

Research Article

Hydrogen Production from the Water-Gas Shift Reaction on Iron Oxide Catalysts

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Unsupported and supported iron oxide catalysts were prepared by incipient wetness impregnation method and studied in the water-gas shift reaction (WGS) in the temperature range 350–450°C. The techniques of characterization employed were BET, X-ray diffraction, acid-base measurements by microcalorimetry and in situ diffuse reflectance infrared Fourier transform spectroscopy. MgO, TiO₂, or SiO₂ was added in order to (i) obtain a catalyst exempt of chromium oxide and (ii) study the effect of their acid-base properties on catalytic activity of Fe₂O₃. X-ray diffraction studies, and calorimetric and diffuse reflectance infrared Fourier transform measurements reveal a complete change in the physicochemical properties of the iron oxide catalyst after MgO addition due to the formation of the spinel oxide phase. These results could indicate that the MgFe₂O₄ phase stabilizes the reduced iron phase, preventing its sintering under realistic WGS conditions (high H₂O partial pressures).

1. Introduction

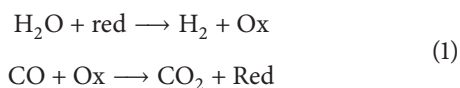
Carbon oxide reacts with water and produces, via the reversible and exothermic reaction: $\text{CO} + \text{H}_2\text{O} = \text{CO}_2 + \text{H}_2$, carbon dioxide with pure hydrogen. In recent years, this reaction has received considerable interest due to the possibility to reduce a large amount of carbon monoxide from reformed fuels ($\text{CO} + \text{H}_2$) into additional hydrogen production. This reaction is catalyzed with a large variety of metals and metal oxides like Fe [1–3], Cu [2, 4], Au [2, 5, 6], Ru [2, 7], and Pt [8, 9] and is often performed in two steps to achieve rates for commercial purposes. At lower temperature (150–250°C) the catalyst of choice is based on copper Cu-ZnO. The iron oxide-based catalysts, Fe₂O₃, are well known in high temperature water-gas shift reaction (350–450°C) and are generally doped with chromium oxide, Cr₂O₃, which prevents the sintering of iron oxide crystallites. Before the high temperature shift catalysts can be used, hematite must be converted to magnetite which is believed to

be the active phase. This reduction is carried out with process gas mixtures of hydrogen, nitrogen, carbon oxide, carbon dioxide, and water vapour and is controlled to avoid further reduction of magnetite active material to lower oxides or to metallic iron species. Metallic iron is an active catalyst for the methanation of CO and the Fischer-Tropsch processes, which is undesirable here, since all generated hydrogen is consumed. To solve this problem, it is suitable to develop iron oxide stable catalysts that would be more difficult to reduce to metallic iron.

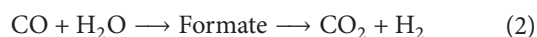
Júnior et al. [10] have indicated that the substitution of chromium by vanadium, in the iron oxide based water-gas shift reaction, produced directly the sought active phase. In a recent study, Martos and his coworkers [11] have replaced chromium by molybdenum in magnetite-based catalysts, by using the oxidation-precipitation and wet impregnation methods preparation and concluded that molybdenum increases thermal stability of the magnetite active phase and prevents metallic iron formation during the reaction.

The oxidation-precipitation method allows obtaining the material directly in the active phase and molybdenum is incorporated into magnetite lattice. Boudjemaa et al. [3] have reported that magnesium could be a good candidate to replace chromium in iron-based catalysts since Mg-rich catalysts are more active than Cr-promoted ones. By adding MgO to Fe₂O₃ [12], it was found that the Fe₂O₃-MgO basic catalyst is 100 times more active than the acidic catalyst Fe₂O₃/SiO₂ and a direct relation between catalytic activity and acid-base properties of catalysts is established.

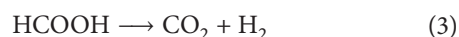
The catalytic conversion of carbon oxide and water to carbon dioxide and hydrogen via the water-gas shift reaction is established to take place principally through two main types of mechanisms, the regenerative mechanism or the associative mechanism. In the first mechanism the catalyst surface is successively oxidized by H₂O and reduced by CO [13]:



In turn, the associative mechanism supposes that the reactants CO and H₂O interact to form a reaction intermediate, such as an adsorbed formate adspecies, which then decomposes to CO₂ and H₂:



It was proposed in several researches that the formic acid species can be used as an intermediate to represent the formate group produced from the reaction between carbon oxide and water in the WGS reaction [2, 9, 13] on the following dehydrogenation process:



The decomposition of formic acid (reaction (3)) to the products of WGS reaction is catalyzed by metals and basic metal oxides.

