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Recent advances in iron-based high-temperature water-gas shift catalysis for hydrogen production

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The high-temperature water-gas shift (HT-WGS) has received tremendous interest for the production of clean hydrogen in large scale. Iron-based oxide catalysts are widely studied for the HT-WGS reaction due to their high activity, durability, and relatively low manufacturing costs. In this review, we discussed the recent findings, especially, the role of different promoters on the HT-WGS performance of the Fe-based oxides catalyst. The review reported the recent attempts to replace the toxic Cr in the Fe/Cr-based catalysts. The article also reviews the structure-activity relations with various characterization techniques. Further, we highlighted the recent progress in understanding the catalyst structure and reaction mechanism during the reaction by *in-situ* and *operando* studies.

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Introduction

Greater and greater scientific attention is being paid to the global energy as its consumption has dramatically increased due to the growth of population and their improved living standards in recent years [1]. Among the various energy sources, hydrogen energy is predicted to solve many of our future energy needs in an environmentally sustainable fashion because it is a clean, renewable and highly efficient energy carrier [2,3]. As a result, the Energy Policy Act of 2005 and the Energy Independence and Security Act of 2007 have come in the United States [4,5]. Although hydrogen can be generated from a wide range of primary energy sources, still most of the world's hydrogen supply (>95%) is produced through the reforming of fossil fuels followed by the water-gas shift (WGS) reaction [6]. Therefore, the WGS reaction is the most important industrial reaction for the sustainable production of hydrogen energy till today. Even though WGS is an exothermic reaction, the reaction rate is lower at lower temperatures. Thus, the WGS is commercially performed in two steps: high-temperature water-gas shift (HT-WGS) at 350–450 °C to increase the reaction rate, followed by low-temperature water-gas shift (LT-WGS) at 200–250 °C to convert the remaining CO in the system. Especially, there is a growing interest in HT-WGS reaction in relation to the production of pure hydrogen from fossil fuels, agricultural and forestry biomass, and municipal waste gasification technology [7,8].

A large number of metal oxides and mixed oxides have been proposed and patented to catalyse the HT-WGS reaction. Among the various systems, formulations containing iron-based oxide materials are widely investigated as promising catalysts for HT-WGS. There have been many efforts to improve the performance of iron-based oxide catalyst by various promoters [9–14]. This short review attempts to discuss the recent advances in developing the efficient Fe-based catalysts for hydrogen production via HT-WGS reaction.

Fe/Cr-based catalysts

Since the discovery of Fe/Cr oxide type catalyst in 1914 for HT-WGS by Bosch and Wild scientists from BASF [15], great efforts have been made to develop Fe/Cr oxide catalyst with new structural and catalytic properties and to identify the active sites. Dufour *et al.* [16] investigated the effect of the iron precursor (Ferrous sulfate and chloride) and Cu and Co promoters on the activity of Fe/Cr magnetite-based catalyst prepared by the oxidation–precipitation method. The Fe/Cr prepared with sulfate precursor showed more CO conversion (%) and H_2 selectivity (%) although it has larger crystallite size and lowers specific surface area compared to the catalyst obtained from chloride precursor. It can be attributed to a decrease in the surface basicity that improves the reducibility and affects to the hydrogen adsorption and CO chemisorption. Moreover, the activity of Fe/Cr catalyst obtained from chloride precursor increased with the incorporation of Cu or Co while the promoters did not affect much of the performance of the materials prepared with sulfate precursor. Meshkani *et al.* [17–22] reported a set of papers on the Fe–Cr–Cu catalyst for HT-WGS in which they synthesized the catalyst by different methods and studied the effect of preparation factors. In some reports, they synthesized the Fe–Cr–Cu catalyst by coprecipitation method and investigated the

effects of precipitation pH, aging temperature, aging time, the concentration of the precursors solution, and calcination temperature on the structural and catalytic properties. The best preparation parameters were reported as pH of 10, precursor concentration of 0.06 M, calcination temperature at 400 °C, aging time of 5 hours and aging temperature at 60 °C [19–21]. In another work, the Fe–Cr–Cu catalyst prepared by coprecipitation method in water-in-oil (W/O) microemulsion exhibited higher activity than the commercial catalyst [17].

