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Effect of Ce on the structural features and catalytic properties of $La_{(0.9-x)}Ce_xFeO_3$ perovskite-like catalysts for the high temperature water–gas shift reaction

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ABSTRACT

$La_{(0.9-x)}Ce_xFeO_3$ perovskite-like catalysts were investigated for the production of hydrogen from simulated coal-derived syngas via the water–gas shift reaction in the temperature range 450–600 °C and at 1 atm. These catalysts exhibited higher activity at high temperatures ($T \geq 550$ °C), compared to that of a commercial high temperature iron–chromium catalyst at 450 °C. Addition of a low Ce content ($x = 0.2$), has little influence on the formation of the $LaFeO_3$ perovskite structure, but enhances catalytic activity especially at high temperatures with 19.17% CO conversion at 550 °C and 40.37% CO conversion at 600 °C. The $LaFeO_3$ perovskite structure and CeO_2 redox properties play an important role in enhancing the water-gas shift activity. Addition of a high Ce content ($x = 0.6$) inhibits the formation of the $LaFeO_3$ perovskite structure and decreases catalyst activity.

1. Introduction

Hydrogen is an important feedstock for use in ammonia synthesis and hydrocarbon processing. Recently, there has been an increasing interest in using hydrogen as a future fuel for use in gas turbines and fuel-cells for power generation in both stationary and transport applications. This will lead to a demand for large-scale central hydrogen production facilities. Production of large quantities of hydrogen will, at least in the first instance, most likely come from fossil fuels and coal is likely to be the primary feedstock because of its relative abundance and low cost.

Although coal gasification is a viable technology for producing hydrogen, there are still some technological challenges to be overcome before this technology becomes feasible for wide-spread commercialization. To produce H_2 from coal, the synthesis gas (a mixture of CO and H_2) from coal gasification needs to be processed in a downstream reactor via the water–gas shift (WGS) reaction for additional H_2 production and preliminary CO clean up as shown below.

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$$CO + H_2O_{(g)} \leftrightarrow H_2 + CO_2 \quad \Delta H^{\circ}_{25^{\circ}C} = -41\ kJ/mol \qquad (1)$$

However, there are some barriers in the application of the WGS reaction to the syngas from coal gasification. One is catalyst stability for this reaction and the other is operating limits. The WGS reaction occurs after coal has been gasified to produce synthesis gas. Impurities contained in the synthesis gas, such as H_2S, may act as poisons that deactivate the catalysts. In addition, the synthesis gas produced from a gasifier exits at a higher temperature (around 800 °C) in comparison to the operating temperature range of commercial WGS catalyst (<450 °C).

Industrially, the WGS reaction is carried out in two separate stages, a high-temperature shift (HTS) at 320–450 °C using Fe_2O_3–CuO–Cr_2O_3 catalyst and a low-temperature shift (LTS) at 200–250 °C using Cu–ZnO catalyst. A heat removal system is coupled with the two reactor system to remove reaction heat and to maintain the gases at optimum reaction temperatures. Accordingly, the synthesis gas should be cooled to below 450 °C for HTS and to below 250 °C for LTS. In a commercial-scale coal gasification process, this step results in a potential loss of overall thermal efficiency from the system, but the efficiency loss can be minimized if the WGS reaction could be conducted at temperatures above 450 °C. There is thus a need to develop high temperature and impurity-tolerant WGS catalysts that are active and stable at higher temperatures. If used in a suitable membrane reactor configuration, that allows in-situ removal of one of the products to drive the equilibrium-limited WGS reaction to the right, essentially total conversion of CO might be achieved in a single reactor, potentially reducing capital costs. However, there are no commercial catalysts suitable for use in WGS reactors that must operate at temperatures above 450 °C [1].

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 [2]. Fe_3O_4 has good activity for the WGS reaction at moderately high temperatures [1], which can be achieved by partial reduction of Fe_2O_3. However, Fe_3O_4 could rapidly sinter and lose its activity under HT-WGS conditions. In commercial high temperature Fe_2O_3–CuO–Cr_2O_3 shift catalysts, the main role of Cr_2O_3 is to stabilise Fe_3O_4 against this sintering and over-reduction. However, Cr_2O_3-containing Fe catalysts have environmental and safety problems because Cr^{6+} has harmful effects on human health such as cancer risks and lung damage [3]. The major challenge in developing novel HT Fe-based catalysts is to design a chromium-free refractory oxide which is able to stabilise Fe_3O_4 at temperatures greater than 500 °C.

