



Long-term WGS stability of Fe/Ce and Fe/Ce/Cr catalysts at high and low steam to CO ratios—XPS and Mössbauer spectroscopic study

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ABSTRACT

Long term time on stream stability of Fe/Ce and Fe/Ce/Cr catalysts has been investigated for high temperature water gas shift (WGS) reaction. Excellent WGS stability was observed for the Fe/Ce catalyst at steam to CO ratio of 3.5 and temperature of 500 °C for 30 days. The Fe/Ce catalyst also exhibited remarkable stability in presence of sulfur since no deactivation was observed in the presence of 400 ppm of sulfur. However, at steam to CO ratio 1.5, Fe/Ce deactivated continuously with time due to continuous formation of carbon and methane. X-ray diffraction measurements reveal that all the catalysts are stable in terms of composition during the WGS reaction irrespective of the steam to CO ratio. However, sintering of the magnetite phase is rapid in the experiment at steam to CO ratio of 1.5. XPS and Mössbauer spectroscopic measurements show that surface and local structural rearrangement of iron ions are taking place in the experiment at steam to CO ratio 1.5. XPS measurements also indicate the carbonate formation during the activation of Fe/Ce catalyst. The present study shows that Ce is a good stabilizer for iron oxide for high temperature WGS reaction only for higher steam to CO ratio applications. At low steam to CO ratio, Ce does not stabilize the Fe³⁺/Fe²⁺ redox couple during the WGS reaction. Addition of Cr to the Fe/Ce catalyst improves the WGS long term stability of Fe/Ce catalyst at steam to CO ratio 1.5. Remarkably, no deactivation was observed for the Fe/Ce/Cr catalyst at steam to CO ratio 1.5 and in presence of 400 ppm of sulfur. Structural and surface characterization measurements suggest that both Ce and Cr prevent the magnetite phase from sintering of and local structural rearrangement of iron ions during the WGS reaction at steam to CO ratio 1.5.

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1. Introduction

The integration of H₂-selective membranes for WGS reactions provides a new effective one step solution, because it allows CO conversion to surpass the thermodynamic equilibrium limitation due to in situ extraction of H₂ according to Le Chatelier's principle [1–3]. Thus, the reaction can be carried out at high temperature and high pressure which benefits both reaction and membrane permeation kinetics, and the conventional low-temperature WGS stage, can be omitted [4,5]. Several variables influence the performance of a membrane reactor. Operating conditions, engineering of the system, membrane characteristics, catalyst used are all parameters to be taken into account for optimizing the efficiency of the process [6–9]. Developing catalyst for membrane reactors for WGS is more challenging than for conventional reactors due to much higher reaction temperatures (450–550 °C) and pressures (1–20 bar) [10,11].

In our previous studies, we introduced a variety of metal dopants (M=Cr, Mn, Co, Ni, Cu, Zn, and Ce) for iron oxide (spinel lattice), and screened their effectiveness for high-temperature water–gas shift reactions. Among the various modified ferrites investigated Ce doped iron spinel exhibited highest activity [12]. The idea was to examine whether ferrite formation can occur with dopants and promote the Fe³⁺ ↔ Fe²⁺ redox couple. Two features are mainly responsible for making cerium a promising material for use either as a support or as a promoter in the WGS reaction. The first one is the ability of ceria to shift between CeO₂ (Ce⁴⁺) and Ce₂O₃ (Ce³⁺) under oxidizing and reducing conditions, respectively and the second is the ease of forming of labile oxygen vacancies, and particularly promote the relatively high mobility of bulk oxygen species [13]. Cerium oxide-containing WGS catalysts are promising also because of the oxygen storage capacity of ceria and the cooperative effect of Ce-metal resulting in highly active sites [14]. Our previous studies also revealed that both iron and ceria undergo a facile charge transfer reaction between Fe³⁺ ↔ Fe²⁺ and Ce⁴⁺ ↔ Ce³⁺ redox couples, respectively; the synergism between the two couples could be responsible for the improved WGS activity [15]. Additionally, at higher temperatures, the rapid transformation of oxygen exchange

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