In this work, we present the results of the effect of acid-base properties created by the support addition oxides on the catalytic activity of Fe₂O₃ in the water-gas shift reaction. An associative mechanistic of hydrogen production in the high temperature shift reaction was also developed on iron oxide catalyst.

2. Experimental

2.1. Materials Synthesis and Characterizations. 30 wt% Fe₂O₃-MO_x systems, with *M* equal to Mg, Ti, or Si, were prepared by incipient wetness impregnation method. This method consists of adsorbing an adequate aqueous solution of iron nitrate salt Fe(NO₃)₃·9 H₂O onto the selected support MgO, TiO₂, or SiO₂. The systems obtained are 30Fe-Mg, 30Fe-Ti, and 30Fe-Si. All these solids were calcined at 400°C.

The concentration of iron oxide in the solution was controlled to obtain the desired Fe content on MgO (5, 10, 20, and 30 wt%). It is about 5Fe-Mg, 10Fe-Mg, 20Fe-Mg, and 30Fe-Mg, respectively.

30Fe-Mg system was calcined for study needs at 200°C and 300°C. These systems are labeled 30Fe-Mg400, 30Fe-Mg300, and 30Fe-Mg200.

The elaborated solids were then characterized by means of techniques of analysis, X-ray powder diffraction, CO₂ and NH₃ adsorptions calorimetry, and the diffuse reflectance infrared Fourier transform spectroscopy. X-ray diffraction studies were obtained with a Philips PW 1050/81 automated powder goniometer, equipped with a diffracted-beam graphite monochromatic Cu (K_α) radiation. CO₂ and NH₃ adsorptions calorimetry was carried out at 80°C after activation under H₂ flow at 200°C. Differential heats of adsorption were measured in a heat flow Setaram HT microcalorimeter linked to a volumetric adsorption system. Successive small doses of CO₂ or NH₃ were sent over the catalytic surface. From the calorimetric and volumetric data, the differential heats of adsorption versus coverage and the corresponding isotherms are plotted. In situ diffuse reflectance infrared Fourier transform studies were performed on a Nicolet Magna IRTF spectrometer with OMNIC software. The reaction was performed in a high temperature Spectratech cell equipped with a ZnSe window. A sample was first treated in a flow of (~35 mL/min) H₂ at 400°C for 30 min (high-temperature treatment) before each experiment. After this treatment, the sample was cooled under helium and then put in contact with the reacting mixture CO + H₂O at increasing temperature from 25 to 450°C.

2.2. CO + H₂O Reaction. Catalytic properties of Fe-only and Fe-supported systems were examined in the reaction of the conversion of carbon oxide to carbon dioxide usually named WGS between 350°C and 450°C. The reduction treatment was carried for all Fe-based catalysts with a mixture of H₂/N₂ at 450°C during 60 min with a heating rate of 5°C·min⁻¹. The mixtures of reactant gases, H₂O/CO = 4.4 at a total flow-rate of 33 mL/min, and products were periodically analysed on line using a TCD chromatograph which contained two 4 m carbosieve B columns (1/8 inch, 100 to 200 mesh). Prior to analysis, the effluent was passed through a water-trap at 0°C in order to remove reaction water.

3. Results and Discussions

3.1. Fe-Cr Systems. Iron and chromium based catalysts, known generally as high temperature shift catalysts, are active within the temperature range of 350–450°C. Three methods of preparation of iron-chromium oxides, described obviously in [3], are chosen to study their catalytic activities in WGS reaction. The hydrogen produced via the CO + H₂O process at 450°C of the Fe-only and Fe-Cr synthesized under various preparation methods is presented in Figure 1. The samples were reduced in a mixture of H₂ + N₂ at 450°C during 60 min before the reaction. The Fe-Cr prepared by substituting Fe by Cr stays almost inactive for all the duration of the study, while Fe-Cr prepared by the coprecipitation technique provides the highest values of H₂ after 90 min of reaction time and Fe-Cr prepared via impregnation method exhibits an intermediate performance. In turn, the Fe-only catalyst presents very high