Oxides with a perovskite structure (ABO_3) are attracting great attention as catalysts in oxidation, hydrogenation and hydrogenolysis reactions due to the great flexibility of their crystal lattice to accommodate cation substitutions, high redox properties and control of their acid–base properties [4,5]. In addition, a variety of metal ions can be introduced into the perovskite structure provided that their ionic radii fit the sizes of the 12 coordinated A and octahedral B sites, where $A > B$, $r_A > 0.90$ Å and $r_B > 0.51$ Å. Furthermore, various oxidation states of the A and B cations can also be present in the perovskite structure. As the Fe^{3+} ionic radius is 0.64 Å, Fe can be introduced into the perovskite structure as component B. The La^{3+} ionic radius is 1.03 Å, so La is eligible as component A for the perovskite structure. Since it lowers the binding energy of oxygen in the electronic configuration of BO_6 octahedra, introducing La^{3+} species can activate the surface oxygen (α-oxygen) and assist in adsorbing CO on the catalyst surface. Therefore, the $LaFeO_3$ perovskite structure may be an ideal host matrix for Fe-containing mixed metal oxides used as HT-WGS catalysts. In addition, adjusting the La/Fe ratio can result in non-stoichiometric perovskite oxides such as $La_{(1-x)}FeO_3$. It has been reported [6] that non-stoichiometric perovskite oxides can easily release oxygen and so become more active than the stoichiometric oxides as catalysts in chemical reactions. Furthermore, partially substituting La by Ce could improve its thermal stability and oxygen storage capacity, thus increasing catalytic activity [7]. Hence, non-stoichiometric perovskite-like oxides of $La_{(0.9-x)}Ce_xFeO_3$ were investigated as catalysts for the WGS reaction at elevated temperatures.

Spinicci et al. [8] have investigated catalyst activity of $La_{(1-\varepsilon)}FeO_{(3-1.5\varepsilon)}$ perovskites for total oxidation of CH_4 and observed that their activity increases significantly from stoichiometric $LaFeO_3$ to non-stoichiometric $La_{0.95}FeO_{2.85}$, but decreases with further increase in Fe/La ratio in $La_{0.8}FeO_{2.70}$ and $La_{0.7}FeO_{2.55}$. They hypothesize that the variation of catalyst activity correlates with the mobility of oxygen species on the catalyst surface. Belessi et al. [9] have studied the activity of the $La_{1-x}FeO_3$ perovskites for the NO + CO reaction and found that $LaFeO_3$ ($x = 0$) exhibited lower activity than $La_{1-x}FeO_3$ (x up to 0.05) due to the higher apparent activation energy in the former than that in the latter (around 70 kJ/mol). However, there are few publications on using $La_{0.9-x}Ce_xFeO_3$ perovskite-like catalysts for the WGS reaction at high temperatures [10].

The objective of this work is to develop $La_{(0.9-x)}Ce_xFeO_3$ perovskite-like catalysts with high activity and stability for the WGS reaction operating in the temperature range 450–600 °C for the production of hydrogen from simulated coal-derived syngas.

2. Experimental

2.1. *Catalyst preparation*

$La_{(0.9-x)}Ce_xFeO_3$ perovskite-like catalyst formulations were designed and their compositions are listed in Table 1 along

Table 1 – Nominal compositions of $La_{(0.9-x)}Ce_xFeO_3$ perovskite-like catalysts and composition of commercial HTC2 catalyst.

Catalyst code	x (Ce)	Catalyst composition (at.%)
CE13	0	$La_{0.9}FeO_3$
CE20	0.2	$La_{0.7}Ce_{0.2}FeO_3$
CE21	0.6	$La_{0.3}Ce_{0.6}FeO_3$
HTC2	–	$Fe_2O_3/Cr_2O_3/CuO$ (80–95 wt.%/ 5–10 wt.%/1–5 wt.%)