

Resolving the Reaction Mechanism for H₂ Formation from High-Temperature Water–Gas Shift by Chromium–Iron Oxide Catalysts

Minghui Zhu and Israel E. Wachs*

Operando Molecular Spectroscopy & Catalysis Laboratory, Department of Chemical and Biomolecular Engineering, Lehigh University, Bethlehem, Pennsylvania 18015, United States

Supporting Information

ABSTRACT: The reaction mechanism of the high-temperature water–gas shift (HT-WGS) reaction catalyzed by chromium–iron oxide catalysts for H_2 production has been studied for 100 years with two reaction mechanisms proposed: redox and associative (involving surface HCOO*). Direct experimental support for either mechanism, however, is still lacking, which hinders a thorough understanding of catalytic roles of each elements and the rational design of Cr-free catalysts. The current study demonstrates, with temperature-programmed surface reaction (TPSR) spectroscopy (CO-TPSR, CO+H₂O-TPSR, and HCOOH-TPSR), for the first time that the HT-WGS reaction follows the redox mechanism and that the associative mechanism does not take place.



KEYWORDS: redox mechanism, formate mechanism, associative mechanism, HT-WGS, iron-based catalysts, hydrogen

 \mathbf{T} he majority of industrial H_2 is currently produced by methane steaming reforming (MSR) followed by the water-gas shift (WGS) reaction to increase or control the $H_2/$ CO ratio and is employed in numerous applications (ammonia synthesis (from H_2/N_2), methanol synthesis (from $H_2/CO/$ CO_2), synthetic fuels (from H_2/CO), etc.). Ammonia synthesis alone is responsible for more than 2% of the world's daily energy use and produces the synthetic fertilizer required to feed the world's growing population.¹ Although there is much interest in developing sustainable H_2 production from photo-catalytic splitting of H_2O^{2-4} and biomass reforming,^{5,6} production of H₂ from fossil fuels (CH₄ \gg hydrocarbons \gg coal) will be around for quite some time given its established technology and cost competitiveness. For example, H₂ fueling stations for fuel cell powered automobiles currently being set up in America and Germany rely on MSR and WGS because of the availability of abundant and inexpensive natural gas.⁷

$$CO + H_2O \leftrightarrow CO_2 + H_2 \quad \Delta H = -40.6 \text{KJ/mol}$$
(1)

The WGS reaction involves carbon monoxide reacting with steam to produce carbon dioxide and hydrogen and was first applied by Bosch and Wild in 1914 with a Cr_2O_3 -Fe₂O₃ catalyst to provide H₂ for the synthesis of ammonia.⁸ Currently, the WGS reaction is commercially performed in several stages with different catalysts to optimize the greater CO equilibrium conversion attained at lower temperatures because the reaction is exothermic and reversible.^{9,10} The low-temperature WGS (LT-WGS) reaction is performed at ~190–250 °C with a Cu/ZnO/Al₂O₃ catalyst, and the high-temperature WGS (HT-WGS) reaction is performed at ~350–450 °C with a Cu-promoted chromium–iron mixed oxide catalyst.

During the HT-WGS reaction, the equilibrated bulk iron oxide phase is present as magnetite (Fe₃O₄), which is prone to deactivation by thermal sintering. Sintering is inhibited by addition of chromium oxide (8–14 wt %) to stabilize the surface area of the magnetite phase.^{9–12} With increasing environmental and health concerns about hexavalent chromium (Cr⁶⁺), which is a potent carcinogen, there has been much interest in developing Cr-free iron oxide HT-WGS catalysts in recent years.^{11,13} Rational design of a Cr-free iron oxide HT-WGS catalyst, however, requires a thorough fundamental understanding of the reaction mechanism.

