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A perspective on chromium-free iron oxide-based catalysts for high temperature water-gas shift reaction

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ABSTRACT

Recent efforts to replace toxic hexavalent chromium oxide in commercial copper-chromium-iron oxide catalysts for the High-Temperature Water-Gas Shift (HT-WGS) reaction are reviewed. Advances in understanding the fundamentals of the HT-WGS reaction catalyzed by copper-chromium-iron oxide reveal that the role of chromium is to act as textural promoter to stabilize the surface area of the iron oxide phase towards sintering. The lack of *in situ/operando* spectroscopic characterization of the bulk and surface phases of the newly designed promoted catalysts, however, severely hampers a thorough understanding of the chemical states as well as the exact role of the non-Cr promoters. Future research studies will need to perform *in situ/operando* spectroscopy studies to fill this void to allow for the rational design of advanced HT-WGS catalysts.

1. Introduction

The water-gas shift (WGS) reaction ($\text{CO} + \text{H}_2\text{O} \leftrightarrow \text{CO}_2 + \text{H}_2$) is an important industrial reaction to adjust the H_2 to CO ratio for ammonia synthesis, methanol synthesis, Fischer-Tropsch process and H_2 production via methane steaming reforming (MSR). Due to the exothermic nature of this reversible reaction, this process is commercially performed in several temperature stages with different catalysts to optimize the higher reaction rates as well as CO equilibrium conversion [1,2]. The high temperature water-gas shift (HT-WGS) reaction is commercially performed at $\sim 350\text{--}450^\circ\text{C}$ with iron oxide-based catalysts and the low temperature water-gas shift (LT-WGS) reaction is typically performed at $\sim 190\text{--}250^\circ\text{C}$ with supported copper-based catalysts [3–7]. Supported noble metal catalysts (Pt, Pd, Au, etc.) and single atom catalysts were also developed recently with a medium operation temperature which is typically below 350°C [8–12]. Industrial reactors typically operate at a range from atmospheric pressure to 8375 kPa [1].

Since initially being developed in 1914 by Bosch and Wild, the iron-chromium oxide has been widely used as an industrial catalyst for HT-WGS reaction to remove CO from the H_2 stream for the Haber-Bosch ammonia synthesis process because CO is a poison for the ammonia synthesis by iron-based catalysts [1]. While the WGS reaction has been

a very active research field during the past four decades, interest in the HT-WGS catalytic reaction has only flourished starting from middle 1980s, as shown in Fig. 1. The research interest for the iron-chromium oxide catalysts has covered many aspects such as the reaction mechanism, nature of active sites and promoters. There has been increasing interest since 2000 on the development of non-Cr catalyst due to the arising environmental and health concern on hexavalent chromium (Cr^{6+}) [1,2].

In this perspective, we do not intend to give a comprehensive overview of iron oxide-based catalysts for the HT-WGS reaction and refer the reader to a recent review on this topic [13]. Instead, we will focus our attention on the recent efforts in replacing chromium in the conventional iron-chromium oxide-based HT-WGS catalysts. We will also highlight recent advances in understanding the fundamentals of the HT-WGS reaction catalyzed by iron oxide-based catalysts. Finally, we will discuss how these fundamental research insights can guide the rational design of chromium-free iron oxide based HT-WGS catalysts.

2. Reaction mechanism

Two competing reaction mechanisms have been proposed for the HT-WGS reaction. One is referred to as the “associative” mechanism

Abbreviations: HT-WGS, high-temperature water-gas shift; LT-WGS, low-temperature water-gas shift; MSR, methane steaming reforming; TPSR, temperature-programmed surface reaction; TPR, temperature-programmed reduction; TPO, temperature-programmed oxidation; TPD, temperature-programmed desorption; TOF, turnover frequency; GA, gravimetric analysis; XANES, X-ray absorption near edge structure; XRD, X-ray diffraction; TG, thermal gravimetry; DSC, differential scanning calorimetry; FTIR, Fourier transform infrared spectroscopy; DRIFTS, diffuse reflectance infrared Fourier transform spectroscopy; HRTEM, high-resolution transmission electron microscopy; SEM, scanning electron microscopy; XPS, X-ray photoelectron spectroscopy; XRM, X-ray microscopy

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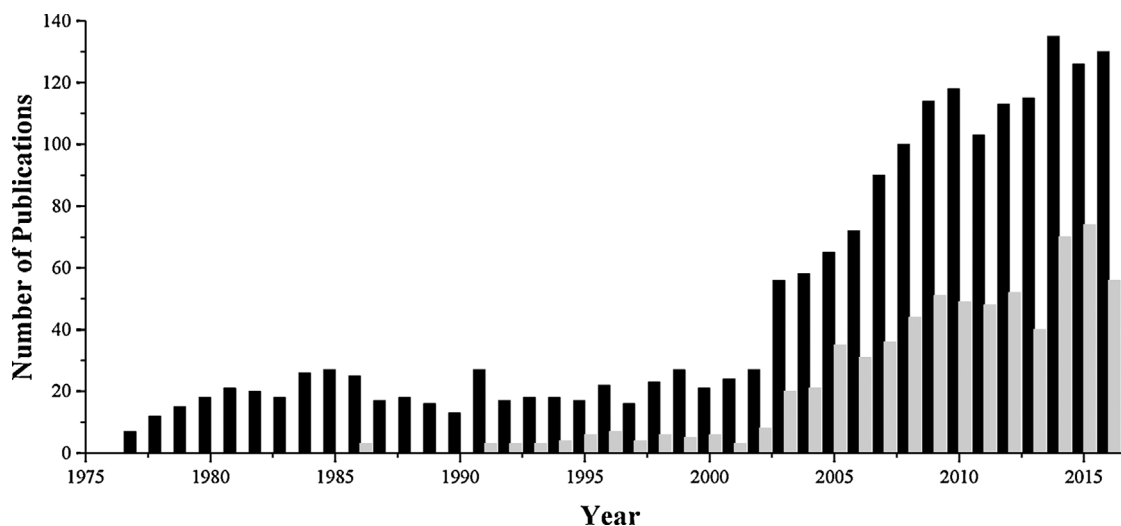
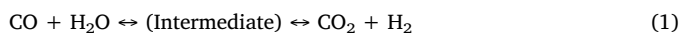


