Journal of $CO_2$ Utilization 21 (2017) 423–428

Contents lists available at ScienceDirect

Journal of $CO_2$ Utilization

journal homepage: www.elsevier.com/locate/jcou

# $CO_2$ valorisation via Reverse Water-Gas Shift reaction using advanced Cs doped Fe-Cu/$Al_2O_3$ catalysts

L. Pastor-Pérez, F. Baibars, E. Le Sache, H. Arellano-García, S. Gu, T.R. Reina*

*Department of Chemical and Process Engineering, University of Surrey, Guildford, GU2 7XH, United Kingdom*

## ARTICLE INFO

*Keywords:*
$CO_2$ conversion
Reverse Water-Gas Shift
Iron catalysts
Caesium promoter

## ABSTRACT

This paper evidences the viability of chemical recycling of $CO_2$ via reverse water-gas shift reaction using advanced heterogeneous catalysts. In particular, we have developed a multicomponent Fe-Cu-Cs/$Al_2O_3$ catalyst able to reach high levels of $CO_2$ conversions and complete selectivity to CO at various reaction conditions (temperature and space velocities). In addition, to the excellent activity, the novel-Cs doped catalyst is fairly stable for continuous operation which suggests its viability for deeper studies in the reverse water-gas shift reaction. The catalytic activity and selectivity of this new material have been carefully compared to that of Fe/$Al_2O_3$, Fe-Cu/$Al_2O_3$ and Fe-Cs/$Al_2O_3$ in order to understand each active component's contribution to the catalyst's performance. This comparison provides some clues to explain the superiority of the multicomponent Fe-Cu-Cs/$Al_2O_3$ catalyst.

## 1. Introduction

Some of the world's most critical issues include anthropogenic induced climate change, depleting fuel resources and pollution. $CO_2$ emissions are ever increasing and due to reliance on fossil fuels and the complications of renewable energy sources, it is necessary to consider the increasingly feasible alternative of capturing $CO_2$ and converting it into fuels and chemicals [1,2]. The Fischer-Tropsch (FT) process has been proposed as a feasible solution for $CO_2$ conversion and is intended to be carried out in conjunction with the Reverse Water-Gas Shift reaction (RWGS) [3,4]. However, the feasibility of this alternative energy source is reliant upon the development of a hydrogen source which is carbon neutral and economically acceptable.

The RWGS reaction (Eq. (1)) is the reversible hydrogenation of $CO_2$ to produce CO and $H_2O$. Due to the chemical stability of $CO_2$, it is a relatively unreactive molecule and so the reaction to convert it to the more reactive CO is energy intensive.

$$CO_2 + H_2 \leftrightarrow CO + H_2O \ \Delta H^{\circ}_{298k} = +41 \text{ kJ mol}^{-1} \quad (1)$$

$$CO_2 + 4H_2 \leftrightarrow CH_4 + 2H_2O \ \Delta H^{\circ}_{298k} = -165 \text{ kJ mol}^{-1} \quad (2)$$

According to Le Châtelier's principle, as the reaction is endothermic, it is thermodynamically favoured by higher temperatures. Increasing the $H_2/CO_2$ ratio maximises the $CO_2$ conversion and favours the RWGS reaction [5]. For this reason, when the reaction is carried out at lower temperatures, the equilibrium will increasingly favour the WGS (reverse of Eq. (1)) and methanation (Eq. (2)) reactions, as they are exothermic and the most prominent side reactions under these conditions. However, this ratio and the temperature are limited to ensure that the conditions applied during the experimental stages are economically beneficial for industrial applications. From previous studies, it has been shown that there is no significant effect of altering pressure on the reaction activity and position of the equilibrium due to the stoichiometry of the reaction [4].

The RWGS reaction is a desired route for industrial applications, most commonly in conjunction with the FT reaction to synthesise hydrocarbon fuels from syngas [3]. The conditions used for the FT reaction lie in the range of 200–375 °C; lower temperatures for long chain alkanes and higher temperatures for shorter. Therefore, an additional reason to improve catalytic activity for the RWGS reaction at lower range temperatures is to reduce heat requirements necessary for the FT process. However, naturally, the thermodynamics of the RWGS reaction require higher temperatures to achieve acceptable levels of activity [6,7].

