^{-1}C_{(s)} \tag{3}$$

$$2CO \rightleftharpoons C_{(s)} + CO_2 \quad\quad \Delta H^{\circ}_{25^{\circ}C} = -172 \; kJ \; mol^{-1}C_{(s)} \tag{4}$$

Another possible carbon-forming reaction is that of CH_4 decomposition:

$$CH_4 \rightleftharpoons C_{(s)} + 2H_2 \quad \Delta H^{\circ}_{25^{\circ}C} = +75 \; kJ \; mol^{-1}C_{(s)} \tag{5}$$
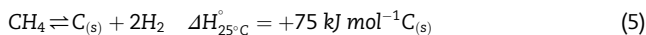
Bradford and Vannice [2] have reported that reaction (3) is the main contributor to carbon formation during SMR. Carbon formation can reduce catalyst lifetime, impair heat transfer efficiency, cause metal dusting and ultimately damages both the reformer tubes and downstream equipment. To reduce the amount of CO and simultaneously produce additional H_2, the WGS reaction is carried out in two separate stages downstream of the reformer namely, a high-temperature shift at 320–450 °C using Fe_2O_3–Cr_2O_3 catalyst and a low-temperature shift at 200–250 °C using Cu–ZnO catalyst.

The integration of a H_2-selective membrane with a SMR catalyst creates a membrane reformer [3,4], in which the in-situ removal of H_2 drives the equilibrium-limited SMR and WGS reactions to the right: essentially total conversion of CH_4 might be achieved in a single reactor at lower temperatures below 600 °C, potentially reducing capital costs. However, such a reactor needs operating at elevated reaction-side pressure to maximise the driving force for H_2 permeation across the membrane. This requires a catalyst that is:

(i) Very active under high pressure and relatively low temperature
(ii) Fully stable under the reaction conditions
(iii) Less prone to carbon formation and metal dusting since both high pressure and low temperature promote carbon formation and metal dusting

There is a growing interest in developing a bimetallic or poly-metallic catalyst for H_2 production since it could enable the catalyst to possess bi- or multiple- functions by the interaction between two metals or metal-support interaction to obtain stable and optimum catalyst performance [5].

The objective of this work is to develop a novel bi-functional catalyst formulation that has the potential for simultaneously conducting SMR and WGS reactions in a membrane reactor, thereby:

• Minimizing P_{CO} in the product gas from the reformer by promoting the in-situ WGS reaction whilst simultaneously producing additional H_2 and
• Reducing carbon formation and metal dusting

Catalyst design

It has been reported that catalytic activity depends strongly on the nature of the active metal and its support, the active phase precursor, the synthesis method, and the pre-treatment used [6]. In order to achieve the current research goal, novel formulations of bi-functional catalyst were designed on the following rationales.

Active metals

Some noble metal-based catalysts are found to have a better performance than the Ni-based ones for SMR [7], but such catalysts are very expensive due to the high cost of the active noble metals components. Noble metal-based catalysts are therefore not practical for industrial-scale reformers. In this study, Ni and Cu have been selected as the active metals. Ni has high activity towards the SMR reaction, and it also shows significant activity towards the WGS reaction. However, Ni can promote carbon deposition on the catalyst surface and the reactor wall and also promotes the methanation reaction (the reverse of reaction (1)) at low temperature. Pieterse et al. [8] indicated that Ni-based catalysts could have sufficient activity to be used in membrane for SMR reactors, but their resistance to carbon formation has to be improved.

Cu has the highest activity for the WGS reaction and no activity for methanation, but it easily sinters at moderate temperatures (>250 °C). However, Cu supported on CeO_2–La_2O_3 catalysts have been recently reported to show high activity and stability for WGS reaction at high temperatures up to 600 °C [1,9]. In addition, Cu is an active metal with lower carbon-metal bonding energy than Ni [10]. This implies that there is a weaker adsorption of carbon over the Cu active sites, thus destabilizing the precursor of solid carbon. It has been reported that addition of Cu to Al_2O_3-based Ni catalysts can enhance the gasification of carbon formed in CH_4 decomposition [11]. Also, the addition of Ni to Cu containing catalysts can improve their WGS activity and inhibit sintering of both Ni and Cu due to the interaction between Cu and Ni [12].

Catalyst supports

Catalyst activity for SMR and WGS reactions is strongly influenced by the type of support used because the support could play a positive role in the reactions. Redox metal oxide-containing multiple metal oxides were designed as support of the bimetallic catalyst because redox metal oxides, such as CeO_2, could provide mobile oxygen and oxygen vacancy to suppress carbon formation and to stabilise Ni as well as Cu [9,13]. Incorporation of La_2O_3 into CeO_2 can enhance the activity and stability CeO_2-based catalyst because the addition can improve oxygen storage capacity and reducibility [14].

Based on the above rationales, two Cu–Ni based catalysts supported on CeO_2–La_2O_3 multiple metal oxides, were designed for this study. The purpose of this design is to enable SMR and WGS reactions over the two bimetallic catalysts to be conducted under experimental conditions far away from equilibrium conversion, thus enabling the relative catalyst activities to be determined.

Experimental

Catalyst preparation

Catalyst support

The urea hydrolysis method has been employed to synthesize CeO_2–La_2O_3 as a bi-functional catalyst support for bi-