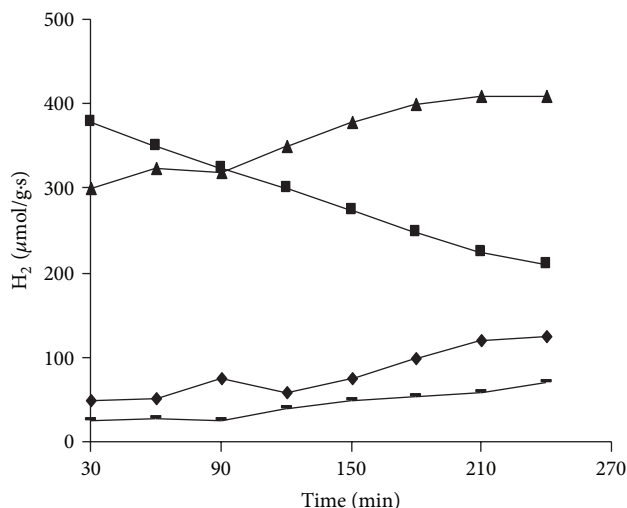


FIGURE 1: Hydrogen generation via WGSR of the calcined and reduced solids prepared by (-) substitution, (◆) impregnation, and (▲) coprecipitation methods. (■) corresponds to Fe_2O_3 .

initial activity which decreased significantly with the reaction time to values one more active than the promoted catalyst Fe-Cr prepared via impregnation method. This loss of activity and stability can be related to the sintering of the iron oxide phase. It has been proved that the addition of chromium oxide to Fe_2O_3 slows the deactivation of the iron oxide [14].

3.2. Fe-Mg Systems. The aim of this part of the study is to promote the iron oxide-based catalyst by replacement of the chromium oxide by MgO which can be apt to improve the catalytic activity of the intermediate active catalyst, in the occurrence Fe-Cr prepared via impregnation method (see Figure 1). Our intent here is for 5Fe-Mg, 10Fe-Mg, 20Fe-Mg, and 30Fe-Mg or 30Fe-Mg400, 30Fe-Mg300, and 30Fe-Mg200 catalysts. The WGS reaction results of Fe-Mg catalysts, expressed by the hydrogen production and the X-ray diffraction patterns of the magnesium promoted catalyst, are given in Figures 2 and 3, respectively.

Figure 2 shows the effect of magnesium additives to iron oxide-based catalysts on the hydrogen production via the WGS reaction at the temperature range 350–450°C. The quantity of hydrogen produced increases significantly with the increase of iron oxide content in the following order 5Fe-Mg < 10Fe-Mg < 20Fe-Mg < 30Fe-Mg. The H_2 production is also found to increase with the rise of reaction temperature. We have reported in previous works [3, 15] that the sample 30Fe-Mg produced a spinel oxide phase of type $MgFe_2O_4$ together with a predominant MgO phase at a temperature of calcination of 400°C and presented excellent performance in the WGS reaction. Furthermore, we projected that a decrease in calcination temperature from 400 to 200°C would not produce the spinel oxide.

The X-ray diffractograms of pure and Fe-supported 5–30 wt% Fe-Mg solids calcined at 400°C and 30 wt% Fe-Mg calcined at 200, 300, and 400°C were studied and illustrated by Figure 3. The analysis of XRD patterns reveals that

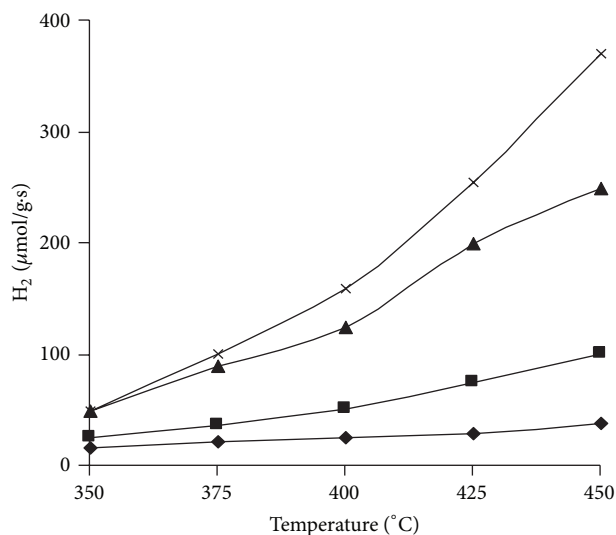


FIGURE 2: Temperature dependence of the H_2 generation from WGS reaction of the samples: (◆) 5Fe-Mg, (■) 10Fe-Mg, (▲) 20Fe-Mg, and (x) 30Fe-Mg after a reduction treatment at 450°C during 60 min. Reactant gas mixture, $H_2O/CO = 4.4$. Total flow-rate of 33 mL/min.