Numerous studies have been carried out regarding catalysis of the RWGS reaction [8–10]. Iron based catalysts are often considered as one of the most successful active metals for higher temperatures, due to its thermal stability and high oxygen mobility [11–13]. Typically iron works in the high temperature range and for lower temperatures copper is often regarded to be successful due to its enhanced adsorption of reaction intermediates at these lower temperatures [14–16]. Also Cu-Fe combinations have been employed for WGS reactions showing some

---

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

http://dx.doi.org/10.1016/j.jcou.2017.08.009
Received 10 July 2017; Received in revised form 10 August 2017; Accepted 14 August 2017

advantages in terms of mechanical properties (i.e. sintering tolerance) and synergistic electronic effects [17,18].

Alkali metals tend to be successful active promoters, as they intensify electrostatic interactions, by promoting electron transfer with reacting molecules. This is known to enhance $CO_2$ adsorption capacity [19,20]. Potassium, in particular, is often regarded as a successful promoter and has been considered in several studies, often with iron as the active metal [4,5]. Furthermore, it is generally accepted that the addition of alkali metal has an important influence on the catalytic performances promoting the dispersion of active sites [21,22]. Within the alkaline materials, Cs has been studied in a lesser extension as a catalysts promoter and it is considered somehow an exotic dopant [23,24]. However, the biggest ionic radius of Cs compared to Na or K makes it a more basic element (i.e. it is more prone to donate electrons) and therefore could be an interesting dopant to promote $CO_2$ activation given the acidic nature of $CO_2$.

Under these premises we have developed a novel Cs-doped CuO-$Fe_2O_3$ catalyst supported on alumina for chemical $CO_2$ recycling via the RWGS reaction. This advanced material has been compared to Fe/Al2O3, Fe-Cu/$Al_2O_3$ and Fe-Cs/$Al_2O_3$ in order to elucidate each active component's chemical contribution to the catalytic behaviour. Furthermore several characterization techniques were employed to gain insights of the chemical properties-catalytic activity correlation.

## 2. Experimental

### 2.1. Catalysts synthesis

The catalysts were synthesised by wet impregnation in excess of solvent. For the Fe/$Al_2O_3$ the necessary amount of iron nitrate (Aldrich, 99.95%) to obtain 15 wt.% $Fe_2O_3$ was dissolved in ethanol. Then PURALOX SCFa-230 alumina support (Sasol, ≥99%) was impregnated during 1 h in a rotary evaporator with the solution containing the metallic precursor. After that, solvent was removed by evaporation and the resultant slurry was dried in at 110 °C for 24 h.

The same procedure was used for the synthesis of Fe-Cu/$Al_2O_3$, Fe-Cs/$Al_2O_3$ and Fe-Cu-Cu/$Al_2O_3$ catalysts by adding in the ethanol solution, in addition to the iron nitrate precursor, the corresponding amount of copper nitrate (Aldrich, 99.95%) and/or caesium carbonate (Aldrich, ≥99%) to obtain 10 wt.% CuO and/or 5 wt.% $Cs_2O$ respectively. All the samples were calcined at 750 °C for 4 h.

### 2.2. Catalysts characterisation

X-Ray Diffraction analysis (XRD) analysis was carried out at room temperature on an X'Pert Pro PANalytical diffractometer. The patterns were obtained using Cu Kα radiation (40 mA, 45 kV) with a 2Θ-range of 10–90° and a step size of 0.05° with a step time of 160 s.

X-Ray fluorescence (XRF) analysis was carried out on an EDAX Eagle III spectrophotometer utilising rhodium as the radiation source.

### 2.3. Thermodynamic simulation

ChemStations' ChemCad software package was used to observe the thermodynamic limits of RWGS reaction over a range of temperatures and $H_2/CO_2$ ratios. The Soave-Redlich-Kwong equation of state was used in a Gibbs reactor. Material flows into the reactor are identical to those intended to be used for experimentation. The results of these simulations are included in the catalytic performance plots.