The reaction mechanism and kinetics of the HT-WGS reaction by Cr_2O_3 —Fe₂O₃ catalysts have been extensively studied for 100 years, yet no consensus has been reached.^{9–11,13,14} The "regenerative" or redox mechanism is the most accepted reaction mechanism involving alternate reduction of the catalyst surface oxygen site (O*), with "*" representing an empty surface site, by gas-phase CO (eq 2) and oxidation of the reduced catalyst surface empty site by H₂O vapor (eq 3).^{15–19} The reversible nature of the WGS reaction also allows reaction steps 2 and 3 to take place from the right to the left, whereby the catalyst is oxidized by CO₂ and reduced by H₂.

$$CO + O^* \leftrightarrow CO_2 + *$$
 (2)

$$H_2O + * \leftrightarrow H_2 + O^* \tag{3}$$

Received: March 5, 2016

Revised: March 28, 2016

ACS Publications © XXXX American Chemical Society

The existing evidence for the redox mechanism is the observation of the bulk $Fe^{2+} \leftrightarrow Fe^{3+}$ redox couple with Mössbauer spectroscopy with bulk Fe²⁺ oxidized to Fe³⁺ by H₂O and bulk Fe³⁺ reduced to Fe²⁺ by CO.^{19,20} In situ gravimetric analysis (GA) demonstrated that the catalyst oxygen content is dependent on the oxyreduction potential of the reaction gases $(H_2/H_2O \text{ and } CO/CO_2)$.¹⁸ It was concluded that the oxygen changes measured with the GA as a function of the oxyreduction environments correspond to that of surface oxygen on the catalyst, but GA measures the total weight of the catalysts and is not able to distinguish between the bulk and surface oxygen content. The redox mechanism has become widely accepted because of these reported studies, which, however, are not able to distinguish between changes taking place in the bulk lattice and surface of the iron oxide catalysts because 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.²¹

The alternative mechanism is referred to as the "associative" mechanism, and it involves surface reaction intermediates formed by reaction between CO and H₂O that subsequently decompose to CO₂ and H₂ (eq 4). The most commonly proposed reaction intermediate is surface formate (HCOO*).^{22–25} The associative mechanism has been criticized mainly by not detecting surface formate species or any other surface intermediates during the HT-WGS reaction,^{26,27} which neglects the possibility of low concentrations and/or transient formation of surface formate species during HT-WGS. Such complexity has intrigued many computational studies that both support and refute the associative mechanism.^{28–30}

$$CO + H_2O \leftrightarrow (intermediate) \leftrightarrow CO_2 + H_2$$
 (4)

The focus of the present work is to resolve the reaction mechanism for H_2 production during HT-WGS by the Cr_2O_3 —Fe₂O₃ mixed oxide catalyst. We will show how employing transient kinetic studies, temperature-programmed surface reaction (TPSR) spectroscopy, allows *for the first time* to finally provide solid experimental evidence that demonstrates the HT-WGS reaction by chromium—iron oxide catalysts only proceeds via the redox mechanism.

The temperature-programmed surface reaction (TPSR) studies were carried out using an Altamira Instruments system (AMI-200) connected to a Dymaxion Dycor mass spectrometer (DME 200MS). The Cr_2O_3 -Fe₂O₃ catalyst was prepared by coprecipitation and consists of 8 wt % Cr_2O_3 and 92 wt % Fe₂O₃. Details of the catalyst preparation synthesis and TPSR experiment details are given in the Supporting Information.

CO-TPSR

The CO-TPSR spectra presented in Figure 1 were collected from an equilibrated catalyst after a 15 min water vapor treatment at 110 °C to enhance the surface hydroxyl concentration. Water does not desorb during the TPSR experiment reflecting the absence of residual molecular water on the initial catalyst surface. Evolution of CO₂ initiates at ~135 °C (Tp = 215 °C) and H₂ formation initiates at ~240 °C (Tp = 285 °C). The CO-TPSR spectra reveal that the formation of CO₂ and H₂ occurs at different temperatures. This indicates that the formation of CO₂ proceeds by reaction between CO and a surface O*, and the formation of H₂O involves reaction of two surface *OH species. TPSR in flowing He, however, does not produce H₂ (see Figure S2). This



Figure 1. MS signals for CO₂, H₂ and H₂O during CO-TPSR.

suggests that the surface oxygen vacancies created by CO oxidation may be required for activation of the surface hydroxyls for H₂ formation. The independent formation of CO₂ and H₂ demonstrates that these two products are not formed by a common reaction intermediate. Above ~285 °C, CO is more extensively oxidized to CO₂ with additional oxygen from the catalyst. Although the CO-TPSR environment is not the actual WGS reaction condition because of the absence of H₂O, the findings reveal that the redox reaction pathway can take place during WGS reaction conditions.

