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Insight towards the role of ceria-based supports for reverse water gas shift reaction over RuFe nanoparticles

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ABSTRACT

Utilization of CO_2 through the reverse water gas shift (RWGS) reaction is a promising solution in managing greenhouse gas emissions. Here, we used the RWGS reaction to evaluate the catalytic conversion of CO_2 over Ru-Fe nanoparticles supported on samarium-doped ceria (SDC) support. Catalysts of different Ru_xFe_{100-x} compositions (x = 100, 80, 45, 20, 0 at.%) have been studied under steady-state conditions in a packed bed reactor in the temperature range 300–800 °C to determine their catalytic activity and selectivity towards CO. The metal-support interaction (MSI) effect for SDC was evaluated to determine its promotional behavior for the RWGS reaction. The catalyst was characterized using TEM, TGA, and ICP-ES techniques. Among all investigated catalysts, $Ru_{45}Fe_{55}$/SDC (2 wt.%) displayed the overall best activity and CO selectivity. A stability test of 100 h at 650 °C confirmed an excellent stability of the $Ru_{45}Fe_{55}$/SDC catalyst. Overall, the use of $Ru_{45}Fe_{55}$/SDC (2 wt.%) is a promising catalyst in the utilization of CO_2, reaching a maximum CO yield of ~47.5% at 800 °C and 100% CO selectivity above 500 °C. Furthermore, $Ru_{45}Fe_{55}$ (2 wt.%) nanoparticles were deposited on un-doped CeO_2 and doped ceria: Gd-CeO_2, Y_2O_3-CeO_2, as well as yttria-stabilized zirconia (YSZ) and carbon supports. Contrary to carbon support, all catalysts containing oxygen conducting-ceramic supports displayed 100% selectivity to CO at temperatures above 600 °C, which can be attributed to the synergistic relationship between Ru-Fe nanoparticles being promoted through the MSI and thermally induced migration of promoting ionic species ($O^{\delta-}$) from oxygen conducting ceramics to the nanoparticles.

1. Introduction

Greenhouse gas emissions have increased by 35% worldwide at a rate of 2.0 ± 0.1 ppm of carbon dioxide (CO_2) per year since 2002 [1,2]. With its ability to retain heat and atmospheric lifetime of at least 200 years, the abundant CO_2 presence in the atmosphere has led to climate change effects including global warming and ocean acidification [2–4]. These increases in emissions are mainly due to the anthropogenic burning of fossil fuels for energy and transportation needs [2,4]. Despite a rapid growth of renewable energy sources, fossil fuels still dominate and CO_2 is being released at a rate faster than it can be used naturally through photosynthesis and ocean absorption. Thus, an ideal method for decarbonization is through the utilization of CO_2 to create useful chemicals in the form of synthetic fuel to accommodate transportation needs.

The RWGS reaction is a promising route, where the reaction of CO_2 and hydrogen (H_2) produces carbon monoxide (CO) and water (H_2O):

$$CO_2 + H_2(\leftrightarrow)CO + H_2O,\ \Delta H = 42.1\ \mathrm{kJ\ mol^{-1}} \quad (1)$$

It is an endothermic reaction that requires a high temperature to allow for the cleavage of the double bond between the carbon and oxygen atoms [5,6]. The RWGS reaction tends to follow two mechanisms – the *redox* mechanism where CO_2 and H_2 adsorb on the catalyst surface and desorb as products CO and H_2O, and the formate mechanism where the intermediate formate (COOH) is formed and is desorbed as CO and OH react with a dissociated H to form H_2O [5,7,8]. Depending on the catalyst used, the methanol synthesis (2) and Sabatier (3) side reactions can also occur, producing methanol (CH_3OH) and methane (CH_4) as their final product instead of CO, as follows:

$$CO_2 + 3H_2 \rightarrow CH_3OH + H_2O,\ \Delta H = -167.0\ \mathrm{kJ\ mol^{-1}} \quad (2)$$

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O,\ \Delta H = -49.5\ \mathrm{kJ\ mol^{-1}} \quad (3)$$

