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A kinetic study on the structural and functional roles of lanthana in iron-based high temperature water–gas shift catalysts

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ABSTRACT

The structural and functional roles of varying amounts of lanthana in co-precipitated high temperature $Fe_2O_3/Cr_2O_3/CuO$ water–gas shift catalysts were studied at 1 atm and 350–425 °C temperature range.

Addition of 0.5 wt% of lanthana enhanced the reducibility of the catalyst, increased its surface area and its WGS activity from 24 to 31 mmol CO/(g_{cat} min), and reduced the deactivation rate at 400 °C from 23% to 11% relative to a similar catalyst with no lanthana. XRD results suggested that 0.5 wt% of lanthana stabilized the iron–chromium cubic spinel structure most efficiently under the operating conditions; however, further additions appeared to disrupt the spinel structure and degrade the performance of the catalysts.

The power-law and Langmuir–Hinshelwood models provided much better fits to the rate data than either the redox or the Eley–Rideal models, suggesting that the reaction tends to follow an adsorptive mechanism. The CO adsorption equilibrium constant was largest for the catalyst with 0.5 wt% lanthana, indicating that the addition of lanthana might facilitate CO adsorption. Water inhibited the reaction as it strongly adsorbed on the catalyst surface.

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Introduction

Hydrogen is a valuable, highly-reactive chemical with a specific energy content of 33 kWh/kg. It is used in numerous industrial processes, such as ammonia synthesis and hydrocarbon cracking [1,2]. It has recently received much attention as a potential fuel for fuel cells that more efficiently meet energy demands.

Industrially, hydrogen is produced as a component of synthesis gas *via* coal gasification, steam reforming of natural gas, or any other autothermal reforming process of an abundant carbon or hydrocarbon source. The toxic CO from the gasification process is generally reacted with steam to produce further hydrogen *via* the reversible water–gas shift (WGS) reaction:

$$CO + H_2O_{(g)} \leftrightarrow CO_2 + H_2 \quad \Delta H^{\circ}_{298\ K} = -41\ \text{kJ/mol} \tag{1}$$

The exothermicity and reversibility of the WGS reaction lead it to be performed in 2 steps in industrial reactors: (1) high-temperature (HT) at ~400 °C and (2) low-temperature

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(LT) at ~220 °C, in order to minimize the CO concentration in the effluent gas stream [3]. The non-catalytic HT WGS reaction operating with supercritical water (above 647 K and 22 MPa) has a reaction rate about 10^7 times slower compared to the reaction in the presence of catalytic iron at non-supercritical conditions [4], which emphasizes the importance of the heterogeneous catalyst. Industrial HT WGS catalysts usually contain iron oxide and chromia (Fe_3O_4/Cr_2O_3), whereas $Cu-ZnO-Al_2O_3$ catalysts are used for the LT WGS reaction [1,3]. The synthesis gas produced from gasified coal has to be purified from any sulfur traces (<1 ppm) and other impurities, such as chlorine and heavy metals, that deactivate the catalyst. The synthesis gas typically cools to about 400 °C, where Fe-based catalytic activity and equilibrium H_2 formation are optimal [3].

Fe_3O_4, which has an inverse spinel structure, serves as the catalytically active phase of iron oxide; however, 8 wt% chromia is added to the iron oxide catalyst to stabilize and decrease sintering of the iron oxide under reaction conditions by forming an iron–chromium normal spinel, for which the lattice parameters are smaller than those for Fe_3O_4 [5–7]. This decrease in unit cell size indicates that chromium stabilizes the structure by making it more compact.

Many promoters have been studied to improve the properties of the iron/chromia HT WGS catalysts. For example, Rhodes et al. [8] experimentally investigated the addition of 2 wt% of B, Cu, Ba, Pb, Hg, and Ag separately on iron oxide-chromia catalysts prepared by co-precipitation. They showed that B poisoned the catalyst and thus decreased its activity, while the other additives improved it. Hg was the most effective promoter, followed by Ag, Ba, Cu, and Pb in decreasing order of effect. Addition of 0.97 wt% rhodium by incipient wetness impregnation to HT WGS catalysts significantly increased the reaction rate [9]. However, Cu has been especially studied as a promoter to these catalysts, as metallic Cu provides actives sites for the HT WGS reaction similar to those available in the LT WGS catalysts [10,11]. Cu also stabilizes the reduction of the catalyst with CO and decreases the apparent activation energy [8,12,13]. Ceria, a rare-earth metal oxide and a promising promoter for HT shift catalysts, is well known for its capability to store and release oxygen and hydrogen and to form intermetallic compounds as well as its ability to cycle between Ce^{4+} and Ce^{3+} oxidation states [14–16]. Hu et al. [17] showed that ceria promotes WGS activity as it facilitates the oxidation of the reduced sites on the catalyst surface by water. Other studies also report increased shift activity in the presence of ceria due to the excellent electronic properties that ceria possesses [18–20].