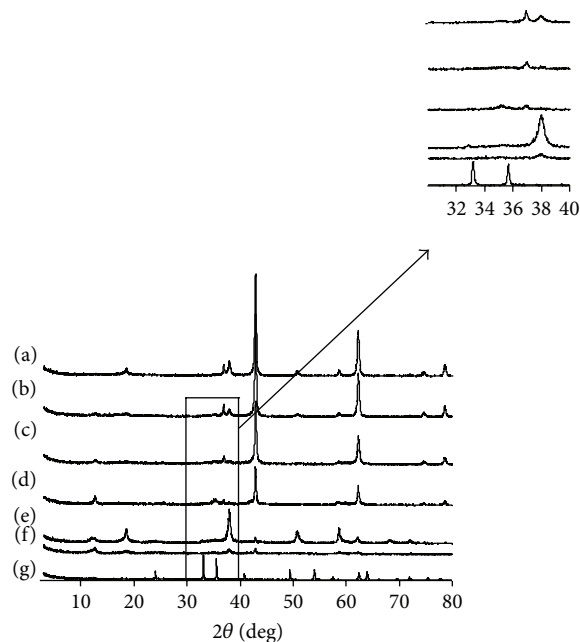


FIGURE 3: X-ray diffraction patterns of the magnesium promoted Fe-Mg catalysts. (a) 5Fe-Mg, (b) 10Fe-Mg, (c) 20Fe-Mg, (d) 30Fe-Mg400, (e) 30Fe-Mg300, (f) 30Fe-Mg200, and (g) Fe-only.

the Fe_2O_3 crystalline phase was detected in the unsupported solid. Iron oxide did not appear on the Fe-supported solids. By looking at 5–30 wt% Fe-Mg spectra, it appears clearly that the intensity of the principal ray assigned to the MgO crystalline phase decreases progressively when the iron oxide charge increases by 5 to 30 wt%. At a charge of 30 wt% Fe_2O_3 (spectrum d), the crystalline fraction of MgO is ostensibly changed by the formation of $MgFe_2O_4$ spinel phase [16].

TABLE 1: S_{BET} , XRD, and DRIFT results of the elaborated catalysts.

Catalyst	BET area ^a ($\text{m}^2\cdot\text{g}^{-1}$)	XRD data ^{a,b}	DRIFT wave numbers ^a (cm^{-1})			
			OH band	CO	OCO species	CH vibration
Fe-only	25.0	Fe_2O_3	— ^c	—	—	—
30Fe-Si	90.7	Fe_2O_3 , SiO_2	—	—	—	—
30Fe-Ti	14.0	Fe_2O_3 , TiO_2	—	2170–2080	—	—
30Fe-Mg	02.2	MgFe_2O_4 , MgO	3570 (3730 ^d) 3040, 3130, 3850	2170–2080	1370 (1510 ^d), 1630, 1720	2850–2700

^aReference [12], ^bsee Figure 3 and Section 3.2, ^cnot detected, and ^dshoulder.

For 30Fe-Mg300 and 30Fe-Mg200 solids a minor MgO phase was observed together with the predominant $\text{Mg}(\text{OH})_2$ phase.

3.3. Fe-Supported Systems. By choosing MgO, TiO_2 , and SiO_2 to support iron oxide in this section, it was expected that the large variety of acid-base strengths of MgO (basic support), TiO_2 (amphiprotic support), or SiO_2 (acidic support) important in determining catalytic activity could be realized. In a previous work [12], we have shown that the most active system is the catalyst containing MgO as a support. $\text{Fe}_2\text{O}_3/\text{MgO}$ is 12 times more active than $\text{Fe}_2\text{O}_3/\text{TiO}_2$, 21 times more active than the unsupported catalyst, and 100 times more active than $\text{Fe}_2\text{O}_3/\text{SiO}_2$.