The advantage of RWGS over reactions (2) and (3) is that it produces CO feedstock to be reacted with H_2 to synthesize long hydrocarbon chains through the Fischer-Tropsch (FT) reaction [9]:

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$$(2n + 1)H_2 + nCO \rightarrow C_nH_{2n+2} + nH_2O \quad (4)$$

The value of *n* can be increased to produce longer hydrocarbon chains, depending on the desired refined end-product (i.e., gasoline, diesel, etc.). The FT reaction is a well-known, mature process to produce liquid fuels from syngas (CO:H_2 ratios of 1:1–1:2) through the gasification of fossil fuels [4,10,11]. Pairing the RWGS reaction with the FT reaction by using CO_2 from carbon capture and H_2 from water electrolysis offers a promising solution in reducing climate change effects and solving transportation needs [12]. For the overall process to be carbon neutral, the conversion reactions and production of H_2 must run on renewable energy; otherwise, it is counterproductive [13].

For the RWGS to be effective, a catalyst is used to increase the rate of conversion of reactants by lowering the required activation energy without it being consumed in the process [14,15]. The ideal RWGS catalyst should be highly active in converting CO_2, selective to CO formation and display a high thermal stability for prolonged periods.

A typical heterogeneous catalyst consists of metal or metal oxide nanoparticles dispersed on a support to increase the number of active sites, improve gas diffusion, increase resistance to attrition, and improve thermal conductivity [14]. Many metals have been studied for the RWGS reaction and each exhibit some sort of concern. Transition metals like Cu, Ni, and Co are commonly used in the water gas shift (WGS) reaction due to their high activity in the forward direction and have been extensively studied for the reverse direction [5,6,16–20]. The main challenges in dealing with these inexpensive metals are lower conversion rates, selectivity to CH_4, coke deposition and stability issues [6]. To deal with the issue of thermal stability, it was observed that when Fe was combined with Cu, its stability was improved, allowing for a stable conversion for long periods, eventually deactivating before 100 h [20]. For Cu and Ni, coke deposition rates are typically proportional to increases in temperature. The conversion rate is therefore limited by operating at lower temperatures to avoid a buildup of coke, thereby deactivating the catalyst. Ni exhibits similar properties to noble metals but displays lower catalytic activity and is more prone to methane formation [21]. Continued research is being done to optimize the performance of transition metal catalysts in order to benefit from their abundance and price when compared to noble metals.

Noble metals such as Pt, Rh, and Ru have been successfully used in the RWGS reaction and display CO_2 conversions close to equilibrium [22–26]. They are advantageous over transition metals since they typically do not exhibit coke deposition and CH_4 formation does not occur past 500 °C [23]. The main issue with noble metals is their high cost and low availability. Ru is the most economical amongst the noble metals, and has shown to display catalytic activity similar to Pt, but is favorable in CH_4 formation [25,27]. Additionally, it accounts for a large number of oxidation states that exhibit high electron transfers, making it a suitable candidate for CO_2 hydrogenation [15]. Pairing Ru with transition metals presents the opportunity of using less noble metals, while not compromising activity and allowing for a synergistic relationship between different metals.