### 2.4. Catalytic behaviour

The activity tests were carried out in a vertical fixed bed reactor in the form of a 7 mm diameter quartz tube. The catalyst was compacted onto quartz wool which was then centrally positioned into the reactor. The reactor was then placed within a cylindrical ceramic furnace. The Carbolite furnace was controlled by the Eurotherm 2416 temperature regulator and a thermocouple installed within the furnace. The product stream was then analysed in an ABB AO2020 Advanced Optima Process Gas Analyser.

Each catalyst was reduced for 1 h under a flow of 10% $H_2$ carried by $N_2$ at 750 °C prior to reactions. All reactions for the activity performance tests of each catalyst were evaluated within a temperature range of 400 to 750 °C. The temperature was increased in 50 °C segments which were held for 20 min with a heating rate between intervals of 15 °C $min^{-1}$. The flow of reactants was held at a constant weight hourly space velocity (WHSV) of 12,500 mL $g^{-1}$ $h^{-1}$ with a $H_2/CO_2$ ratio of 4:1 balanced in nitrogen. For the analysis of the effect of space velocity on catalyst performance, the reaction conditions were tested at the same temperatures and $H_2/CO_2$ ratio at space velocities of 6250, 12,500 and 25,000 mL $g^{-1}$ $h^{-1}$. The conditions for the stability tests were carried out at a space velocity of 12,500 mL $g^{-1}$ $h^{-1}$ with a $H_2/CO_2$ ratio of 4:1 at 500 °C for 50 h.

According to previous studies and the ChemCad simulation of the RWGS reaction, the $CO_2$ conversion can be improved by using higher temperatures (up to 1000 °C) and higher $H_2/CO_2$ ratios [25,26]. This is particularly true for copper containing catalysts which have been reported to be activated by high hydrogen partial pressures [4]. Despite this, the reactions have been carried out at the aforementioned conditions in order to demonstrate that the developed catalyst can perform successfully under more economical conditions, which would be beneficial for industrial application.

The parameters used for measuring catalytic activity of each sample in the investigation were $CO_2$ conversion (Eq. (3)), CO selectivity (Eq. (4)), $CH_4$ selectivity (Eq. (5)) and specific reaction rates [27].

$$CO_2 \text{ conversion } (\%) = ([CO_2]_{In} - [CO_2]_{Out})/([CO_2]_{In}) \times 100 \tag{3}$$

$$CO \text{ selectivity } (\%) = ([CO]_{Out})/([CO_2]_{In} - [CO_2]_{Out}) \times 100 \tag{4}$$

$$CH_4 \text{ selectivity } (\%) = ([CH_4]_{Out})/([CO_2]_{In} - [CO_2]_{Out}) \times 100 \tag{5}$$

where $[CO_2]_{Out}$ and $[CH_4]_{Out}$ are the concentrations of $CO_2$ and $CH_4$ in the outlet of the reactor and $[CO_2]_{In}$ in the $CO_2$ concentration in the initial gas mixture. The error in $CO_2$ conversion and $CO/CH_4$ selectivities for all the experiments is within ± 0.5%

## 3. Results and discussion

### 3.1. Characterisation

Prior to reactions, the composition and structural properties of each fresh catalyst sample was characterised by XRD, and XRF. Table 1 summarises the results of the actual composition of each catalyst from an XRF analysis. As shown in the table the nominal values of the active components (Cu and Fe) as well as the promoter (Cs) loading agrees very well with the nominal composition which validate the synthesis procedure.

As for the chemical structure, the XRD patterns presented in Fig. 1A reveals the crystalline composition of the prepared materials. As shown in the figure the samples are mainly composed by crystalline iron oxide particles with hematite $Fe_2O_3$ structure (JCPDS# 4-0784).

**Table 1**
XRF characterisation results.

| Catalysts | Composition (w/w%) | | |
|---|---|---|---|
| | $Fe_2O_3$ | CuO | $Cs_2O$ |
| Fe/$Al_2O_3$ | 15.1 | – | – |
| Fe-Cu/$Al_2O_3$ | 14.8 | 10.2 | – |
| Fe-Cs/$Al_2O_3$ | 14.6 | – | 4.2 |
| Fe-Cu-Cs/$Al_2O_3$ | 14.1 | 9.2 | 4.5 |