CO+H₂O-TPSR

The evolution of H₂O, CO, CO₂, and H₂ during CO+H₂O-TPSR are shown in Figure 2a, and the normalized CO_2 and H_2 signals are exhibited in Figure 2b. For the normalized spectra, the MS signals were rescaled to the same maximum and minimum intensity to better compare their transient behavior. The slight increase in H₂O evolution may be related to water desorption from the catalyst surface at these low temperatures. Formation of CO₂ initiates at \sim 125 °C, but the appearance of H_2 is significantly delayed to ~240 °C, indicating that the CO₂ production between 125 and 240 °C involves CO oxidation by surface O*. This behavior was already observed above during CO-TPSR. Even when both CO_2 and H_2 are simultaneously formed above 240 $^{\circ}$ C, the evolution of H₂ is retarded relative to CO_2 and the H_2/CO_2 ratio is less than 1, which finally reaches 1 as equilibrium is achieved at \sim 500 °C. The initial delay in H₂ formation relative to CO₂ evolution has also been previously observed in constant temperature transient partial pressure experiments.^{31,32} The different kinetic responses of CO₂ and H₂ during CO+H₂O-TPSR reveal that these two products are not generated by a common surface reaction intermediate undergoing the same elementary reaction step.

HCOOH-TPSR

Formic acid (HCOOH) is known to decompose to CO_2 and H_2 from HCOO* which is the most proposed reaction intermediate of associative mechanism.^{22,33} The evolution of CO_2 and H_2 from formic acid decomposition during HCOOH-TPSR on the equilibrated Cr_2O_3 -Fe₂O₃ catalyst is presented in Figure 3. The modest increase in HCOOH evolution at lower temperatures may be related to formic acid desorption from the catalyst surface. The production of the CO_2 and H_2



Figure 2. (a) MS signals for evolution of H_2O , CO, CO₂, and H_2 during CO+H₂O-TPSR from the equilibrated Cr₂O₃-Fe₂O₃ catalyst and (b) the normalized CO₂ and H₂ MS signals (CO: $H_2O = 1:1$).



Figure 3. Normalized MS signals for HCOOH, CO_2 , and H_2 during HCOOH-TPSR on equilibrated Cr_2O_3 -Fe₂O₃ catalyst.

decomposition products initiates at ~225 °C. The evolution of CO_2 and H_2 from HCOOH decomposition follows the exact same kinetics between 225 and 300 °C as would be expected for their origin from the same surface reaction intermediate.

The evolution of CO_2 and H_2 from $CO+H_2$ -TPSR and HCOOH-TPSR are compared in Figure 4. As indicated above,



Figure 4. Normalized MS signals for CO₂ and H₂ evolution during HCOOH-TPSR and CO+H₂O-TPSR on equilibrated Cr_2O_3 -Fe₂O₃ catalyst.

evolution of CO₂ and H₂ from HCOOH decomposition initiates at the same temperature and follows the exact same kinetics as expected for decomposition of a common surface reaction intermediate (HCOO*), which is the rate-determining-step.³⁴ In contrast, the production of $CO_2/(CO+H_2O)$ begins at a much earlier temperature than $H_2/(CO+H_2O)$ formation because of CO oxidation by surface O*. The kinetics for evolution of $CO_2/(CO+H_2O)$ and $H_2/(CO+H_2O)$ above 250 °C are not the same with more CO_2 being initially formed than H₂. Furthermore, the kinetics for CO₂ and H₂ evolution from CO+H2O-TPSR are also different than found for the kinetics for CO₂ and H₂O production from the decomposition of formic acid. The TPSR findings demonstrate that (i) an associated mechanism through a common surface intermediate, especially formic acid or formate, is not supported by the current findings and (ii) the current findings are only consistent with a redox or regenerative mechanism.