Smirniotis *et al.* [23] developed various Ce-promoted Fe/M (M=Cr, Co, Zr, Hf, and Mo) spinel type catalysts and tested for HT-WGS at low steam to CO ratios and in the presence of sulfur. Although all the catalysts have good stability in the presence of sulfur, only Cr-doped and Co-doped Fe/Ce catalysts exhibited excellent activity even at low steam/CO ratio = 1.5. Mössbauer spectral analysis revealed that Cr and Co occupy the octahedral sites of the magnetite during the activation and promote the WGS activity of Fe/Ce, whereas Zr, Hf, and Mo have little or no effect on the structure of Fe/Ce during the activation [23]. The stability of the catalyst is industrially indispensable as it can reduce the catalyst manufacturing cost. The Fe/Ce catalyst itself showed a remarkable long-term WGS time on stream stability for 30 days at steam to CO ratio of 3.5 and temperature of 500 °C even in the presence of sulfur (Figure 1a and b). Nevertheless, it was deactivated continuously with time at steam to CO ratio of 1.5 due to the rapid formation of methane (Figure 1c). The Mössbauer characterization of Fe/Ce catalyst showed a similar octahedral (O_h)/tetrahedral (T_d) fraction before (2.44) and after the WGS at steam to CO ratio of 3.5 (2.3). However, spent Fe/Ce catalyst at steam to CO ratio of 1.5 exhibited a significant change in the O_h/T_d fraction of Fe ions (1.1) compared to the activated catalyst (2.44). This indicates the severe local structural rearrangement of Fe^{2+} and Fe^{3+} ions in the catalyst during the WGS which could be responsible for its deactivation at steam to CO ratio of 1.5. Further, with the addition of Cr, the Fe/Ce catalyst showed improved long-term time on stream stability at steam to CO ratio of 1.5. Interestingly, Mössbauer results revealed that there was no significant change in the O_h/T_d fraction (2.72) value even after the 30 days of the WGS reaction as compared to the activated catalyst (2.9). This indicated that the Cr stabilizes the Fe/Ce catalyst during the WGS at steam to CO ratio of 1.5. These findings were also in agreement with their XPS results [24].

Recently, we have optimized Fe–Ce–Cr catalyst composition for HT-WGS and found that the catalyst with Fe/Ce/Cr atomic ratio of 10:1:1 showed higher activity compared the other compositions. From the surface and structural characterizations, we concluded that the better performance of the Fe–Ce–Cr (10:1:1) catalyst was due to its higher lattice strain or disorder and excellent surface redox properties among the catalysts with different compositions [25•]. In another work, Smirniotis and co-workers also synthesized Fe/M/Cu (M=Cr, Ce, Ni, Co, Mn, and Zn) ferrite catalysts for HT-WGS reaction. In this study, Cu act as a promoter for all M-modified ferrites except for the Fe/Ce/Cu catalyst in which Cu acts as an inhibitor for the reaction. This abnormal behavior of the Cu in the catalyst is due to the formation of the wustite phase during the activation as suggested by Mössbauer measurements, which is in line with their XRD and XPS results [14,26,27].

Cr-free Fe-based catalysts

The research focus has been shifted towards the development of Cr-free iron-based catalysts for HT-WGS since 2000 due to the environmental concerns related to chromium. There have been many efforts in the open literature to replace Cr in the formulation while maintaining the high activity and stability of the catalyst for HT-WGS. Araújo *et al.* in 2000 reported that the Al-doped Fe–Cu catalyst has similar HT-WGS activity as compared to the commercial Fe–Cr–Cu catalyst [28]. The Fe–Th–Cu was shown to be a promising catalyst than the Fe–Cr–Cu catalyst for the HT-WGS reaction by Costa *et al.* [29]. Natesakhawat *et al.* [30] studied Al, Ga, Mn as a substitute for Cr and found Al was a potential promoter for chromium replacement in HT-WGS catalyst. They have also investigated the effects of Fe/Al ratio, precipitation medium pH, and calcination temperature on the Fe–Al catalyst and observed the best activity at Fe/Al = 10, pH = 9, and 450 °C calcination temperature. Na *et al.* [31] studied the effect of preparation method on Fe/Al/Cu oxide catalyst for HT-WGS and reported that the co-precipitated catalyst showed the highest CO conversion with stable activity than the catalysts synthesized by impregnation and sol-gel methods. Such improved performance of the co-precipitated catalyst was ascribed to the high surface area, the small crystallite size of the Fe_3O_4, the ease of reducibility, and formation of a reduced form of the Cu species. Meshkani *et al.* [32] screened the Ni, Co, and Cu as a structural promoter to Fe–Al catalyst and found that the Cu-promoted Fe-Al exhibited the highest activity than the Co-promoted and Ni-promoted catalysts. They also optimized both the Al and Cu contents in the catalyst for HT-WGS and claimed that the catalyst with Fe/Al = 10 and Fe/Cu = 10 showed the highest CO conversion. In other works, they studied the promoted Fe_2O_3–Al_2O_3–CuO catalysts with Ba, Ca, Mg, Sr, Ce, La, Zn, Y, and Mn and revealed that the Ba and Mn were the promising promoters for the catalyst. The effect of Ba and Mn contents on the catalyst was also evaluated and indicated that the catalyst with 9 wt% Ba and 12 wt% Mn showed the highest activity among the other catalysts tested [33,34].