Fig. 1. Number of annual WGS publications since 1975 with: (black bar) “water-gas shift” in title; (gray bar) “water-gas shift” in title and “high temperature” in title, abstract or keywords, according to Web of Science.

which involves a surface reaction intermediate on the catalyst formed by reaction between CO and H₂O that subsequently decompose to produce CO₂ and H₂ (Eq. (1)). The most commonly proposed reaction intermediate is surface formate (HCOO*) which is usually observed on LT-WGS catalysts under reaction conditions [14–17]. The associative mechanism was proposed since 1920s but has been criticized mainly by the absence of any detectable surface intermediates with *in situ* IR spectroscopy during the HT-WGS reaction [18,19], which neglects the possibility of low concentrations and/or transient formation of surface formate species during HT-WGS.



The second proposed reaction mechanism, named “regenerative” or redox mechanism, is the most accepted reaction mechanism involving alternate reduction and re-oxidation of the catalyst [20–22].



The existing evidence for the redox mechanism is the observation of the bulk Fe²⁺ ↔ Fe³⁺ redox couple with Mössbauer spectroscopy showing bulk Fe²⁺ is oxidized to Fe³⁺ by H₂O and bulk Fe³⁺ reduced to Fe²⁺ by CO [22,23]. *In situ* gravimetric analysis (GA) demonstrated that the catalyst oxygen content is dependent on the oxyreduction potential of the reaction gases (H₂/H₂O and CO/CO₂) [20]. Both Mössbauer spectroscopy and gravimetric analysis, however, are not able to distinguish between changes taking place individually in the bulk lattice and surface of the iron oxide catalysts since they monitor the entire volume of the catalyst. The dynamic nature of the iron oxide catalyst bulk phases upon gas oxyreduction potential further complicates the above conclusions [24].

To resolve the debate about the HT-WGS reaction mechanism, a series of temperature-programmed surface reaction (TPSR) spectroscopy studies were undertaken [25]. The decomposition of formic acid during HCOOH-TPSR on Cr₂O₃-Fe₂O₃ catalysts, that had been activated under HT-WGS reaction conditions, mimics the second half of the associative pathway (Eq. (1)) and provides the kinetics of surface formate (HCOO*) decomposition. The same formation kinetics for CO₂ and H₂ is consistent with the fact that they are produced from a common intermediate (formate), which is the key feature of associative mechanism. The formation of CO₂ during CO/H₂O-TPSR on activated Cr₂O₃-Fe₂O₃, however, preceded the formation of H₂ indicating that they do not arise from a common surface reaction intermediate. While the different dynamics of CO₂ and H₂ evolution during transient HT-WGS were

previously reported by other researchers, it’s the first time that we provide a direct comparison between surface formate decomposition kinetics (mimic for the associative mechanism) and the actual HT-WGS kinetics, which confirms that the HT-WGS reaction by Cr₂O₃-Fe₂O₃ catalysts follows a redox mechanism as schematically shown in Fig. 2.

The participation of catalyst oxygen in the HT-WGS reaction was also examined via isotope switch experiments [26]. Upon switching from C¹⁶O₂/H₂ to C¹⁸O₂/H₂ during steady-state reaction conditions, the transient production of H₂¹⁶O vanishes within 2 min while ~90% of ¹⁶O still remains in the catalyst (determined by H₂-TPR since iron oxide reduces to metallic iron in H₂). This clearly shows only surface oxygen directly participates in the HT-WGS reaction and that a Mars-van Krevelen (MvK) mechanism employing bulk lattice oxygen doesn’t operate. The proposed HT-WGS reaction mechanism is presented in Fig. 2. A method was also developed to calculate the number of catalytic active sites (Ns) by quantifying the amount of ¹⁶O-containing products during the C¹⁸O₂/H₂ isotope switch that allowed for the first time quantification of the turnover frequency (TOF = number of CO molecules converted per active site per second) of iron oxide-based HT-WGS catalysts [26].

3. Knowledge of chromium as promoter

It was known that under HT-WGS reaction conditions, the hematite

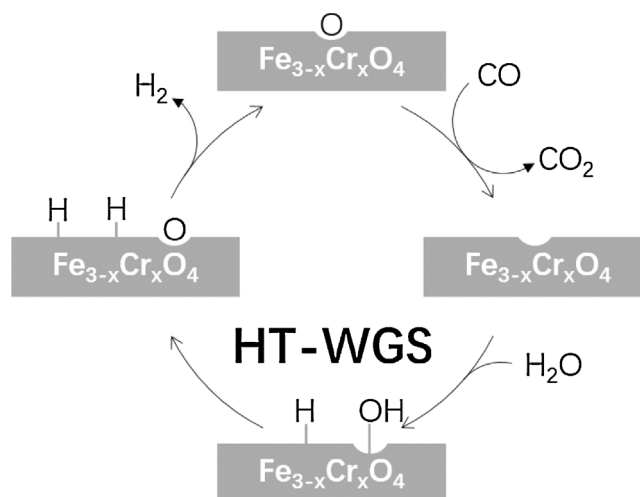


Fig. 2. Proposed surface redox mechanism on iron oxide-based catalyst during HT-WGS. Reproduced with permission from reference [25].

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