The X-ray crystalline phases of the elaborated Fe-only, 30Fe-Mg, 30Fe-Ti, and 30Fe-Si systems are given in Table 1 with the results of calorimetric and DRIFT measurements data. MgFe_2O_4 was identified with mainly MgO support phase in the 30Fe-Mg solid system. On the three other systems, iron was found at the Fe (3+) state in its $\alpha\text{-Fe}_2\text{O}_3$ allotropic variety (JCPDS number 89-0598).

3.3.1. Calorimetric Data. In order to establish correlation between catalytic activity and the acid-base properties of the catalyst surface, it is essential to determine the nature and the strength of the acid-base sites by adsorption of a probe molecule.

The differential heats of carbon dioxide adsorption, at 80°C , versus coverage, are illustrated in Figure 4. As can be seen from these illustrations, the evolution of the differential heat of carbon dioxide is strongly marked by the nature of the added support. 30Fe-Mg sample shows evidence of a much larger amount of strong strength basic sites with an initial heat of adsorption of $150\text{ kJ}\cdot\text{mol}^{-1}$ as indicated in Figure 4 by dark diamond-shaped symbols. This MgO modified solid exhibits a second population of strong strength of basic surface sites at around $130\text{ kJ}\cdot\text{mol}^{-1}$ then a continual decrease of the strength of basic sites. The presence of the second population of basic sites can be attributed to bulk MgO ($\sim 120\text{ kJ}\cdot\text{mol}^{-1}$) in good agreement with XRD data (see Table 1). On 30Fe-Ti and 30Fe-Si surfaces, we noted that the basicity strength declines rapidly by replacing MgO by TiO_2 and SiO_2 , respectively. The acidic properties of 30Fe-Si are confirmed by the results presented in Figure 5. Finally, the distribution of the strength of CO_2 adsorption, that is, basicity, is strongly dependent

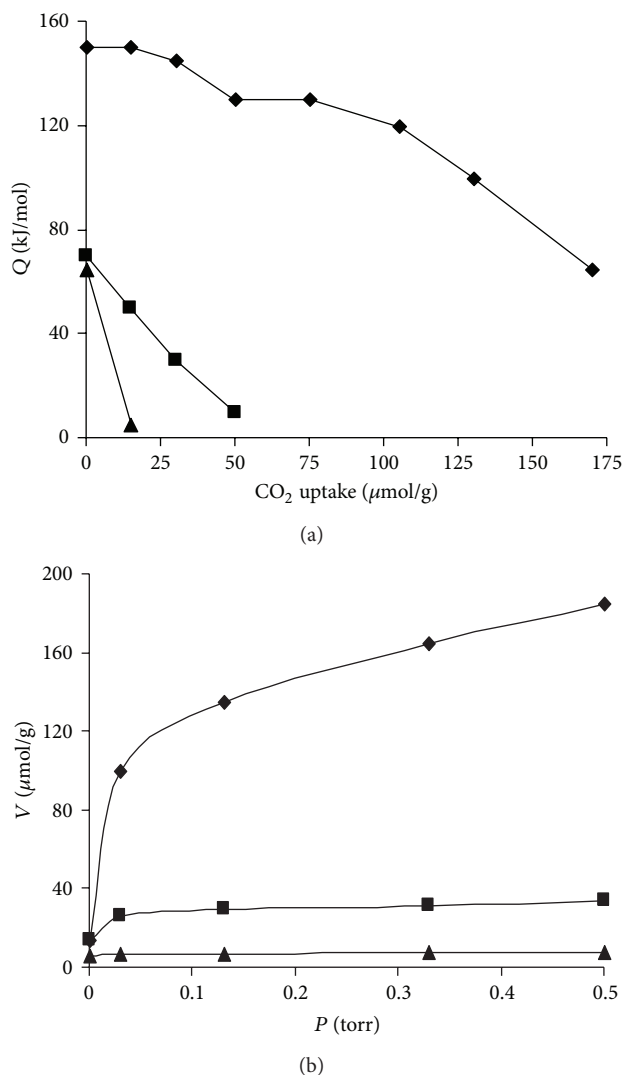


FIGURE 4: Differential heats of CO_2 adsorption at 80°C . (▲) 30Fe-Si, (■) 30Fe-Ti, and (◆) 30Fe-Mg.

on the nature of added support: $30\text{Fe-Mg} \gg 30\text{Fe-Ti} > \text{Fe-only} \gg 30\text{Fe-Si}$.