The new insights suggest the following redox reaction mechanism for the HT-WGS reaction by chromium–iron mixed oxide catalysts.

$$CO + O^* \leftrightarrow CO_2^*$$
 (5)

$$\mathrm{CO}_2^* \leftrightarrow \mathrm{CO}_2 + ^*$$
 (6)

$$H_2O + * \leftrightarrow H_2O^* \tag{7}$$

$$H_2O^* + * \leftrightarrow OH^* + H^* \tag{8}$$

$$OH^* + * \leftrightarrow O^* + H^* \tag{9}$$

$$\mathrm{H}^* + \mathrm{H}^* \leftrightarrow \mathrm{H}_2 + 2^* \tag{10}$$

The oxidation of CO by surface O* appears rather straightforward, but isotopic oxygen studies showed rapid oxygen scrambling that also implicates the presence of surface carbonates (CO₃*) during the HT-WGS.³⁵ The surface carbonates may just be formed by complexation of the CO₂ product with surface O* and not directly involved in the HT-WGS reaction.³⁶ The details of the elementary steps involved in water decomposition during HT-WGS are not completely clear at present because formation of H₂ must involve several reaction steps such as reactions 8–10. The current findings also suggest that activation of surface hydroxyls to yield H_2 involves formation of surface vacant sites by CO oxidation. It appears that the HT-WGS shift reaction is much more complex involving multiple elementary steps than originally conceived as reflected by eqs 2 and 3.

In conclusion, the evolution of CO_2 and H_2 from $CO+H_2O$ -TPSR with equilibrated $Cr_2O_3-Fe_2O_3$ catalysts has, for the first time, been able to provide experimental evidence that the HT-WGS reaction follows a redox mechanism where the catalyst surface is alternatively reduced by CO and reoxidized by H_2O . The alternatively proposed associative reaction mechanism for CO_2 and H_2 formation proceeding through a common surface reaction intermediate and elementary decomposition step is disproved by the current findings. The new mechanistic insight will contribute toward the discovery of a nontoxic Cr-free HT-WGS catalyst for manufacture of clean H_2 fuel.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acscatal.6b00659.

Catalyst synthesis; in situ Raman spectroscopy details; temperature-programmed surface reaction (TPSR) spectroscopy; Raman spectra of Fe_2O_3 and Cr_2O_3 - Fe_2O_3 under dehydrated and reaction conditions (Figure S1); MS signals during He-TPSR for equilibrated Cr_2O_3 - Fe_2O_3 catalyst (Figure S2) (PDF)

AUTHOR INFORMATION

Corresponding Author

*E-mail: iew0@lehigh.edu.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The authors gratefully acknowledge financial support from National Science Foundation Grant CBET- 1511689.

REFERENCES

(1) Licht, S.; Cui, B. C.; Wang, B. H.; Li, F. F.; Lau, J.; Liu, S. Z. Science **2014**, 345, 637–640.

- (2) Kudo, A.; Miseki, Y. Chem. Soc. Rev. 2009, 38, 253-278.
- (3) Walter, M. G.; Warren, E. L.; McKone, J. R.; Boettcher, S. W.; Mi,
- Q. X.; Santori, E. A.; Lewis, N. S. Chem. Rev. 2010, 110, 6446–6473.
- (4) Bard, A. J.; Fox, M. A. Acc. Chem. Res. 1995, 28, 141–145.
- (5) Navarro, R. M.; Peña, M. A.; Fierro, J. L. G. Chem. Rev. 2007, 107, 3952-3991.
- (6) Navarro, R. M.; Sanchez-Sanchez, M. C.; Alvarez-Galvan, M. C.; del Valle, F.; Fierro, J. L. G. *Energy Environ. Sci.* 2009, 2, 35-54.
- (7) Calo, E.; Giannini, A.; Monteleone, G. Int. J. Hydrogen Energy 2010, 35, 9828-9835.
- (8) Bosch, C.; Wild, W. U.S. Patent US11130966A, October 6, 1914. (9) Newsome, D. S. *Catal. Rev.: Sci. Eng.* **1980**, *21*, 275–318.
- (10) Ratnasamy, C.; Wagner, J. P. Catal. Rev.: Sci. Eng. 2009, 51, 325-440.
- (11) Lee, D. W.; Lee, M. S.; Lee, J. Y.; Kim, S.; Eom, H. J.; Moon, D. J.; Lee, K. Y. *Catal. Today* **2013**, *210*, 2–9.