The present study investigates the role of another rare earth oxide, lanthana (La_2O_3), on $Fe_3O_4/Cr_2O_3/CuO$ HT WGS catalysts. Lanthana exhibits thermal stability and has a large coordination number [21,22]. Lanthana addition to chromia-free iron oxide WGS catalysts creates a perovskite-like structure with a chemical formula of $La_{0.9-x}Ce_xFeO_3$, which provides the catalyst with higher activity at temperatures above 550 °C, compared to the standard industrial Fe–Cr catalysts [23,24]. (In both of these studies [23,24], small amounts of cerium, up to 0.22 atom fraction, were included with the lanthanum. Small amounts of cerium ($0.2 < x < 0.6$) produced high WGS activity. Higher amounts of cerium ($x > 0.6$) prevented the formation of the perovskite structure.) Wang et al. [25] studied the effect of lanthana addition on Zr–Co/activated carbon catalysts for Fischer–Tropsch synthesis and concluded that 0.2 wt% La enhanced the activity of the catalyst and the selectivity to long-chain hydrocarbon (C_{5+}) due to increased thermal stability of the catalysts.

Many studies on HT WGS reaction kinetics have been conducted over the last 30 years during which over 20 mechanisms and kinetic models have been proposed, a few of which are most accepted [3,26]. Power-law, Langmuir–Hinshelwood (LH), and regenerative (redox) models generally best fit and represent the steady-state kinetics of the high-temperature WGS reactions [26,27]. The Langmuir–Hinshelwood model follows an adsorptive mechanism, in which the reactants adsorb on the catalyst surface to react to products that then desorb, as shown in equations (2)–(6), where *s* represents a vacant adsorbing site. (The dissociation of water and reaction of its products with adsorbed CO likely proceed through more complicated steps than shown in this simplified mechanism. This is also true for the redox model presented below. However, the rate expressions from these more complicated mechanistic steps retain similar forms to the ones presented. Derivation details for each of the following rate expressions is included in Appendix A.)

$$H_2O + s \Leftrightarrow H_2O - s \tag{2}$$

$$CO + s \Leftrightarrow CO - s \tag{3}$$

$$CO - s + H_2O - s \Leftrightarrow CO_2 - s + H_2 - s \tag{4}$$

$$CO_2 - s \Leftrightarrow CO_2 + s \tag{5}$$

$$H_2 - s \Leftrightarrow H_2 + s \tag{6}$$

The general expression for the LH model is depicted in equation (7):

$$-r_{CO} = \frac{kK_{CO}K_{H_2O}([CO][H_2O] - [CO_2][H_2]/K)}{(1 + K_{CO}[CO] + K_{H_2O}[H_2O] + K_{CO_2}[CO_2] + K_{H_2}[H_2])^2} \tag{7}$$

where *r* is the reaction rate, *k* is the rate constant, K_i is the adsorption equilibrium constant for species *i*, *K* is the WGS reaction equilibrium constant, and [i] is the concentration of species *i*. The proposed LH model assumes non-dissociative adsorption of water (in Equation (2)); therefore, water dissociation occurs as part of the rate-determining step (Equation (4)). In contrast, only one reactant adsorbs on the surface and the denominator is raised to the first power in the Eley–Rideal model, as shown in equation (8):

$$-r_{CO} = \frac{kK_i([CO][H_2O] - [CO_2][H_2]/K)}{1 + K_i[i]} \tag{8}$$

The regenerative model follows an oxidation–reduction mechanism, hence the name redox, in which H_2O oxidizes a reduced center on the catalyst surface to form H_2, and then CO reduces the oxidized center to form CO_2, completing the catalytic cycle. The mechanism can be written in two steps, where * and O*, respectively, represent a reduced and an oxidized active site on the surface of the catalyst, as follows:

$$H_2O + * \Leftrightarrow H_2 + O* \tag{9}$$

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