3.3.2. DRIFTS Data. The DRIFTS data of Fe-only, 30Fe-Si, 30Fe-Ti, and 30Fe-Mg catalysts are presented in Table 1. The spectrum of 30Fe-Mg reduced solid system shows, at

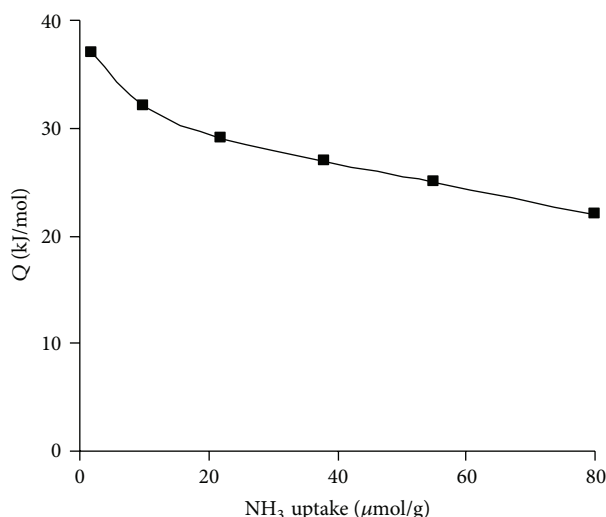
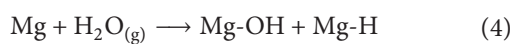


FIGURE 5: Differential heat of NH₃ adsorption at 80°C of 30Fe-Si sample.

the reaction temperature of 450°C, a large adsorption band and its maximum at 3570 cm⁻¹ (with a shoulder at 3730 cm⁻¹) which is related to the interaction of H₂O with the medium basic groups of MgO revealed by calorimetric study in Section 3.3.1:



In addition to the large OH band abovementioned, other smaller band adsorbed species are detected in the range 3130–3040 cm⁻¹. From this observation, it comes that these bands correspond to Fe(OH) still present even after reduction due to the remaining traces of H₂O always present in the dynamic DRIFT cell.

Furthermore, the small bands emerging at 2170–2080 cm⁻¹ are characteristic of the gaseous CO via the following reaction:

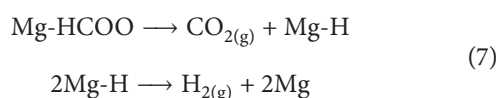


The doublet at the 2400–2330 cm⁻¹ region corresponds to adsorbed and/or gaseous CO₂.

Elsewhere, the dosing of the gas mixture CO + H₂O onto reduced 30Fe-Mg produced formate adspecies (1720, 1630, and 1370 cm⁻¹) as a surface intermediate:



The latter adsorbed species are considered as an active intermediate of the water-gas shift reaction process:



As opposed to 30Fe-Mg, no infrared contribution from formate adsorbed species was observed on the reduced 30Fe-Ti system. After contacting this catalyst with CO + H₂O

mixture gas, two new bands are detected in the carbonate species region (1550–1630 cm⁻¹) with the doublet at 2170–2080 cm⁻¹, a characteristic of the CO gaseous (Table 1). Based on this observation, we can conclude that this system does not work like the 30Fe-Mg basic catalyst in the water-gas shift reaction.

From the data in Table 1, one can see that no formate or carbonate bands were detected on the reduced 30Fe-Si and Fe-only catalysts in line with Rethwisch and Dumesic works [1].

4. Conclusion

In this study, one can conclude that magnesium oxide-modified Fe, free from chromium samples, is a good catalyst for the high temperature shift reaction. By adding MgO to Fe₂O₃, a spinel oxide phase of type MgFe₂O₄, initially detected as a minor phase after calcinations at 200 and 300°C, was reinforced and formed, at a temperature of calcination of 400°C, one of the main crystallized phases. These results could indicate that the MgFe₂O₄ phase stabilizes the reduced iron phase, preventing its sintering under realistic WGS conditions (high H₂O partial pressures).

An associative mechanistic of the hydrogen production via the high temperature shift reaction was also developed on this type of catalyst.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

Acknowledgment

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