It is well known that the catalytic activity of a catalyst depends on many factors: particle size, size distribution, catalyst dispersion, surface and bulk composition, and the nature of the support [15]. The latter is known as the metal-support interaction (MSI) effect. The MSI can be tailored to enhance the RWGS reaction through the selection of the metal and support used and the catalyst preparation method. The combination of metals deposited on support governs the performance of the MSI. Most common catalyst supports include aluminum oxide (Al_2O_3), silica (SiO_2), zirconia (ZrO_2) and activated carbon [19]. In recent years, the use of mixed ionic-electronic conductive (MIEC) oxide supports such as ceria (CeO_2), titania (TiO_2) and ionically conductive yttria-stabilized zirconia (YSZ), samarium doped ceria (Sm-CeO_2 or SDC), beta-alumina (β-Al_2O_3) have been on the rise since they enhance the MSI effect [28,29]. CeO_2 has been proven to be an active support for the RWGS due to its high reducibility, high ability to adsorb CO_2 and its high oxygen ion (O^{2-}) conductivity [19,30–33]. Oxygen vacancies for CeO_2 are created through redox cycles between Ce^{4+} and Ce^{3+} where the vacancies act as storage and release sites. *Nolan* et al. determined that the activity of ceria is due to an oxygen hopping mechanism where one O molecule from CO_2 fills up the oxygen vacancy resulting in CO desorption, and two H molecules adsorbs to the O molecule to produce H_2O [34]. This leaves behind an oxygen vacancy which serves to repeat the process all over again [34]. Furthermore, the MSI effect with these types of supports is functionally similar to the mechanism of electrochemical promotion of catalysis (EPOC) or non-Faradaic modification of catalytic activity (NEMCA) [28,35–37]. The model of electrochemical promotion regards the phenomenon as catalysis in the presence of an electrically controlled effective double layer formed by ion spillover/backspillover at the catalyst surface. This double layer is formed upon application of electrical stimuli and is in-situ controlled. For metal or metal oxide catalysts dispersed on ionically conducting supports (yttria-stabilized zirconia (YSZ) (O^{2-} conductor) [28,38–40], K-β″-Al_2O_3 (K^+ conductor) and Na-β″-Al_2O_3 (Na^+ conductor) [41,42] or MIEC, the charge built up by the electronic effect may induce migration of ions to the catalyst/support interface and vice versa. The population of the surface with dipoles increases the surface potential, and the concomitant increase in work function affects the binding strength of chemisorbed species and as a result the catalyst activity and often selectivity. The close analogy between EPOC and MSI is well postulated, and they may be considered as two functionally identical and only operationally different phenomena [43,44]. Several studies on nanostructured film catalysts [28,43] or nanoparticles dispersed on active supports [29,45,46] showed that when no potential or current is applied, even the operational difference vanishes under steady-state reaction conditions and the MSI effect is due to migration (spillover/backspillover) of charged species such as O^{2-}, H^+, Li^+, K^+, Na^+, F^-, etc.

In the present study, the catalytic activity of mono- and bimetallic Ru, Fe and Ru_xFe_{100-x} (x = 100, 80, 45, 20, 0 at.%) nanoparticles (1.5–2 nm) supported on CeO_2, MIEC and ionically conductive doped-CeO_2 (Sm-CeO_2 (SDC), Gd-CeO_2 and Y_2O_3-CeO_2) and YSZ, and non-conductive carbon were examined for the RWGS reaction in order to shed light on MSI effect and role of O^{2-} from the support. The effect of Ru to Fe atomic ratio along with the overall metal loading on SDC support was examined to reduce the amount of Ru while ensuring high activity. Furthermore, the gas composition (H_2:CO_2 ratios) and the stability of the best-performed catalyst, as well as its activity for water gas shift (WGS) reaction have been investigated.

2. Experimental

2.1. Synthesis of colloidal nanoparticles

Ru, Fe and Ru-Fe nanoparticles were synthesized using the polyol synthesis method, described in Ref. [47]. This method consists of mixing metal precursors with ethylene glycol and sodium hydroxide (NaOH): ethylene glycol acting as a reaction medium and a reducing agent [48], and NaOH to increase the pH of the solution, which governs the size of the nanoparticles by allowing the ethylene glycol to act as a stabilizer. Ruthenium chloride ($RuCl_3$) (anhydrous, Sigma Aldrich) and iron (III) nitrate ($Fe(NO_3)_3$) (nanohydrate, Fischer Scientific) were synthesized in 50 mL ethylene glycol (Fischer-Scientific certified grade) containing 0.08 M NaOH. For example, the $Ru_{45}Fe_{55}$ colloid solution was prepared with 0.123 g and 0.2916 g of $RuCl_3$ and $Fe(NO_3)_3$, respectively. The colloid solution was mixed for 1 h at room temperature where the pH increased to 11. It was then refluxed for 3 h at 160 °C, cooled, and then stored at room temperature. The final mixture for bimetallic $Ru_{45}Fe_{55}$ colloid was dark brown in color. The remainder of the colloids were prepared by the same method with their respective concentrations and were all dark brown in color.