(12) Grunwaldt, J. D.; Kappen, P.; Hammershoi, B. S.; Troger, L.; Clausen, B. S. J. Synchrotron Radiat. 2001, 8, 572–574.

- (13) Zhu, M.; Wachs, I. E. ACS Catal. 2016, 6, 722-732.
- (14) Byron Smith, R. J.; Loganathan, M.; Shantha, M. S. Int. J. Chem. React. Eng. 2010, 8, 1–32.
- (15) Kulkova, N. V.; Temkin, M. I. Zh. Fiz. Khim. 1949, 23, 695-698.

- (16) Shchibrya, G. G.; Morozov, N. M.; Temkin, M. I. Kinet. Catal. 1965, 6, 1057–1059.
- (17) Temkin, M. I. Adv. Catal. 1979, 28, 173-291.
- (18) Kubsh, J. E.; Dumesic, J. A. AIChE J. 1982, 28, 793-800.
- (19) Boreskov, G. K.; Yurieva, T. M.; Sergeeva, A. S. Kinet. Catal. 1970, 11, 374–381.
- (20) Topsoe, H.; Boudart, M. J. Catal. 1973, 31, 346-359.
- (21) Cherkezova-Zheleva, Z.; Mitov, I. Journal of Physics: Conference Series 2010, 217, 012044.
- (22) Armstrong, E. F.; Hilditch, T. P. Proc. R. Soc. London, Ser. A 1920, 97, 265–273.
- (23) Oki, S.; Mezaki, R. J. Phys. Chem. 1973, 77, 1601-1605.
- (24) Botes, F. G. Appl. Catal., A 2007, 328, 237-242.
- (25) Van der Laan, G. P.; Beenackers, A. A. C. M. Appl. Catal., A 2000, 193, 39–53.
- (26) Boudjemaa, A.; Daniel, C.; Mirodatos, C.; Trari, M.; Auroux, A.; Bouarab, R. C. R. Chim. **2011**, *14*, 534–538.
- (27) Diagne, C.; Vos, P. J.; Kiennemann, A.; Perrez, M. J.; Portela, M. F. *React. Kinet. Catal. Lett.* **1990**, *42*, 25–31.
- (28) Chen, L.; Ni, G.; Han, B.; Zhou, C. G.; Wu, J. P. Acta Chim. Sin. **2011**, *69*, 393–398.
- (29) Huang, L.; Han, B.; Zhang, Q.; Fan, M.; Cheng, H. J. Phys. Chem. C 2015, 119, 28934–28945.
- (30) Van Natter, R. M.; Coleman, J. S.; Lund, C. R. F. J. Mol. Catal. A: Chem. 2009, 311, 17–22.
- (31) Salmi, T.; Lindfors, L. E.; Bostrom, S. Chem. Eng. Sci. 1986, 41, 929–936.
- (32) Salmi, T.; Bostrom, S.; Lindfors, L. E. J. Catal. 1988, 112, 345–356.

(33) Rhodes, C.; Hutchings, G. J.; Ward, A. M. Catal. Today 1995, 23, 43–58.

- (34) Poulston, S.; Rowbotham, E.; Stone, P.; Parlett, P.; Bowker, M. *Catal. Lett.* **1998**, *52*, 63–67.
- (35) Zhu, M.; Wachs, I. E. ACS Catal. 2016, 6, 1764-1767.
- (36) Kalamaras, C. M.; Olympiou, G. G.; Efstathiou, A. M. Catal.
- Today 2008, 138, 228–234.